

NUTRIENT CYCLING HOTSPOTS IN SUBURBAN WATERSHEDS:
STORMWATER DETENTION BASINS, GRASSED ROAD DITCHES, AND
LAWNS

A Dissertation

Presented to the Faculty of the Graduate School
of Cornell University

In Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy

by

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August 2016

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Cornell University 2016

As urbanization has increased across the United States and the world, we have manipulated the way that water and nutrients move around the landscape. This creates potential conditions for nutrient cycling hotspots- zones of higher reaction rates relative to surrounding areas- in certain features of developed landscapes. While there has been research on various aspects of biogeochemical processes in urban and suburban landscapes, we still lack a comprehensive understanding of where and when particular urbanized features act as hotspots for certain nutrient cycling processes. This research fills this gap by investigating how hydrology and nutrient availability control the occurrence of hotspots, with a focus on stormwater control measures (SCMs) in suburban watersheds in central New York State. In a field comparison of wet and dry stormwater detention basins, wet basins were hotspots for both methane (CH_4) emissions and potential denitrification. A follow-up study focusing on organic matter amendments in stormwater basins compared a bioretention-style basin with compost in its soil media to a grassed detention basin. High nutrient content in the bioretention basin media made it a hotspot for export of dissolved carbon, nitrogen and phosphorus and elevated carbon dioxide (CO_2) emissions. A third study applied similar techniques to study nutrient cycling in different suburban landscape features- grassed roadside ditches and lawns. Here, ditches- like the wet basins- were a hotspot

for CH₄ emissions but also for nitrate removal via denitrification. Nutrient availability thanks to fertilization drove greenhouse gas emissions in adjacent lawns, which demonstrated higher rates of nitrous oxide (N₂O) and CO₂ emissions compared to ditches. With all of these findings, we can inform improved design of suburban landscapes and SCMs, so that we can maximize beneficial water quality services like denitrification and minimize disservices like greenhouse gas emissions.

BIOGRAPHICAL SKETCH

Lauren grew up in Montgomery, New York where she spent ample time exploring the woods, playing in the mud, and generally gaining a strong love for science and nature. She earned her B.S in Science of Earth Systems in 2007 from Cornell University where she dappled in soil microbiology and snow hydrology research and participated in the Cornell Earth and Environmental Systems Program in Hawai'i. Lauren then spent three years working for the U.S. Geological Survey in Reston, Virginia as a research associate on projects related to stream and wetland hydrology and biogeochemistry. From there, she returned to Cornell to pursue graduate studies in Biological and Environmental Engineering and enjoy further exploring Ithaca and beautiful central New York. She completed an M.S. degree in 2013 on nitrogen cycling in agricultural stream riparian areas. For her dissertation work, she moved into more urbanized systems to study nutrient cycling dynamics related to stormwater management. She is broadly interested in understanding human impacts on land and water resources and informing more sustainable development practices.

To my wonderful family that has supported me in all of my endeavors, especially my parents Bob and Robin McPhillips and my husband and partner-in-life Matt Herndon

ACKNOWLEDGEMENTS

I'm immensely thankful for the guidance, support, and laughs provided by my advisor Todd Walter, as well as for the helpful insight, feedback, and encouragement provided by committee members Christy Goodale, Peter Groffman, Susan Riha and Rebecca Schneider. For assistance with getting lab instrumentation to behave, I'm grateful to Shree Giri and Brian Richards. For assistance with carrying out all of the field and lab work, I'm indebted to many undergraduate research assistants, including Julia Dagum, Andrea Fortman, Christine Georgakakos, Peri Gerson, Liza Johnson, Breann Liebermann, Brandon Roosenboom and Rachel Whiteheart. For helping me maintain my sanity and (almost) always making 'work' fun, I'm thankful for my many Soil and Water Labmates. For providing access to and information on research sites, I'm appreciative to Bob Chiang of Cornell Engineering and Linda Aarismaa of Cornell Environmental Compliance as well as the residents of the road ditch study watershed. I'm also immensely grateful to my husband Matt Herndon for his support and encouragement, including taking care of our son Rolin while I was off writing this dissertation! Finally, this work was made financially possible thanks to funding from the National Science Foundation Graduate Research Fellowship Program under Grant No. 1144153, the Cornell Cross-Scale Biogeochemistry & Climate IGERT under NSF Grant No. 1069193, the New York Water Resources Institute, and the New York Water Environment Association under the NG Kaul Award.

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LIST OF ABBREVIATIONS

C	Carbon
CO ₂ Equiv	CO ₂ equivalents
DOC	Dissolved organic carbon
GHG	Greenhouse gas
GWP	Global warming potential
i.d.	Inner diameter
NO _x	NO ₃ ⁻ + NO ₂ ⁻
LOI	Loss-on-ignition
N	Nitrogen
OM	Organic matter
SCM	Stormwater control measure
SRP	Soluble reactive phosphorus
VWC	Volumetric water content

CHAPTER 1

Introduction

As development and urbanization has increased around the world, so has the coverage of impervious surface on the landscape. This impervious surface - in the form of buildings, parking lots and roads - prevents water from infiltrating soils and thus has led to redistribution of water around urbanized landscapes. The runoff generated from these impervious surfaces has created numerous challenges and undesired consequences, including flooding of various critical infrastructures and flooding, pollution, and associated degradation of streams and rivers.

In response, stormwater control measures (SCMs) have been implemented to route, detain, and/or treat stormwater runoff generated by impervious surfaces (NRC, 2009). Along many roads, ditches or swales have been constructed to accept runoff from the road and route it away to prevent the road from flooding. For ditches, managing the volume of storm runoff has typically been the only goal in design and implementation. As water bodies in urbanized regions became increasingly degraded from routing of runoff quickly to streams (Walsh et al., 2005), it became clear that new management solutions needed to be implemented. In the last several decades, SCMs have been built in developed areas with the intention of detaining and/or infiltrating stormwater. These ponds or basins have been constructed with the primary goal of reducing peak stormflows in downstream water bodies and they have been increasingly designed to also improve water quality of incoming stormwater (Davis and McCuen, 2005).

This routing of stormwater around the landscape and into various types of SCMs has implications for biogeochemical cycling. The convergence of storm flows into certain portions of the landscape combined with the availability of particular substrates in the stormwater or soil

could promote development of biogeochemical hotspots. The concept of biogeochemical hotspots refers to a zone of increased reaction rate relative to surrounding areas (McClain et al., 2003). There has been much focus on identification of hotspots at the terrestrial-aquatic interface where water plays both the role of affecting redox status and thus what reactions would be thermodynamically favored as well as the role of carrying in new substrates for transformation. Stream riparian areas have been traditionally seen as a hotspot given that they represent this sort of terrestrial-aquatic interface. Given the wide variety of nutrients and pollutants present in urban systems, SCMs could harbor biogeochemical hotspots for many processes. The type and magnitude of biogeochemical processes occurring is of interest because they control the fate of pollutants.

One nutrient of concern is nitrogen (N), given its role in promoting eutrophication of downstream waterbodies as well as being able to be transformed into a potent greenhouse gas (GHG), nitrous oxide (N_2O). A major source of N in urban environments includes vehicle exhaust and atmospheric deposition on impervious surfaces, particularly roads (Bettez et al., 2013; Bettez and Groffman, 2013). Fertilizers containing N are applied to some residential or commercial lawns and when applied in excess amounts or shortly before a storm event can provide a substantial N source. Leakage of septic or sanitary sewer systems and pet waste provide additional urban N sources (Kaushal et al., 2006).

Denitrification is a microbially mediated process which can remove excess nitrogen from urban soils or water by transforming reactive nitrate (NO_3^-) into inert dinitrogen gas (N_2) (Seitzinger et al., 2006). The conditions under which this transformation is promoted can be present in SCMs. Denitrification is favored under low oxygen concentrations, which often occur in areas of high soil moisture. As receptors of runoff during storm events, SCMs are likely to

have at least periodic increases in soil moisture. In addition to available NO_3^- , the process also requires a substrate to act as an electron donor, which is often carbon (Burgin and Hamilton, 2007). Organic carbon could be present in dissolved or particulate forms in storm runoff as well as in SCM soils.

Though denitrification can act as a beneficial water quality improvement process, it can also generate GHGs, which are a concern given their role in driving global climate change (Solomon et al., 2007). N_2O is produced as an intermediate in the denitrification pathway and may not always be reduced to N_2 gas. Controls on N_2O versus N_2 production can include soil oxygen status, where increased O_2 concentrations can drive increased N_2O emissions (Burgin and Groffman, 2012a). NO_3^- availability can also influence denitrification end products since NO_3^- is preferred over N_2O as an electron acceptor, and thus more N_2O can be produced under conditions when NO_3^- is in excess (Firestone et al., 1980). N_2O can also be generated as an intermediary of nitrification, in which ammonium (NH_4^+) is oxidized to NO_3^- (Firestone and Davidson, 1989). Nitrification occurs under oxic conditions (Firestone and Davidson, 1989); thus cycling between anoxic and oxic conditions could generate N_2O in SCMs. Given that N_2O has 298 times the warming potential of carbon dioxide (CO_2) (Solomon et al., 2007), it is critical to determine whether SCMs act as hotspots for emissions of this GHG.

Some of the same conditions which promote denitrification and N_2O emission could also make SCMs hotspots for other GHG-generating processes. Methanogenesis yields methane (CH_4), which has 25 times greater warming potential compared to CO_2 (Solomon et al., 2007). This process is favored under anoxic conditions and involves reduction of CO_2 or anaerobic respiration of organic carbon to create CH_4 (Schlesinger, 1997). Under oxic conditions, respiration of organic carbon generates CO_2 , another GHG (Schlesinger and Andrews, 2000).

CH₄ can also be oxidized under these conditions; thus this is another instance how cycling of SCMs between oxic and anoxic conditions could control GHG dynamics.

Though nutrient cycling and GHG emissions have been fairly well studied in many environments, there are still many gaps in our knowledge of their dynamics in urbanized systems. Previous research in urban areas has focused primarily on lawns (Byrne et al., 2008; Kaye et al., 2004; Raciti et al., 2011b) and urban forests (Groffman et al., 2009b; Groffman and Pouyat, 2009). Limited work has focused on nutrient cycling in SCMs. Research focusing on denitrification includes a study in Baltimore, Maryland which investigated potential denitrification in a range of traditional SCMs (Bettez and Groffman, 2012) and another study which surveyed the distribution of denitrification genes in a single stormwater basin (Chen et al., 2013). Another investigation using laboratory mesocosm SCM representations with varying plant compositions evaluated denitrification and N uptake and assimilation (Payne et al., 2014b). The only known study of GHG emissions from SCMs evaluated adjacent stormwater infiltration basins in the temperate coastal climate of Melbourne, Australia (Grover et al., 2013).

With the expansion of urban landscapes and increasing implementation of SCMs, it is important to understand whether they are hotspots for certain biogeochemical processes such as denitrification, GHG emissions or nutrient leaching. While some research studies have started to provide insight to some of these processes in certain SCMs, there are still many gaps in knowledge remaining, particularly with regards to how hydrologic conditions and nutrient availability influence the occurrence of these nutrient cycling processes. With the potential to alter the way that we plan and engineer urbanized landscapes, it is critical to determine how environmental, landscape or design factors influence these processes. This will allow us to

manage urban landscapes to maximize beneficial biogeochemical processes and minimize those which produce undesirable outcomes such as GHG production.

This dissertation research addresses these gaps through the following field-based investigations of nutrient cycling processes in multiple suburban landscape features:

- (1) Evaluation of hydrologic conditions as a control on denitrification and soil GHG emissions in stormwater detention basins with different drainage regimes
- (2) Evaluation of organic matter additions as a control on nutrient leaching and soil GHG emissions in a traditional grassed stormwater basin and a bioretention-style stormwater basin with compost-amended soil media, mulch and diverse plantings
- (3) Evaluation of hydrologic conditions and nutrient availability as controls on denitrification and soil GHG emissions in grassed roadside ditches and adjacent lawns with varying drainage patterns and fertilization regimes

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CHAPTER 2

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

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.

2.1. 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., 2001a).

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, 2012b; 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 basins in Melbourne, Australia (Grover et al., 2013). Bioretention systems expand on the typical wet or dry detention basin to include an infiltration zone and plants to stimulate soil microbial activity to provide overall better pollutant removal. The researchers found the basins to be slight sources of N_2O and sinks of CH_4 under most conditions, but observed pulses of both gases after

simulated rain events (Grover et al., 2013).

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

2.1.1. Objectives/ Hypotheses

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

2.2. Methods

2.2.1. Study site

The four stormwater basins (Figure 2.1a) 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 ((Northeast Regional Climate Center (NRCC), 2016). 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 2.1). 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 2.2) 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 2.1b). 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.

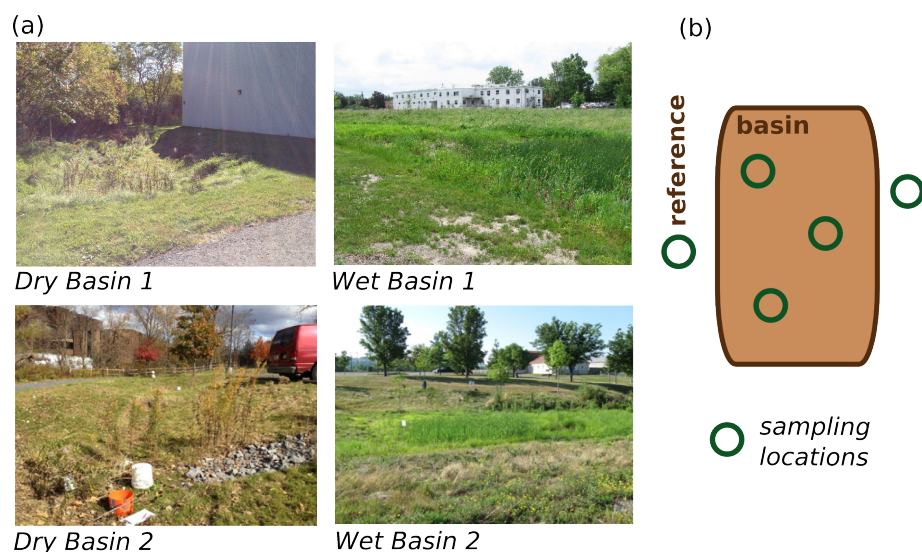


Figure 2.1. (a) Photographs of four stormwater detention basins and (b) layout of sampling locations used for soil and gas flux measurements

Table 2.1. 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

2.2.2. 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 (Northeast Regional Climate Center (NRCC), 2016). 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 N_2 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 N_2O and 20 ppm CH_4 (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 ($\mu\text{g gas m}^{-2} \text{ hr}^{-1}$) using the ideal gas law.

2.2.3. 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 NO_3^- -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 N_2 gas twice. 10 mL acetylene gas was added to each bottle to begin the assay, and inhibit production of N_2 from denitrification. 15 mL gas samples were taken from each bottle at 0, 20, 40 and 60 minute intervals and injected into pre-evacuated vials. Following each sample extraction, 15 mL N_2 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 N_2O concentration on the same gas chromatograph as described previously (section 2.2). N_2O fluxes were determined using the linear slope of the concentrations of the four time-points and converted to denitrification rates in $\text{mg N kg}^{-1} \text{ hr}^{-1}$ using the dry mass of the soil subsamples.

2.2.4. 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.

2.2.5. *Water quality sampling*

Inflowing stormwater was sampled at each of the four basins to characterize dissolved NO_x ($\text{NO}_3^- + \text{NO}_2^-$) 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 0.45 μm 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 NO_3^- and NO_2^- was performed on a Dionex ICS-2000 Ion Chromatograph with an IonPac AS-18 analytical column.

2.2.6. *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 2 cm

diameter and 5 cm deep 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

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

where LOI is % loss-on-ignition.

2.2.7. 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.

2.3. Results and Discussion

2.3.1. Soil conditions

Soil texture was the same across all basin and reference locations (loamy sand; Table 2.2). 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 2.2). Across all sites, soil OM was significantly positively correlated with VWC (Table 2.3), possibly due to decreased mineralization and subsequent accumulation of OM under wetter conditions (Bridgman 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 2.2: 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 2.3. Pearson correlation coefficients for measured variables at the four basin and four reference sites. For measurements made more than once throughout the year, average values were used in the analysis.

	N₂O μg N m ⁻² hr ⁻¹	CH₄ μg C m ⁻² hr ⁻¹	Denit. Potential mg N kg ⁻¹ hr ⁻¹	Soil VWC vol ⁻¹ vol ⁻¹	OM %
N₂O					
CH₄	-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

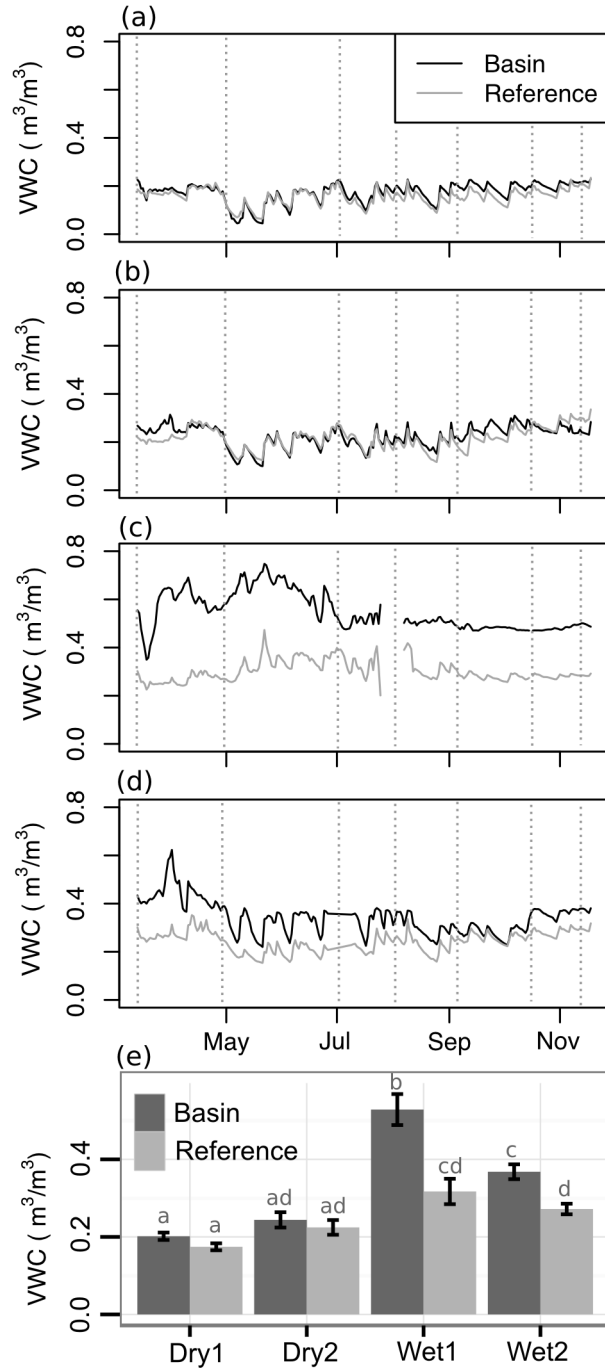


Figure 2.2. Volumetric water content (VWC; $\text{m}^3 \text{ m}^{-3}$) during the 2013 sampling period for (a) Dry Basin 1, (b) Dry Basin 2, (c) Wet Basin 1 and (d) Wet Basin 2. Vertical dotted lines indicate dates on which GHG fluxes were measured. A barplot of average VWC (e) is shown for all sites, for the dates when GHG fluxes were measured. Error bars represent standard error. Letters indicate which sites are significantly ($p < 0.05$) different than each other based on statistical tests.

2.3.2. Greenhouse gas emissions

2.3.2.1. Nitrous Oxide

N₂O fluxes were low across all basin and reference sites (Table 2.4) 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 2.3). 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 2.3). 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 2.2), 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 2.2), 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 basins 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. Mean N₂O emissions for all basins (4.6 $\mu\text{g N m}^{-2} \text{ hr}^{-1}$) were higher than the mean emissions in forested riparian wetlands in upstate New York 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., 2009b; Raciti et al., 2011a). Higher emissions have been observed in fertilized lawns, up to 720 $\mu\text{g N m}^{-2} \text{ hr}^{-1}$ (Townsend-Small and Czimeczik, 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 2.4: 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 μg N m ⁻² hr ⁻¹	CH ₄ Flux μg 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

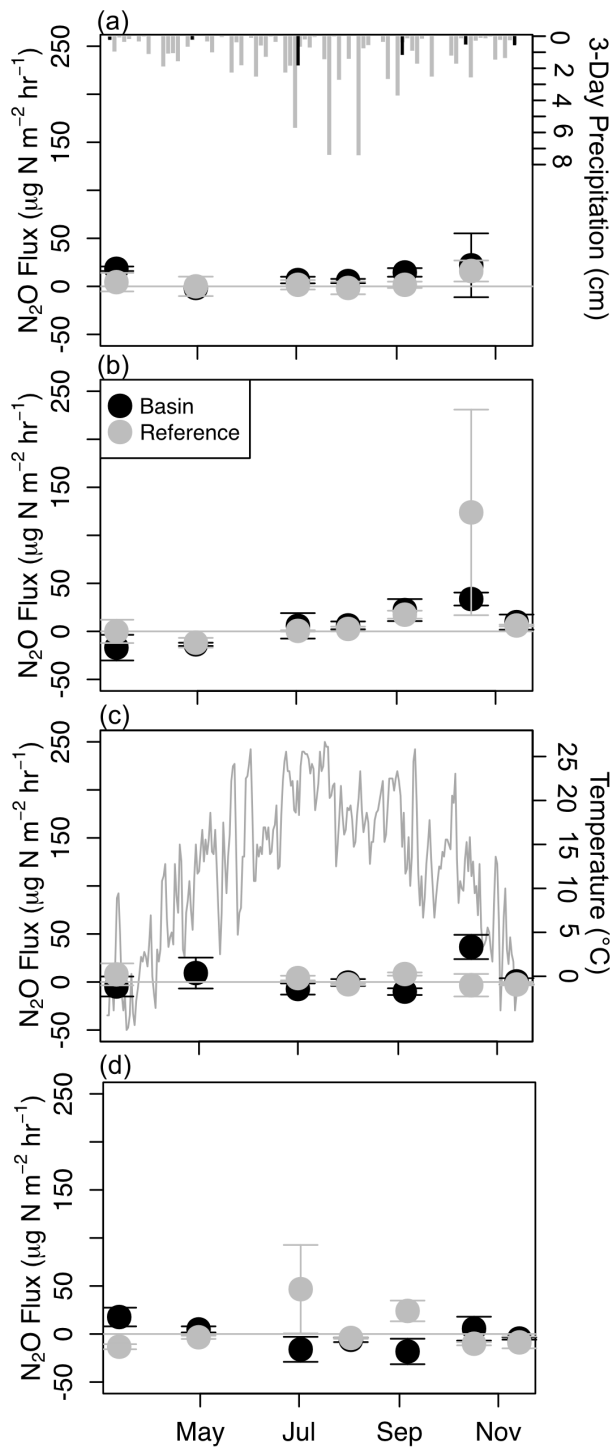


Figure 2.3: N_2O fluxes for seven measurement points in 2013 at (a) Dry Basin 1, (b) Dry Basin 2, (c) Wet Basin 1, and (d) Wet Basin 2. 3-day averaged precipitation (a) and daily air temperature (c) obtained from a campus weather station are also shown. 3-day precipitation prior to gas flux sampling is indicated as black bars (a).

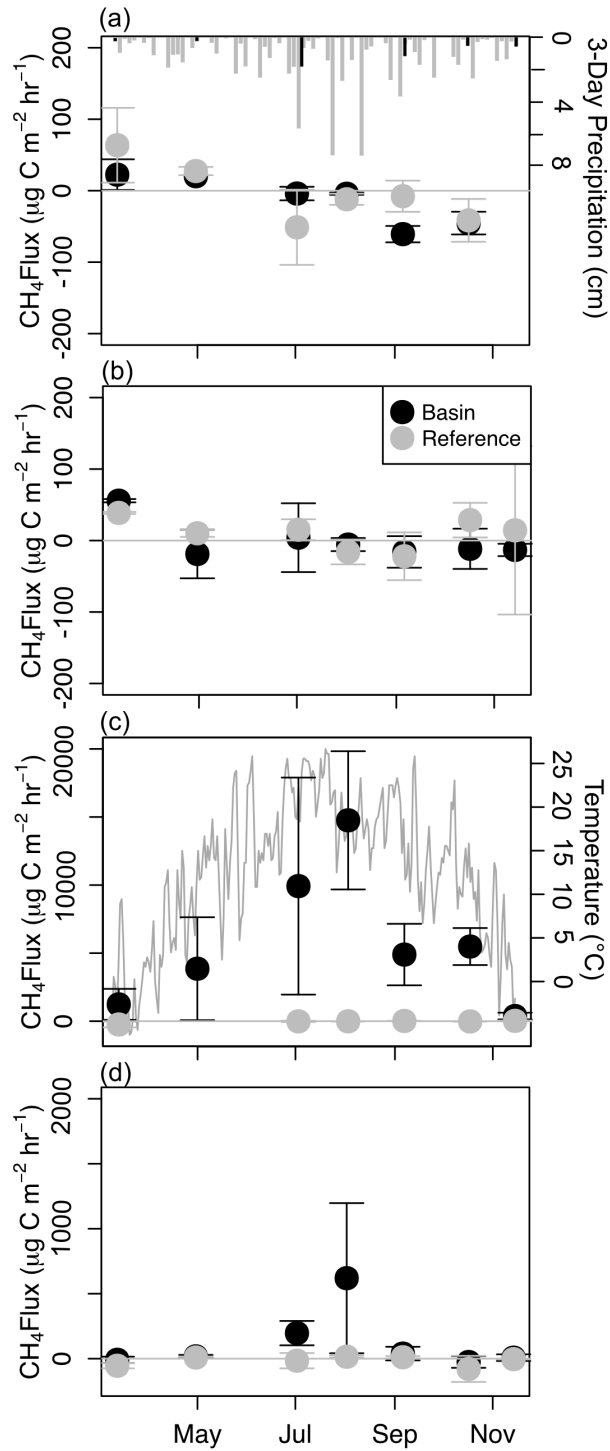


Figure 2.4: CH₄ fluxes for seven measurement points in 2013 at (a) Dry Basin 1, (b) Dry Basin 2, (c) Wet Basin 1, and (d) Wet Basin 2. 3-day averaged precipitation (a) and daily air temperature (c) obtained from a campus weather station are also shown. 3-day precipitation prior to gas flux sampling is indicated as black bars (a)

2.3.2.2. Methane

CH₄ fluxes were low across the dry basins (Table 2.4) 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 2.4a). 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 2.4c), 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 2.4d) 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 basins 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 CH_4 fluxes (Table 2.3). Additionally, soil OM was significantly positively related to CH_4 fluxes, consistent with the function of OM as the substrate that is transformed by microbes to generate CH_4 .

2.3.3. Denitrification

Potential denitrification was significantly higher ($p < 0.05$) within each of the wet basins compared to either dry basin (Figure 2.5; Table 2.4). 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 2.3). 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 2.3). 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 2.3.

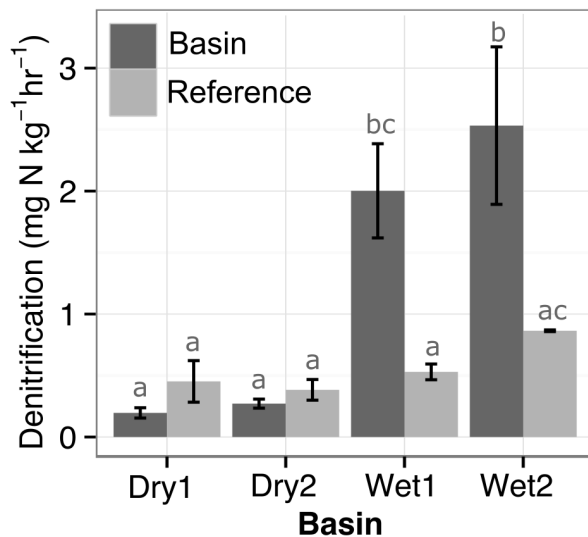


Figure 2.5: Denitrification potential ($\text{mg N kg soil}^{-1} \text{ hr}^{-1}$) for soils within each basin and at reference locations directly outside of basins. Error bars denote standard error. Superscripted letters indicate which sites are significantly ($p < 0.05$) different than each other based 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 ($1.2 \text{ mg N kg soil}^{-1} \text{ hr}^{-1}$), where

overall climate is similar to that of our study (Bettez and Groffman, 2012). Slightly lower average rates of $0.74 \text{ mg N kg soil}^{-1} \text{ hr}^{-1}$ were measured in grassed dry detention basins in Arizona; grassed city parks in the same system also had an average rate of $0.74 \text{ mg N kg soil}^{-1} \text{ hr}^{-1}$ (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., 2014b). 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.

2.3.4 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., 2014c). 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 basin with a subsurface saturated zone was included in Grover et al.'s (2013) study, in which they observed minimal CH_4 emissions, but also elevated N_2O 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). 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.

2.4. 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. CH₄ 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.

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CHAPTER 3

Nutrient leaching and greenhouse gas emissions in grassed detention and bioretention stormwater basins

Abstract

Stormwater detention basins are increasingly implemented to manage storm runoff from impervious surfaces. Historically, the design objectives have been to dampen storm pulses and remove sediment and associated pollutants (e.g. metals). Managing nutrients has not often been a design priority, though excess nutrients can contribute to downstream eutrophication and greenhouse gas (GHG) production. We compared a grassed detention basin and a bioretention basin that has been amended with compost, mulch, and diverse plantings. We monitored concentrations of dissolved nitrogen (N), phosphorus (P), and carbon (C) in basin inflows and outflows as well as emissions of greenhouse gases methane (CH₄), carbon dioxide (CO₂) and nitrous oxide (N₂O) from basin soils during 2014 and 2015. Though these basins are intended to improve storm runoff quality, we found that the bioretention basin was a source of nitrate + nitrite (NO_x), soluble reactive phosphorus (SRP) and dissolved organic carbon (DOC). The SRP and DOC leaching was driven by high P and C content of the bioretention soil media and NO_x leaching was driven by the low C:N of added compost. Emissions of N₂O and CH₄ were overall low from both basins, though there were periodically high N₂O emission rates at both sites, reaching 133 µg N m⁻² hr⁻¹. CO₂ emissions (average= 368 mg C m⁻² hr⁻¹) were greater from the bioretention basin, where soil C content was greater. Based on these results, bioretention basin design should minimize OM additions to soil media and choose OM with high C:N (>20) and low P content in order to minimize availability of excess nutrients for leaching or GHG production.

3.1. Introduction

Over the last two decades, stormwater management practices have been increasingly implemented to mitigate flooding and water quality issues associated with urbanization. These practices are intended to intercept and detain stormwater for a period of time, and provide some water quality treatment through physical and/or biological means (Davis and McCuen, 2005). Traditionally, these structures have included stormwater ponds and wetlands or grassed detention basins. Over time, designs have diversified to meet additional needs, such as having smaller or differently shaped footprints, having improved remediation capabilities for certain pollutants, or providing other ecosystem services.

Bioretention systems, also known as biofiltration systems, have become a popular stormwater management practice. Originating in Maryland USA in the mid-1990's, they typically include a sand or soil-based media with some organic matter (OM) amendment, a surface mulch layer, and a diverse suite of vegetation. These systems are intended to provide both physical and biological remediation of pollutants, with soil media promoting physical filtration and sorption and microbial metabolism of pollutants and plants providing water and pollutant uptake (Roy-Poirier et al., 2010; Liu et al., 2014). Features like diverse vegetation may also be providing additional ecosystem services beyond runoff reduction and water quality improvement such as pollinator habitat (Lundholm, 2015; Salisbury et al., 2015). Typically, these systems are underlaid by an underdrain, which routes infiltrated runoff into the storm sewer system.

Numerous studies have been performed on field installations of bioretention systems or laboratory mesocosm or column representations, in order to evaluate hydrologic and water

quality performance. Greater than 90% reduction in concentration and/or load of sediment and heavy metals (including copper, lead, and zinc) in stormwater inflows has consistently been observed in field and lab settings (Davis et al., 2001a, 2003; Hatt et al., 2009; Hsieh and Davis, 2005). Nutrient removal performance has been less consistent. While some studies have observed phosphorus (P) retention, others have noted increases in total P concentrations in bioretention outflow (Chahal et al., 2016; DeBusk and Wynn, 2011; Hatt et al., 2009; Hunt et al., 2006). Nitrogen (N) removal performance has also varied, particularly with regards to different species. Increased concentrations of nitrate (NO_3^-) in bioretention outflows relative to inflows have been observed in multiple cases (Chahal et al., 2016; Davis et al., 2001b; Hatt et al., 2009) while both release and retention have been observed for total N and ammonium (NH_4^+) (Davis et al., 2001b; Hsieh and Davis, 2005; Hunt et al., 2006). In some cases where increases in concentration of N and/or P were observed, there were still overall reductions in exported loads due to substantial (>50%) decreases in flow between the basin inlet and underdrain outflow (Hunt et al., 2006; DeBusk and Wynn, 2011).

If bioretention systems are indeed contributing N and/or P, especially as bioavailable forms such as NO_3^- , NH_4^+ or dissolved P to downstream water bodies, they are exacerbating issues of nutrient pollution and eutrophication (e.g. Smith et al., 1999). Additionally, availability of excess nutrients, primarily N and carbon (C), can also lead to production of greenhouse gases (GHGs). N_2O , a GHG with 298 times the global warming potential of CO_2 (Solomon et al., 2007), can be produced through two major microbially-mediated pathways. Reduction of NO_3^- to N_2O can occur during denitrification and N_2O can also be produced during the nitrification of NH_4^+ to NO_3^- (Firestone and Davidson, 1989). Additionally, C in inflowing stormwater or in basin media can be microbially transformed during methanogenesis to CH_4 , a GHG with 25

times the warming potential of CO₂ (Solomon et al., 2007), and CO₂ can also be produced through autotrophic and heterotrophic respiration processes (Schlesinger, 1997).

At this time, there has only been one study of GHG emissions in bioretention systems. In a field evaluation of two bioretention basins in Melbourne, Australia, GHG emissions were found to be similar to those from urban soils or lawns. However, there were periodic ‘hot moments’ of N₂O and CH₄ emissions following precipitation events (Grover et al., 2013).

As bioretention systems continue to be implemented, it is important to understand their nutrient dynamics and how we can better design these systems to maximize beneficial services like pollutant removal and minimize detrimental functions such as nutrient leaching and GHG emissions. With differing organic matter additions and vegetation compared to grassed detention basins, there may be differences in nutrient cycling in these two design approaches. However, there is a lack of field investigations directly comparing function of different types of stormwater management practices. Additionally, since most field studies only include one or two stormwater management practices given the expense of monitoring, there is still a need to build the overall body of knowledge on biogeochemical function of these structures. Here we provide a field evaluation of nutrient cycling in a grassed detention basin and a retrofitted bioretention basin. In each, we collected data on export of dissolved nutrients as well as emission of GHGs from basin soils. We complemented these data with soil assessment to further understand controls on the nutrient cycling processes of interest.

3.2. Methods

3.2.1. *Experimental set-up*

The two stormwater basins were located on the Cornell University campus in Ithaca, New

York USA (Figure 3.1a & b; Table 3.1). This region is characterized by a temperate climate, with an average temperature of 8.1°C and annual average precipitation of 947 mm (Northeast Regional Climate Center (NRCC), 2016). Both basins were originally designed as dry detention basins in 2005 and 2007 and were planted with turfgrass (primarily perennial ryegrass- *Lolium perenne*) which is regularly mowed. The basins had 10-15 cm topsoil which was underlain by native silt loam in the sloped portions of the basins and 46 cm of sand along the bottom of the basins. Below the sand was an underdrain (perforated pipe) that connected to the campus storm sewer system and was intended to route water away from the basin during periods of saturation. Both basins were intended to drain within approximately 24 hours.

In April 2014, one basin was modified to the style of a bioretention system by horticultural students as part of a class project (Figure 3.1b). The modification included the tilling of the existing turfgrass and top ~38 cm of soil. This soil was then amended with 15 cm of organic matter which consisted of a compost mix (nutrient specifications in Table A1) obtained from the Cornell Grounds Department. The organic matter was incorporated to ~38 cm depth. The basin was planted with a mix of perennial shrubs, with the most abundant types including *Forsythia*, *Rosa rugosa* and *Spiraea japonica*. A full list of plantings is available in Appendix Table A2. A layer of woody mulch was added to the soil surface and this mulch was refreshed in spring 2015 as well. Beginning in late May 2014, both the modified basin and grassed basin were monitored for soil greenhouse gas emissions, soil nutrients, and stormwater inflows and outflow water quality.

Table 3.1. Basin design characteristics

	Basin Area (m²)	Watershed Area (m²)	Watershed Area: Basin Area	Year Built	Year Modified
Grassed	260	2300	8.8	2007	n/a
Bioretention	400	2100	5.3	2005	2014



Figure 3.1. The grassed detention basin (a), bioretention basin (b), and schematic of greenhouse gas, soil, and water sampling in the basins (c)

3.2.2. *Water quality assessment*

Stormwater was sampled from the inlet and outlet of both detention basins (Figure 3.1c) over seven occasions between May and August 2014 and 2015. Samples were only retrieved when water was flowing from the inlet and outlet in both basins. For the seven sampling dates, there were 1.02 to 5.13 cm of daily precipitation and all but one date had at least 2.54 cm of precipitation over the three day period up to and including the sampling date (Figure 3.2a). Samples were obtained manually from the stone spillway inlets and underdrain catch basin outlets using 125 mL HDPE bottles and each was taken in replicate. The water was immediately filtered using 0.45 μ m Pall mixed cellulose ester filters and filtrate was stored at 4°C until analysis. Analysis of NO_3^- , NO_2^- , and Cl^- was performed on a Dionex ICS-2000 Ion Chromatograph with an IonPac AS-18 analytical column. Analysis of soluble reactive phosphorus (SRP) was performed on an OI Analytical Phosphorus Analyzer Model 3000. Analysis of NH_4^+ was performed on a Lachat QuikChem 8000 Flow Injection Analyzer using the salicylate method. Analysis of dissolved organic carbon (DOC) was performed on an OI Analytical Total Carbon Analyzer Model 1010. Stormwater flow was not measured as part of this study, but ambient Cl^- was used as a tracer to determine whether there was an increase in dissolved nutrient loads in basin outflow relative to inflow for both study basins.

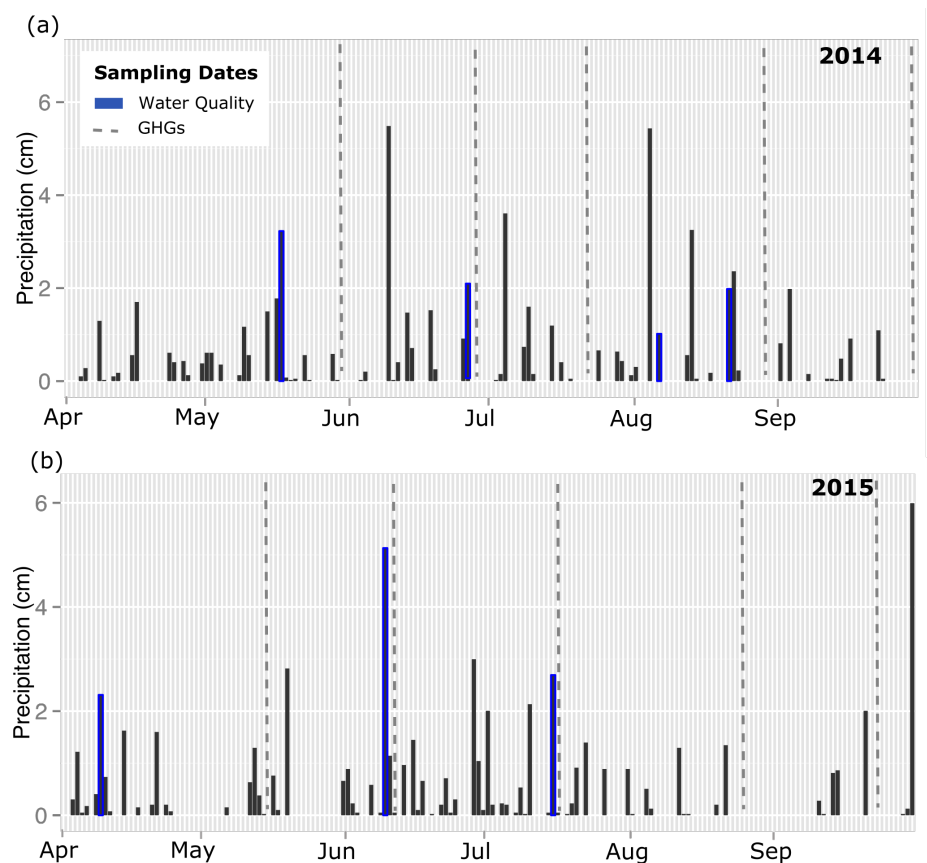


Figure 3.2. Daily precipitation during the (a) 2014 and (b) 2015 sampling periods. Sampling dates for water quality are indicated by the blue precipitation bars and sampling dates for GHGs are indicated by the grey dotted lines

3.2.3. Greenhouse gas emissions

Soil greenhouse gas fluxes were measured at three locations within each basin and two reference locations directly outside of each basin (Figure 3.1c). The outside locations provided references where the soil media was the same as within the basin itself, but which did not receive the same inputs of stormwater and nutrients as the basin. Flux measurements were made monthly between late May 2014 and September 2014 and between late May 2015 and September 2015 (n=10). Fluxes were over the same time period for the two years in order to assess whether there were any differences in emissions between the two years. N_2O and CH_4 were measured during 2014 and 2015, while CO_2 was only measured during 2015 (n=5). Average air temperature for

the ten dates ranged from 5.0 to 21.1°C and precipitation in the three preceding days for each measurement date ranged from 0 to 6.3 cm (Figure 3.2b).

Fluxes were measured using *in situ* static chambers which were 30 cm in diameter and constructed using two opaque 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. A 5 cm wide rubber band was placed around each chamber base, and the bases were installed prior to the gas flux measurement, taking care to minimize soil disturbance. 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 N₂O and CH₄ using an Agilent 6890N gas chromatograph equipped with a HP 7694 Headspace Autosampler (Hewlett-Packard Co.). N₂O separation was performed using a Supel-Q™ PLOT capillary column (Supelco Inc.) and a μ ECD (electron capture detector). CH₄ separation was performed using a Carboxen 1006 PLOT capillary column (Supelco, Inc.) and an FID (flame ionization detector). CO₂ was analyzed with the gas chromatograph FID after installation of a methanizer in 2015. Calibration curves were made using a series of standard gas mixes (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 (μ g

gas $\text{m}^{-2} \text{hr}^{-1}$) using the ideal gas law.

At the time of gas sampling, field measurements were also made to characterize soil conditions at each of the basin and reference sampling locations. A digital thermometer was used to record soil temperature. Soil moisture was assessed as volumetric water content (VWC) using a Campbell Scientific Hydrosense II probe.

3.2.4. *Soil nutrient analysis*

Soils from basin and reference sampling sites were analyzed for nutrient content. Organic matter concentration was quantified via loss-on-ignition at 500°C for 2 hours (Ferguson and Swenson, n.d.). Total carbon and nitrogen were analyzed using an Elementar Vario EL Cube elemental analyzer on samples dried at 105°C and ground and sieved $<2\text{mm}$. Extractable soil NO_x and NH_4^+ were assessed on fresh soil samples with gravel removed using a 1 M KCl extraction (Robertson et al., 1999) where NO_x and NH_4^+ were analyzed on a Lachat QuikChem 8000 Flow Injection Analyzer. Extractable phosphorus was evaluated using a Mehlich-3 extraction on field moist soil and organic matter samples (Sims et al., 2002). Extractant was analyzed for phosphorus concentration on an OI Analytical Phosphorus Analyzer Model 3000.

3.2.5. *Statistical analysis*

Statistical analyses were conducted in R v. 3.1.3. (The R Project for Statistical Computing). For both gas and water samples, replicate samples at each site were averaged for all analyses. One-way analysis of variance (ANOVA) with Tukey honestly significant difference (HSD) pairwise comparison was used to assess differences between inflow and outflow at both sites for all water quality constituents and for soil nutrient content at both basin and reference

sites. One-way ANOVA with repeated measures was used to assess differences between GHG fluxes across all sites and dates. If GHG flux distribution was not normal, lognormal transformation was applied prior to use of ANOVA. Temperature and moisture effects on GHG fluxes were assessed using linear mixed effects models (R package lme4) in which sites were treated as a random effect to account for having multiple timepoints from each site. Results were considered significant for p-values less than 0.05.

3.3. Results

3.3.1. *Greenhouse gas emissions*

Across both basins and reference sites, there were no significant differences in fluxes of N₂O or CH₄ over the sampling period (Figure 3.3a & b). Average N₂O flux was 13.1 and 23.4 $\mu\text{g N m}^{-2} \text{ hr}^{-1}$ in the grassed and bioretention basins, respectively (Table A3). Periodic pulses of higher N₂O emissions occurred at all sites, with these ‘hot moments’ generally occurring in late spring. The highest emission of 152.4 $\mu\text{g N m}^{-2} \text{ hr}^{-1}$ occurred at the grassed reference in May 2014 while the next highest emissions of 133.4 and 125.0 $\mu\text{g N m}^{-2} \text{ hr}^{-1}$ occurred at the grassed and bioretention basins, respectively, in May 2015. Average CH₄ flux was 18.9 and 45.4 $\mu\text{g C m}^{-2} \text{ hr}^{-1}$ in the grassed and bioretention basins, respectively (Table A2). As with N₂O, there were periodic pulses of CH₄. The five highest emissions occurred in May and June 2014, included all four basin and reference sites, and ranged from 161.9 to 1422.0 $\mu\text{g C m}^{-2} \text{ hr}^{-1}$. Given that CH₄ pulses occurred at all sites, the emissions were likely linked to overall wetter conditions due to lingering effects of snowmelt and spring precipitation. However, linear mixed effects models did not indicate any significant relationship between soil moisture and CH₄. There were no differences in fluxes of either N₂O or CH₄ at a given site between 2014 and 2015. CO₂ fluxes

were significantly higher at the bioretention basin (average= 367.9 mg C m⁻² hr⁻¹; Figure 3.3c, Table A2) compared to the grassed basin and reference (average=198.5 and 130.5 mg C m⁻² hr⁻¹). The highest CO₂ emissions during the May to September 2015 measurement period occurred during May and June 2015, peaking at 904.8 mg C m⁻² hr⁻¹ in the bioretention basin.

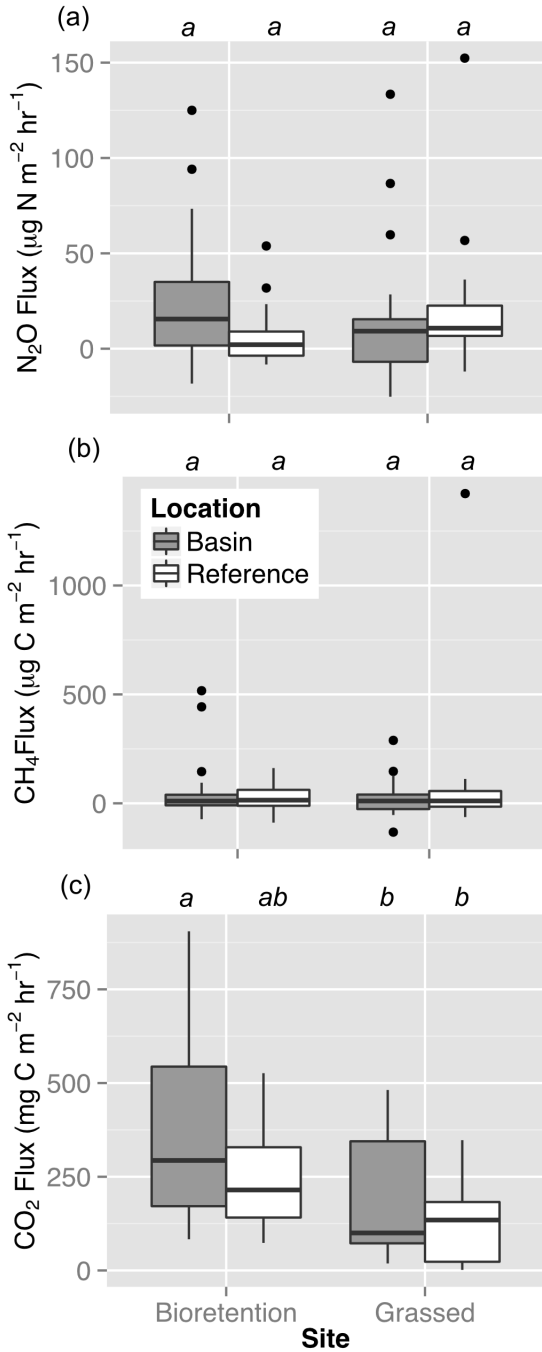


Figure 3.3. Boxplots of (a) CH_4 , (b) N_2O , and (c) CO_2 fluxes for the grassed and bioretention basins and reference sites across all sampling dates. Horizontal black lines show the data median, the box boundaries mark the first and third quartiles, the whiskers indicate 1.5 times the interquartile range, and the points represent extreme values. Italicized letters denote statistical significance.

3.3.2. Water quality

Trends in water quality varied by constituent. Average NH_4^+ outflow concentration was

roughly half that of inflow at both basins (~ 0.04 vs. 0.08 mg N L^{-1} ; Figure 3.4a, Table A4); however inflow and outflow concentrations over the sampling period were not statistically different. Average NO_x outflow concentration was several times higher than inflow concentration at both basins, but the difference was only significant at the bioretention basin (Figure 3.4b). The highest NO_x concentrations were observed at the first outflow sample for the bioretention basin in May 2014, averaging 4.5 mg N L^{-1} (Table A4). For the grassed basin, both SRP and DOC concentrations were similar in the inflow and outflow, but the bioretention basin exhibited significantly higher outflow concentrations (average SRP = 1.53 mg L^{-1} and DOC = 14.5 mg L^{-1} ; Table A3) relative to inflow (Figure 3.4c & d). The highest SRP concentrations occurred in the first sample of both 2014 and 2015 at the bioretention basin outflow, averaging 1.96 and 3.46 mg P L^{-1} . The highest DOC concentration occurred in the first outflow sample for the bioretention basin in May 2014, averaging 35.5 mg C L^{-1} .

Examining nutrient concentrations relative to Cl, the two basins exhibited different patterns (Figure 3.5). The grassed basin consistently had lower ratios of NO_x to Cl and SRP to Cl in outflow compared to inflow, indicating a net loss of NO_x and SRP relative to Cl. The bioretention basin had higher ratios of NO_x to Cl, indicating a net gain of NO_x and SRP relative to Cl.

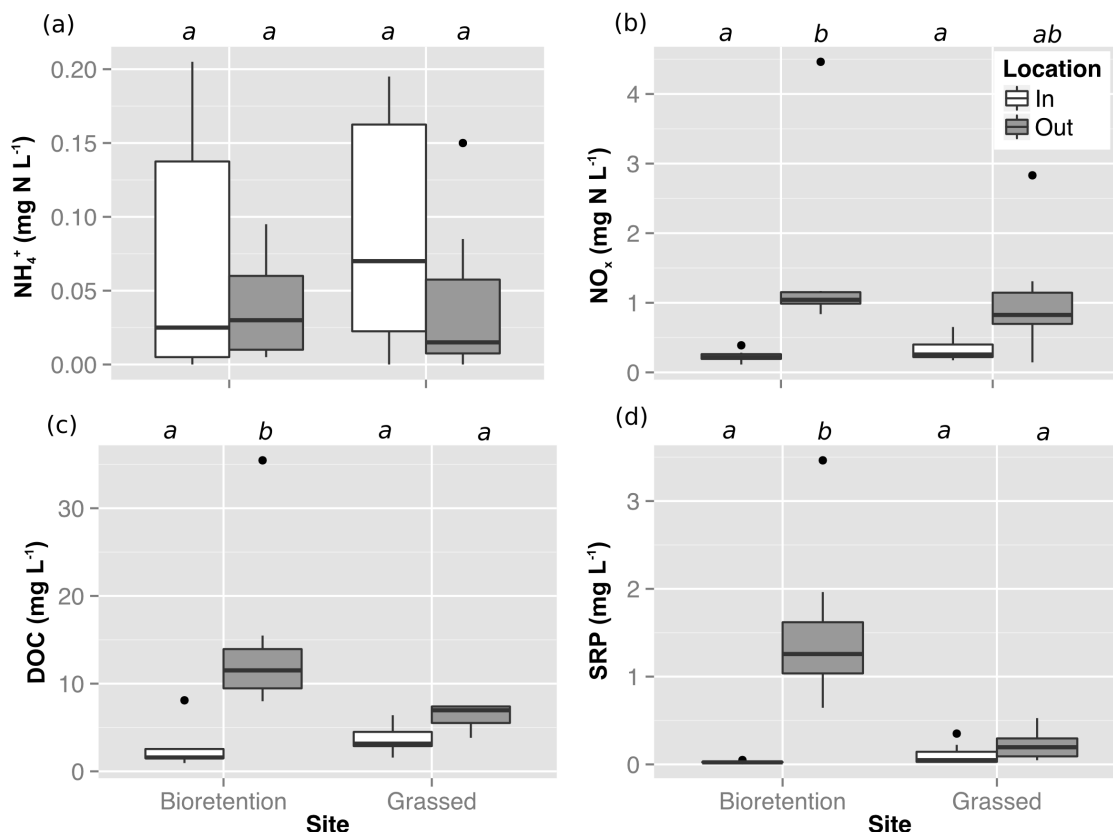


Figure 3.4. Boxplots of (a) NH_4^+ , (b) NO_x , (c) DOC, and (d) SRP inflow and outflow concentrations for the grassed and bioretention basins across all sampling dates ($n=7$). Horizontal black lines show the data median, the box boundaries mark the first and third quartiles, the whiskers indicate 1.5 times the interquartile range, and the points represent extreme values. Italicized letters denote statistical significance between inflow and outflow concentrations.

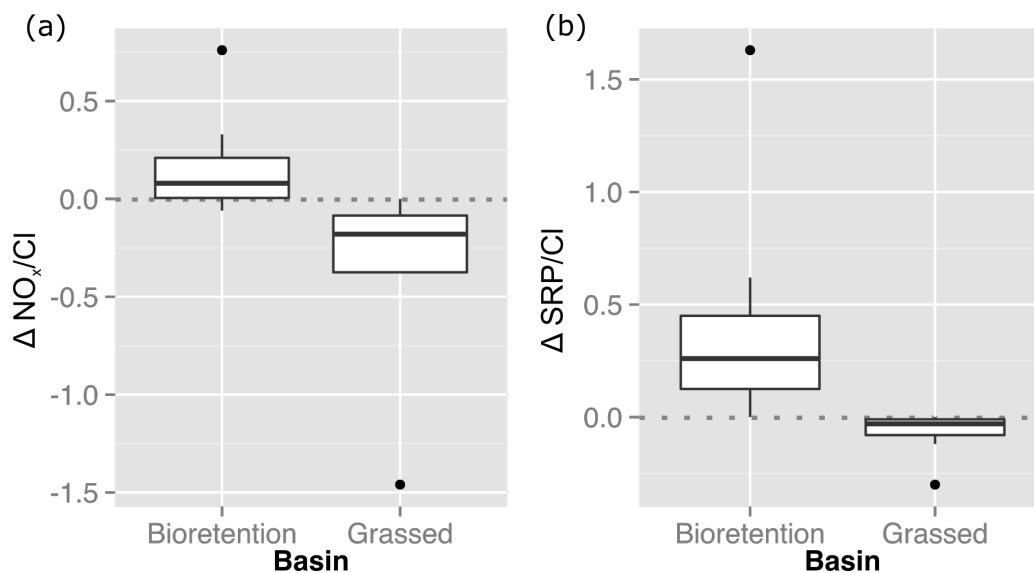


Figure 3.5. (a) NO_x and (b) SRP concentrations relative to CI for seven stormwater sampling events at both basins. Δ represents the difference between outflow and inflow chemistry.

3.3.3. Soil analysis

Average soil nutrient content was higher in both the bioretention reference and basin soils when compared to the grassed reference and basin soils (Table 3.2). Mehlich-3 P was significantly higher at the bioretention basin and reference compared to the grassed basin; there was not a significant difference compared to the grassed reference due to considerable variability in P between the reference locations sampled around the basin. Soil C, N, and OM content were higher at the bioretention basin and reference, but the difference compared to the grassed sites was not significant. However, the ratio of C to N (C:N) was significantly higher at both the bioretention reference and basin when compared to the grassed reference and basin.

Table 3.2. Average basin soil characteristics. Superscripted letters indicate which sites are significantly ($p < 0.05$) different than each other based on statistical tests.

		OM (%)	C (%)	N (%)	C:N	NO ₃ ⁻ (mg kg ⁻¹)	NH ₄ ⁺ (mg kg ⁻¹)	Mehlich-3 P (mg kg ⁻¹)
Grassed	Basin	7.5 ^a	6.58 ^a	0.38 ^a	17.6 ^a	4.3 ^a	4.7 ^a	156.1 ^a
	Reference	6.9 ^a	5.90 ^a	0.37 ^a	16.1 ^a	6.4 ^a	7.9 ^a	280.1 ^{ab}
Bio retention	Basin	13.8 ^a	12.12 ^a	0.55 ^a	21.8 ^b	4.7 ^a	10.0 ^a	410.2 ^b
	Reference	12.2 ^a	9.78 ^a	0.44 ^a	22.6 ^b	1.9 ^a	2.8 ^a	433.7 ^b

3.4. Discussion

3.4.1. Greenhouse gas emissions

These results showed a lack of difference in N₂O and CH₄ emissions between the grassed and bioretention basins and their respective reference sites. The overall magnitude of fluxes was similar to those documented in other urban features. For N₂O, average emissions resembled those in other bioretention basins (13.7 and 65.6 µg N m⁻² hr⁻¹ for two basins; Grover et al., 2013), lawns (17-28 µg N m⁻² hr⁻¹ depending on fertilization and irrigation treatments) and

mulched garden beds ($14 \mu\text{g N m}^{-2} \text{ hr}^{-1}$; Livesley et al., 2010) in Melbourne, Australia. Average emissions were slightly higher than observations in lawns in the western United States ($10 \mu\text{g N m}^{-2} \text{ hr}^{-1}$; Kaye et al., 2004; Townsend-Small and Czimeczik, 2010) and in other dry grassed ($9.5 \mu\text{g N m}^{-2} \text{ hr}^{-1}$) and wet grassed ($0.5 \mu\text{g N m}^{-2} \text{ hr}^{-1}$) detention basins in upstate New York (McPhillips and Walter, 2015). However, maximum N_2O emissions in this study were lower than those observed in most of these other investigations, which were often several hundred to $1100 \mu\text{g N m}^{-2} \text{ hr}^{-1}$. Recent rain (Grover et al., 2013) or fertilization events (Townsend-Small and Czimeczik, 2010) were indicated as drivers of these elevated emissions. In our study, precipitation does not appear to be the primary driver of the May N_2O pulses, as three day antecedent precipitation was 0.6 and 1.7 cm for the May 2014 and 2015 dates respectively. Nutrient availability likely instigated the pulses of N_2O emissions. Fertilization may have played a role, since fertilizer is periodically applied to adjacent campus lawns. Spring pulses of N_2O have also been linked to post-thaw increases in nutrient availability and subsequent microbial activity (Wagner-Riddle et al., 2008).

CH_4 emissions in the grassed and bioretention basins were somewhat higher than average fluxes in some urban lawns (Groffman and Pouyat, 2009; Kaye et al., 2004; Livesley et al., 2010) and well-draining bioretention (Grover et al., 2013) or grassed detention basins (McPhillips and Walter, 2015). Average fluxes in these investigations were all were negative, indicating CH_4 uptake. Emissions in this study were much lower than those in wetter stormwater features, such as wet detention basins ($2755 \mu\text{g C m}^{-2} \text{ hr}^{-1}$; McPhillips and Walter, 2015), grassed road ditches ($625 \mu\text{g C m}^{-2} \text{ hr}^{-1}$; McPhillips et al., In Prep), and stormwater ponds ($53592 \mu\text{g C m}^{-2} \text{ hr}^{-1}$; Sims et al., 2013). Average CH_4 emissions were most similar to those observed from a study of urban lawns in central New York, which also occurred over 2014-2015 (McPhillips et

al., In Prep). Average soil moisture in these lawns (41% VWC) was similar to moisture levels in this study (30.0-34.4% VWC for the four sites), whereas soil moisture in the other lawn studies ranged from around 10-40% VWC (Groffman and Pouyat, 2009; Livesley et al., 2010). Thus CH₄ fluxes here were most similar to the wetter lawns and much less than wet stormwater basins, likely because of broadly similar conditions of soil moisture and oxygen levels, which are major influences on methanogenesis and methane oxidation (Walter and Heimann, 2000).

CO₂ was the only GHG that differed significantly across sites, with the bioretention basin having overall higher CO₂ emissions than the grassed basin and reference. Fluxes from the grassed basin and reference were similar to average fluxes in two bioretention basins in the temperate coastal environment of Melbourne, Australia (98.3 and 102.2 mg C m⁻² hr⁻¹; Grover et al., 2013) and lawns in central New York (151.0 mg C m⁻² hr⁻¹; McPhillips et al., In Prep) and eastern Massachusetts (194.1 mg C m⁻² hr⁻¹; Decina et al., 2016). The higher CO₂ emissions measured in our bioretention basin were more similar to average emissions from mulched garden beds in Melbourne (~360 mg C m⁻² hr⁻¹; Livesley et al., 2010) and landscaped cover in residential areas in eastern Massachusetts (291.0 mg C m⁻² hr⁻¹; Decina et al., 2016). The higher emissions in the bioretention sites corresponded to higher soil OM and C contents relative to the grassed sites (Table 3.2) which follows previously described positive correlations between C substrate availability and soil respiration (Wang et al., 2003) and between respiration and C to N ratios (Gödde et al., 1996). Despite increased CO₂ emissions with the increased organic matter content in the bioretention basin, this organic matter serves additional purposes, such as supplying plants with nutrients, decreasing soil bulk density and promoting sorption of metals (Hunt et al., 2012). Additionally, this study did not examine C sequestration in these basins, which has the potential to offset these CO₂ emissions from respiration. Primary production of the

woody shrubs in the bioretention basin has the potential to exceed that of the turfgrass ecosystem of the grassed detention basin (Jo and McPherson, 1995). Annual inputs of new woody mulch to the bioretention basin may further increase potential for C retention in basin soils.

3.4.2. *Water quality*

NO_3^- is viewed as a challenging pollutant with regards to stormwater management. It can be generated *in situ* in treatment structures from mineralization of organic N and nitrification of NH_4^+ and its removal depends on the biological processes of plant uptake or denitrification to N gases (Payne et al., 2014a). Previous field investigations of bioretention cells in the eastern and central United States and Melbourne, Australia have documented mediocre success in reducing NO_3^- concentrations. In these studies, average NO_x concentrations in outflow were similar to or slightly reduced relative to inflows (Hsieh and Davis, 2005; Hunt et al., 2006; Hatt et al., 2009; Chen et al., 2013), although increases in NO_x from inflow to basin outflow were observed in some individual storm events (Hatt et al., 2009). In the grassed and bioretention basins in this study, NO_x concentrations consistently increased from inflow to outflow.

While average inflow NO_x concentrations (grassed = 0.33 mg N L^{-1} , bioretention = 0.23 mg N L^{-1}) were similar to those in previous bioretention studies, outflow concentrations were consistently higher for both of our basins. Outflow concentrations sometimes exceeded 1 mg N L^{-1} , particularly in the bioretention basin. One main source of NO_x was likely to have been mineralization and nitrification of soil media, particularly in the bioretention basin where soil N concentration was somewhat higher. The low C:N of the added compost (14.3) would have promoted net mineralization of N, according to stoichiometric constraints on microbial nutrient cycling (Chapin et al., 2011). The very high initial NO_x outflow concentration at the bioretention

basin can be explained by mineralization of labile fine organic N present from the addition of compost during the re-design of this basin in the prior month. This is supported by high concentrations of SRP and DOC also observed in this same May 2014 sample. Additional NO_x in this initial outflow may have come from mineralization and nitrification of turfgrass, given that the grass originally growing in the basin was tilled under when the compost was added in spring 2014. In the grassed basin, the majority of NO_x in outflow likely came from mineralization and nitrification of soil organic matter during the dormant season. There also may have been inorganic N application as fertilizer periodically to adjacent campus lawns, but data are unavailable to confirm this; although, extractable NO_3^- and NH_4^+ were both high in the adjacent grassed reference (Table 3.2).

Trends in SRP in our basins largely resembled those observed in other stormwater field studies, where increases in concentration between inflow and outflow- sometimes by several hundred percent- have often been observed (Hatt et al., 2009; Hunt et al., 2006). The moderate, but not statistically significant, increases in SRP measured in the grassed basin (mean inflow= 0.11 to mean outflow= 0.22 mg P L⁻¹) were similar to those observed in three bioretention basins in Melbourne, Australia (0.006 to 0.10-0.11 mg P L⁻¹; (Hatt et al., 2009) and a bioretention basin in North Carolina (0.05 to 0.52 mg P L⁻¹; (Hunt et al., 2006). The large increases in SRP documented in our bioretention basin (0.03 to 1.53 mg P L⁻¹) were more similar to those observed in a bioretention basin in North Carolina with a high P- containing soil media (0.06 to 2.2 mg P L⁻¹; (Hunt et al., 2006)). That soil media had a ‘high’ (86-100) Mehlich-3 P Index, which indicated that the soil was saturated with P and there was ample P for plant growth by agronomic standards (Hardy et al., 2014). High soil P availability, particularly in the bioretention basin, also drove the elevated SRP in our basin outflows. Mehlich-3 P levels in the bioretention

soils were several times greater than amounts considered optimal for plant growth (51-100 mg P kg⁻¹ or P-Index 51-100; Hardy et al., 2014; Sims et al., 2002), and well into the range where the soil is over-saturated with respect to P.

Loads of NO_x and SRP could not be calculated due to the lack of stormflow data for these basins. Data on Cl were available and Cl is a conservative element that is not biologically transformed as nutrients are. Thus comparison of ratios of nutrients and Cl concentrations in stormwater basin inflows and outflows can indicate retention/ removal versus production of nutrients. Since NO_x/Cl and SRP/Cl were consistently lower in outflows from the grassed basin relative to inflows, the basin was retaining these nutrients, despite sometimes having slightly elevated concentrations in outflow. In the bioretention basin, NO_x/Cl and SRP/Cl indicated that that basin was exporting both NO_x and SRP, so not only were the concentrations of these nutrients elevated in outflow but so was the overall mass.

Chloride is typically used as a conservative tracer due to its minimal biological interactions (Schlesinger, 1997), and thus can be a good indicator of water loss due to evapotranspiration where flow data are not available. In this system, Cl is not necessary an ideal tracer due to seasonally biased inputs from de-icing salts during winter. However, both sites were located on the same campus and are managed by the same entity and thus likely have similar application rates of de-icing salt to the adjacent parking lots. All water sampling in this study took place after de-icer application, as can be seen by the temporal decrease in Cl concentrations (Table A4) as Cl is being gradually leached out of detention basin soils. Despite this, the overall pattern of NO_x or SRP export is still very consistent within each basin, which lends confidence to the conclusion that the grassed basin is retaining NO_x and SRP while the bioretention basin is exporting these nutrients.

DOC has rarely been measured in other investigations of stormwater basin function. It represents a broad range of compounds which primarily include humic substances derived from organic debris in inflowing stormwater or basin soil media. Studies of DOC dynamics in forest soils have identified positive relationships between DOC availability and soil OM as well as C:N ratio (Kalbitz et al., 2000). Significant increases in DOC concentration were observed in our bioretention outflow, and this basin also had higher soil OM and C concentrations and a higher C:N ratio than the grassed basin. Export of DOC was also observed in a recent column study using bioretention media containing 40% compost addition by volume. The DOC was found to complex with copper from the soil media and drive export of copper as well, though the researchers noted that these complexes would be less biologically available to aquatic organisms downstream (Chahal et al., 2016).

Given that the nutrient export from the bioretention basin was linked to the compost added during the spring 2014 basin modification, it is possible that this pattern of export could dissipate as this nutrient reservoir mineralizes and is depleted. A column study investigating solute export from compost-amended bioretention media found several fold reductions in export of NO_x , PO_4^{3-} and DOC over numerous simulated storm events (Chahal et al., 2016). Similarly to our study though, these researchers observed the largest drop in nutrient export after the first storm event and long-term trends were less clear. With regards to GHG emissions, there were no differences observed in N_2O or CH_4 fluxes from any of the research sites between 2014 and 2015. Year-to-year changes in CO_2 were unable to be evaluated given that only one year of data was available. Re-evaluating these basins several years from now could elucidate how long the bioretention basin will continue to export nutrients or whether there will be any changes in GHG emissions.

Concentrations of outflowing nutrients are particularly important with regards to water quality standards intended to prevent eutrophication and harmful algal blooms in downstream waterbodies. According to the US Environmental Protection Agency (US EPA), recommended nutrient criteria for rivers and streams in Ecoregion 7 (in which central New York is located) are 0.54 mg N L⁻¹ for total N and 0.033 mg P L⁻¹ for total P (US EPA, 2000). In this study, we did not quantify nutrient concentrations in the receiving waterbodies. However, it is concerning that our measured concentrations of SRP, the most biologically available form of P (Prestigiacomio et al., 2016), were at times two orders of magnitude larger than the total P standard for flowing waters. There are no criteria for dissolved organic C as it is not considered a pollutant, though it's important to understand its dynamics as its availability- particularly relative to N and P- can influence nutrient limitation and biological activity in downstream water bodies.

3.4.3. Recommendations for bioretention and rain garden design

Our findings in this comparison of two stormwater basin designs can help inform improved design of future stormwater infrastructure. Recommendations based on our observations of nutrient balances along with insight from other similar studies include:

- 1) Optimize OM basin additions to only what is necessary for plant health and pollutant retention, while minimizing availability of excess nutrients for GHG emissions and leaching. In our bioretention basin, approximately 40% compost by volume was added to the upper soil layer of the basin, which drove high availability of C, N and P. In a review of bioretention design, Davis et al. (2009) note that recommendations for OM additions range from 3-5% in North Carolina to 60% peat moss and mulch in Delaware. In addition to the overall amount of OM added, the relative content of nutrients is important. P content should be limited to less than 100

mg P kg⁻¹, as assessed by the Mehlich-3 P soil test, in order to keep soil P below saturation (Sims et al., 2002). Greater C to N ratio of soil media also minimizes N availability for leaching or transformation to N₂O, and increases C availability for promoting immobilization of other nutrients (Booth et al., 2005) as well as sorption of pollutants (Hunt et al., 2012). Based on stoichiometry of microbial nutrient utilization, C:N greater than ~20 should promote immobilization of N as opposed to mineralization (Chapin et al., 2011). Thus using compost from woody mulch and/or leaves would be preferable over compost with a higher N content such as that derived from grass or food scraps.

2) Maintain well-draining, primarily aerobic upper soils underlain by an anaerobic zone to promote better NO_x removal. In both basins in this study, basin media was relatively uniform and porous, allowing drainage of stormwater within several hours of a storm event. While these primarily aerobic conditions were beneficial in avoiding N₂O and CH₄ production, they also promoted nitrification and reduced opportunities for removing excess NO_x via denitrification. Other studies have found that addition of a subsurface saturated zone can promote NO_x removal via denitrification (Kim et al., 2003).

Some of these design considerations can also be transferred to rain gardens, a less engineered type of storm runoff control system relative of bioretention basins, that are being recommended for implementation in residential areas to treat rooftop and/or driveway runoff. Guidelines can be found on many state cooperative extension websites or state environmental conservation/protection agency websites. These rain gardens typically consist of a 6-8 inch deep leveled depression that is planted with a variety of suitable vegetation and topped with a 2-3 inch

layer of mulch. Similar to bioretention soil media specifications, many rain garden guidelines advise adding compost to the soil prior to planting, in amounts ranging from 5-50% by volume. However, these rain garden soils with high compost additions would likely experience the same nutrient leaching issues as observed in our and other bioretention basins. Rutgers Cooperative Extension recommends that homeowners have a soil test performed prior to rain garden installation, in order to determine whether any amendments would be recommended to improve soil texture or nutrient content. We encourage other organizations to include a similar guideline, where rain garden designers would only add compost if the soil was nutrient deficient.

3.5. Conclusion

In this study, we evaluated nutrient balances in two different kinds of stormwater detention basins- a grassed basin and an OM-amended bioretention basin. With respect to greenhouse gas production, we didn't find any significant differences in emission of N_2O and CH_4 between the basins and adjacent reference sites, but did measure significantly higher CO_2 emissions from the bioretention basin compared to the grassed basin. Focusing on water quality, we found that the bioretention basin was a source of NO_x , SRP and DOC. This leaching could be attributed to the high content of these nutrients in the soil media used in the bioretention basin.

With these findings, we can work to minimize GHG emissions and leaching of excess nutrients and maximize retention of nutrients and other pollutants. It is important to note that there are other ecosystem services provided by these basins that were not considered here, such as C sequestration and pollinator habitat and aesthetics. The type and magnitude of these services may differ between the two basin designs and should also be considered when deciding on the optimal stormwater management strategy.

Supplementary Material

Appendix A contains tables of greenhouse gas and water quality summary data, a full list of bioretention vegetation and additional figures.

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CHAPTER 4

Nutrient cycling in grassed roadside ditches and lawns in a suburban watershed

Abstract

Roadside ditches are ubiquitous in developed landscapes. They are designed to route water from roads for safety, with little consideration of water quality or biogeochemical implications. Periodically saturated conditions along with nutrient influxes may make them hotspots for nitrogen removal via denitrification, as well as production of biologically produced greenhouse gases (GHGs) nitrous oxide (N₂O), methane (CH₄), and carbon dioxide (CO₂). We measured these processes using *in situ* static chambers and laboratory assays in twelve grassed ditches and adjacent lawns in a suburban watershed in central New York. Potential denitrification in ditches was significantly higher than lawns and rates were comparable to those in stream riparian areas, features traditionally viewed as denitrification hotspots. Ditches also had higher rates of CH₄ emissions, particularly in the wettest ditches. Lawns were hotspots for N₂O and CO₂ respiratory emissions, which were driven by nutrient availability and fertilizer application. Scaling up to the watershed, grassed ditches have the potential to remove substantial N loads via denitrification if managed optimally. Ditch GHG emissions across the watershed were minimal compared to lawns, which were the greater contributor of GHGs. These findings suggest that road ditches may offer new design or management opportunities for mitigating nonpoint source N-pollution in residential watersheds.

4.1. Introduction

Peri-urban areas are a growing fraction of the landscape in the United States, increasing

in area by more than 500% since 1950 (Brown et al., 2005). With this increased development has come construction of roads for transportation, with public roads in the United States totaling 6.3 million kilometers and covering approximately 1% of land by area (NRC, 1997). The majority of these roads are flanked by ditches, which help quickly route stormwater off of roads for safety purposes. This introduction of road ditches into watersheds causes substantial manipulation of landscape hydrology (Buchanan et al., 2013; Forman et al., 2003).

Even in watersheds with low development density, road ditches can intercept ~30% runoff generated in the watershed (Buchanan et al., 2013). This results in substantial redistribution of both water and associated solutes or particulates in the watershed. Previous research in rural watersheds in central New York has found that road ditches negatively influence downstream water quality, serving as ‘efficient conduits’ of sediment, phosphorus, and *E. coli* to receiving streams (Buchanan et al., 2013; Falbo et al., 2013). Though there has been some investigation of pollutant transport in ditches, there has been little work investigating biogeochemical transformations of various solutes in ditch soils. With their intermittent pulses of water and associated solutes, grassed ditches could be hotspots for biogeochemical processes that remediate pollutants or generate greenhouse gases (GHGs).

Nitrogen (N) is of particular interest, given its potential to contribute to downstream water quality impairment and GHG production. In suburban watersheds, which often have a high density of roads and corresponding ditches, potential N sources to ditches include fertilizer applied to residential and commercial lawns (Raciti et al., 2011b) as well as automobile exhaust and atmospheric deposition (Bettez and Groffman, 2013). The microbially-mediated process of denitrification, which transforms nitrate (NO_3^-) into nitrous oxide (N_2O) or dinitrogen (N_2) gas (Tiedje, 1994), may be occurring in vegetated ditches and acting as an important nitrate removal

pathway. However, N_2O is a GHG with 298 times the global warming potential (GWP) of carbon dioxide (CO_2). In addition to being a possible by-product of denitrification, N_2O can also be produced by nitrification (Firestone and Davidson, 1989).

Previous research has documented the occurrence of denitrification hotspots- zones of increased denitrification rates relative to surroundings- in the environment where there is the convergence of nutrient inputs and high soil moisture and low oxygen conditions (Groffman et al., 2009a; McClain et al., 2003). Though road ditches are typically characterized by flashy, intermittent flow (Buchanan et al., 2013), there could be periods of time during and shortly after storm events which satisfy the conditions needed for denitrification. Some of these conditions (e.g. high soil moisture and availability of carbon (C) and nitrogen (N) substrate) also influence production of other GHGs. Methane (CH_4) is a GHG with 25 times the GWP of CO_2 , which is produced by soil microbes via methanogenesis when there is high soil moisture and ample soil C (Walter and Heimann, 2000). CO_2 itself can also be produced by multiple respiratory processes occurring in soils (Schlesinger and Andrews, 2000).

Denitrification and GHG production have been studied in various features of suburban landscapes. Previous research has focused on lawns (Byrne et al., 2008; Groffman and Pouyat, 2009; Kaye et al., 2004; Livesley et al., 2010), stormwater control measures (Bettez and Groffman, 2012; Grover et al., 2013; McPhillips and Walter, 2015) and streams and their riparian areas (Groffman and Crawford, 2003; Kaushal et al., 2008). Despite the fact that roadside ditches are a common feature in suburban landscapes, there is limited knowledge of their water quality impacts and virtually no understanding of their role in nutrient cycling in developed landscapes. Research in agricultural ditches has documented high nitrogen removal potential via denitrification (Roley et al., 2011), though these ditches are typically more

continuously flowing compared to roadside ditches and thus nutrient cycling dynamics may differ. As a built feature, an improved understanding of biogeochemical dynamics in roadside ditches can inform better ditch design and landscape management practices.

The primary objective of this study was to quantify denitrification and GHG emissions in twelve grassed roadside ditches and compare these processes to those in adjacent lawns, given that lawns have similar soil properties and management to the ditches but do not receive the stormflows that the ditches do. Additionally, we sought to link any observed patterns in biogeochemical processes to environmental factors or landscape or management characteristics, estimate the impact of ditches and lawns on denitrification and GHG processes across the watershed, and recommend improvements to management of suburban landscapes in order to maximize water quality services like denitrification and minimize greenhouse gas emissions.

4.2. Experimental methods

The experimental sites were located in the watershed of a first order (unnamed) stream in Tompkins County, NY (within the Town of Ithaca and Villages of Cayuga Heights and Lansing; 42.477°N, -76.485°W) that drains to Cayuga Lake (Figure 4.1). 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, 2016). The 293 ha mixed use watershed is representative of many suburban watersheds across New York State, containing developed land (including residential, school, and commercial land), forest, wetland and open water. Existing stormwater infrastructure in the watershed includes detention ponds, road ditches (almost all are vegetated), and minimal storm sewers, all of which discharge within the watershed (Easton and Petrovic, 2008). Soils are predominantly silt loam (US Department of Agriculture, 2015), though

sand or gravel amendments were likely added during the construction of detention ponds or ditches.

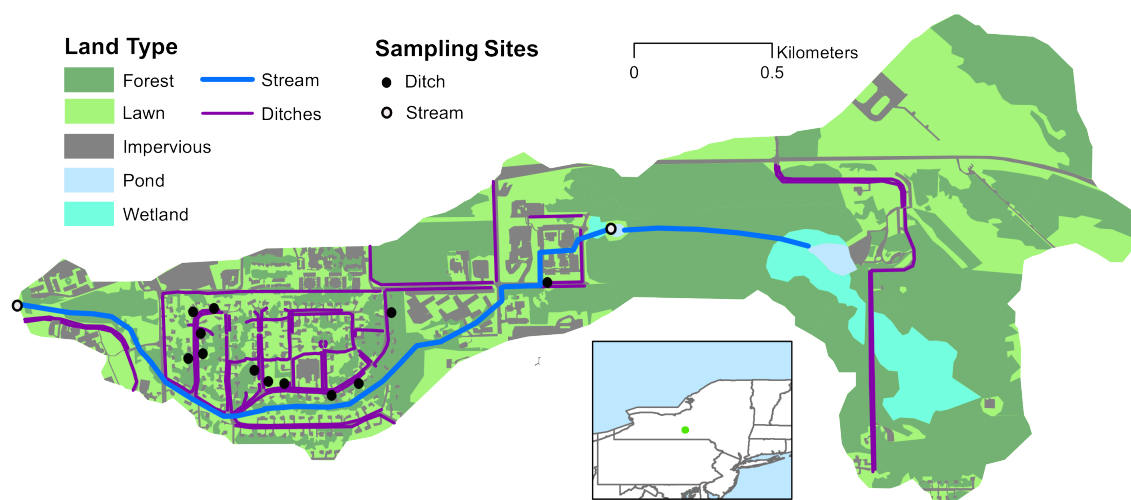


Figure 4.1. Map of study watershed displaying land cover types and locations of ditch and stream sampling sites, with inset map displaying location of the watershed in New York

Potential experimental sites were identified through use of a homeowner survey. Information was mailed to homes adjacent to ditches within the study watershed. Homeowners who were interested in allowing their ditch and adjacent lawn to be a research site were directed to an online survey form. The survey was granted an exemption from the Cornell Institutional Review Board as it did not solicit personal information or pose a risk to participants. The survey solicited information on lawn maintenance (including mulching and fertilizer application) as well as road ditch conditions (such as how often it had water flowing). Using this information, twelve grassed road ditches were selected as experimental sites (example photograph, Figure B1), such that they represented a range of lawn care practices and ditch moisture regimes (Appendix Table B1).

Fluxes of CO_2 , CH_4 and N_2O were measured in the ditches on six dates between July 2014 and June 2015 that spanned a range of temperature and moisture conditions (Figure B2).

Precipitation and air temperatures during this period were close to the climatic annual average for 1981-2010, where precipitation was 0.9 cm below the average of 94.7 cm and mean air temperature was 1.3°C below the average of 8.1°C (NRCC, 2016). 3-day antecedent precipitation for the sampling dates ranged from 0.28 to 3.8 cm and soil temperature at time of sampling ranged from 7.4 to 26.8°C.

On each sampling event (Table B2), GHG fluxes were measured over two consecutive days in which there was minimal average temperature change and no new precipitation. Six ditch sites were measured on each of the two days, during the same time period on each day. At each ditch, flux measurements were made at two locations within the ditch and at two locations in the lawn adjacent to the ditch. Fluxes were measured using *in situ* static white PVC chambers (10.16 cm i.d.). Dark chambers were used to prevent heating effects from solar radiation; thus CO₂ fluxes as measured using these chambers represent soil respiration rather than net ecosystem production. The chamber bottom consisted of a 5 cm long, 10.16 cm diameter PVC pipe with a beveled edge to minimize soil disturbance; in several cases, a 7.62 cm long base was used where there was standing water. Bases were installed immediately prior to sampling. Prior to collecting gas samples, a standard rubber band was placed around the PVC base. The chamber top was a PVC cap (4 in. i.d.). Two rubber septa were installed equidistant from the center of the lid; one was used for sampling and a 21 gauge syringe needle was inserted through the other to serve as a vent (Hutchinson and Mosier, 1981).

For a single gas flux measurement, the chamber top was mounted and a 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 N₂O and CH₄ using an Agilent 6890N gas chromatograph equipped with a HP 7694 Headspace Autosampler (Hewlett-Packard Co.). N₂O separation was performed using a Supel-Q™ PLOT capillary column (Supelco Inc.) and a μ ECD (electron capture detector). CH₄ separation was performed using a Carboxen 1006 PLOT capillary column (Supelco, Inc.) and an FID (flame ionization detector). CO₂ concentrations were analyzed on a LI-6200 Portable Photosynthesis System attached to an LI-6250 CO₂ Analyzer (LI-COR, Inc.) during 2014. For 2015 samples, CO₂ was analyzed with the gas chromatograph FID after installation of a methanizer. Calibration curves were made using a series of standard gas mixes (Airgas Inc.) Gas fluxes were calculated by determining the linear slope of the concentrations of the four time-points (Rochette and Bertrand, 2008). Fluxes were converted from volumetric to mass-based units ($\mu\text{g gas m}^{-2} \text{ hr}^{-1}$) using the ideal gas law.

At the time of gas sampling, field measurements were also made to characterize soil conditions at each of the ditch and lawn sampling locations. A digital thermometer was used to record soil temperature. Soil moisture was assessed as volumetric water content (VWC) using a Campbell Scientific Hydrosense II probe.

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 ditch in October 2014. For each of the two within-ditch and two lawn 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 following the methodology of McPhillips et al. (2015). Briefly, nutrient media containing NO₃⁻ and glucose was added, along with acetylene to block conversion of N₂O

to N₂ gas. Gas samples for N₂O analysis were taken at 20 min intervals over 60 min and analyzed via gas chromatograph. N₂O fluxes were converted to denitrification rates in mg N kg⁻¹ hr⁻¹ using the dry mass of the soil subsamples.

Soil organic matter was assessed for dried, ground, and sieved (<2mm) soil samples from all sites. Percent organic matter was quantified via loss-on-ignition at 500°C for 2 hours (Ferguson and Swenson, n.d.). Percent carbon and nitrogen was quantified using a Carlo Erba NC2500 Elemental Analyzer. Extractable soil NO₃⁻ was assessed on fresh soil samples with gravel removed using a deionized water extraction (Barrett et al., 2009) where NO₃⁻ was analyzed on a Dionex ICS-2000 Ion Chromatograph. Soil pH was measured on a 1:2 soil and water slurry (Robertson et al., 1999).

Ditch water samples were taken during or immediately following six storm events between July 2014 and June 2015. Water samples were obtained in all ditches except one which never had observed flow. Additionally, stream water samples were obtained at least monthly from upstream (above majority of ditches in watershed) and watershed outlet locations (Figure 4.1). Water samples were filtered to 0.45 µm and analyzed within two days for NO_x (NO₃⁻ + NO₂⁻) using a Dionex ICS-2000 Ion Chromatograph. Samples were acidified to pH=2 and analyzed for dissolved organic carbon (DOC) using an OI Analytical Total Carbon Analyzer Model 1010. NO_x loads were also estimated in ditches to compare to up-scaled estimates of denitrification N removal capacity in ditches. Annual ditch NO_x load was calculated using the average NO_x concentration across all ditch sites and sample events, which was multiplied by annual ditch discharge (July 2014-June 2015). Ditch discharge was determined from total watershed stormflow, since field observations indicated that the ditches in the study watershed only flowed during and directly after storm events. Total watershed stormflow was calculated

using hydrograph separation as performed by the Web-based Hydrograph Analysis Tool (<https://engineering.purdue.edu/~what/>). The stream discharge analyzed with the tool was obtained using a HOBO water level sensor at the watershed outlet and a stage-discharge rating curve developed during the study period using a Marsh-McBirney FloMate electromagnetic velocity sensor. In order to calculate the discharge contributed directly from the ditches, total watershed stormflow was scaled by the percent watershed area that is drained by ditches.

In order to scale up gas flux measurements to the entire watershed, a detailed land use map (Figure 4.1) was created in ArcGIS using orthoimagery and ground surveying of road ditches. Total watershed area for each land use was calculated. For the two land uses investigated in this study (ditches and lawns), areas were multiplied by average gas fluxes in order to generate area-weighted emissions. Emissions were expressed as CO₂ equivalents (CO₂Equiv) by multiplying by each gas's 100 year global warming potential (GWP). Potential denitrification was scaled up in ditches by converting the rate to an areal basis using soil bulk density and multiplying the rate by total ditch area and a depth of 5 cm, the depth for which the denitrification assay was performed.

Statistical analyses were conducted in R v. 3.1.3 (*The R Project for Statistical Computing*, 2015). The two replicate sampling locations within each ditch or lawn site were averaged for all analyses. Given the skewed distribution of the gas fluxes, a paired Wilcoxon rank sum non-parametric test was used to assess differences between gas fluxes and potential denitrification at the ditch and lawn sites, where ditch and lawn measurements at a given location were paired. To assess any correlations between measured variables (including annual averages for gas fluxes and VWC and one-time measurements for all other variables), Pearson product-moment correlation analysis was used. Additionally, temperature and moisture effects on GHG

fluxes were assessed using linear mixed effects models (R packages lme4 and lmerTest) that were applied to transformed gas fluxes. Lognormal or Box-Cox transformations were applied to fluxes with a constant added such that all fluxes for that gas were greater than zero and the transformation was determined according to which improved normality the most. For temperature models, sites were treated as a random effect in order to account for having multiple timepoints from each site. For moisture models, both sites and sample dates were treated as a random effect, since moisture varied widely and without any consistent temporal trend for the sample dates. Significance for all tests was determined based on p-values less than 0.05.

4.3. Results and discussion

4.3.1. *Potential denitrification*

Potential denitrification was significantly higher in the ditches compared to the adjacent lawn sites (Figure 4.2). Average potential denitrification in the ditches was $3.45 \text{ mg N kg}^{-1} \text{ hr}^{-1}$. This is similar to mean values measured in stormwater detention basins ($1.2 \text{ mg N kg}^{-1} \text{ hr}^{-1}$) (Bettez and Groffman, 2012; McPhillips and Walter, 2015) and stream riparian areas ($0.4\text{-}3.6 \text{ mg N kg}^{-1} \text{ hr}^{-1}$) (Bettez and Groffman, 2012; Groffman and Crawford, 2003), which are other landscape features considered to be ‘biogeochemical hotspots’. Thus, these ditches are potentially able to provide the valuable service of removing some excess N from stormwater before it pollutes downstream water bodies. Despite findings in other studies that denitrification is positively correlated to soil organic matter (OM) and moisture (Bettez and Groffman, 2012; Groffman and Crawford, 2003), in this investigation denitrification was not significantly correlated to either of these variables. The lack of correlation with OM in this study may be due to a narrower range (4-10%) than that observed in these other studies (~5-20%) (Bettez and

Groffman, 2012; Groffman and Crawford, 2003) The only significant relationship was between denitrification rates in ditch sites and average DOC concentration in ditch stormwater (Table 4.1; Table B3). This implies an influence of inflowing stormwater composition- particularly C availability- on nutrient cycling processes occurring in ditch soils.

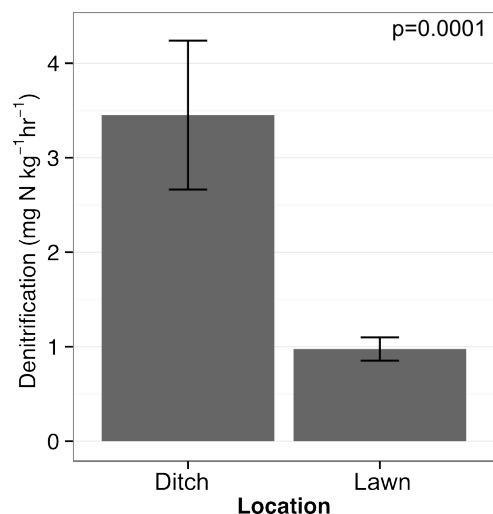


Figure 4.2. Denitrification potential (mg N kg soil⁻¹ hr⁻¹) for soils within all ditches (n= 12) and adjacent lawns (n = 12) sampled in October 2014. Error bars denote standard error.

Table 4.1. Pearson correlation coefficients for measured variables. For measurements made more than once throughout the year, average values were used in the analysis. Superscripted stars indicate statistical significance, where $\ast=p<0.05$, $\ast\ast=p<0.01$, and $\ast\ast\ast=p<0.001$.

	Soil NO _x	Soil pH	Inflow DOC	Inflow NO _x	Soil C	Soil N	Soil OM	Soil VWC	Denit	CO ₂	CH ₄	N ₂ O
N ₂ O	0.42*	0.07	0.46	0.53	0.25	0.26	-0.30	-0.21	0.06	0.47*	0.20	
CH ₄	-0.11	0.43*	-0.01	0.13	0.08	0.13	-0.06	0.61***	0.13	-0.34		
CO ₂	0.49*	0.00	0.55	0.01	0.50**	0.46*	-0.12	-0.49*	-0.12			
Denit	-0.12	-0.04	0.65*	0.33	0.16	0.27	0.13	0.33				
Soil VWC	-0.3	0.22	-0.12	-0.28	0.08	0.16	0.24					
Soil OM	-0.41*	0.13	0.20	-0.22	0.28	0.33						
Soil N	0.04	0.16	0.35	0.35	0.91***							
Soil C	0.18	0.22	0.27	0.14								
Inflow NO _x	0.01	-0.05	0.25									
Inflow DOC	0.45	0.10										
Soil pH	0.17											

4.3.2. Greenhouse gas emissions

CH₄ emissions were significantly higher in ditches compared to adjacent lawn sites (Figure 4.3a; Table B4). This trend was driven by higher average soil moisture in the ditches compared to the lawn sites (61% vs 41% VWC). Across all the sites, average CH₄ fluxes were significantly, positively correlated with average soil VWC and pH (Table 4.1). Across all timepoints, the mixed effects model also identified a positive correlation between CH₄ and VWC (Table 4.2). The model also indicated that more variance was explained by site to site wetness differences than by temporal changes in moisture. CH₄ emissions were particularly high (> 500 µg C m⁻² hr⁻¹) in ditches where standing water was often observed, and reached a maximum of 23,070 µg CH₄-C m⁻² hr⁻¹.

Table 4.2. Parameters and results for linear mixed effects models for GHG fluxes

GHG	Transformation	Fixed Effect	Random Effect	Estimate of Fixed Effect	p-value
CH ₄	Box-Cox	VWC	Site+Date	9.3x10 ⁻²	5.4x10 ⁻³
	<i>Lambda</i> =-0.25	Temp	Site	1.7x10 ⁻³	2.1x10 ⁻¹
N ₂ O	Box-Cox	VWC	Site+Date	-8.9x10 ⁻²	3.6x10 ⁻¹
	<i>Lambda</i> =-0.5	Temp	Site	6.1x10 ⁻³	1.3x10 ⁻¹
CO ₂	Lognormal	VWC	Site+Date	-2.7x10 ⁻¹	7.3x10 ⁻³
		Temp	Site	1.7x10 ⁻²	2x10 ⁻⁴

CH₄ emissions in ditch sites, particularly those with the highest soil VWC, were comparable to those measured in natural wetlands as well as wet stormwater detention basins. In natural fens in central New York and southeastern New Hampshire, mean fluxes of 734- 5,933 µg CH₄-C m⁻² hr⁻¹ have been observed (Frolking and Crill, 1994; Smemo and Yavitt, 2006). In wet stormwater detention basins in central New York, mean fluxes of 2,756 µg CH₄-C m⁻² hr⁻¹ were observed (McPhillips and Walter, 2015). CH₄ emissions at the lawn sites were similar, but

somewhat higher, than those observed in other lawn studies. While some lawn studies have recorded slightly negative mean fluxes, reflecting net uptake or oxidation of CH₄ (Groffman and Pouyat, 2009; Kaye et al., 2004; Livesley et al., 2010), lawn sites in this study averaged 30.9 µg CH₄-C m⁻² hr⁻¹. This may be due to elevated average soil moisture in lawns in this study (average=41% VWC) compared to moisture levels observed in other lawn studies, which ranged from around 10-40% VWC (Groffman and Pouyat, 2009; Livesley et al., 2010). Additionally, the relatively high CH₄ fluxes at these lawn sites may be due to reduced CH₄ uptake, which has previously been documented in urban and N-fertilized soils (Costa and Groffman, 2013; Groffman and Pouyat, 2009; Steudler et al., 1989).

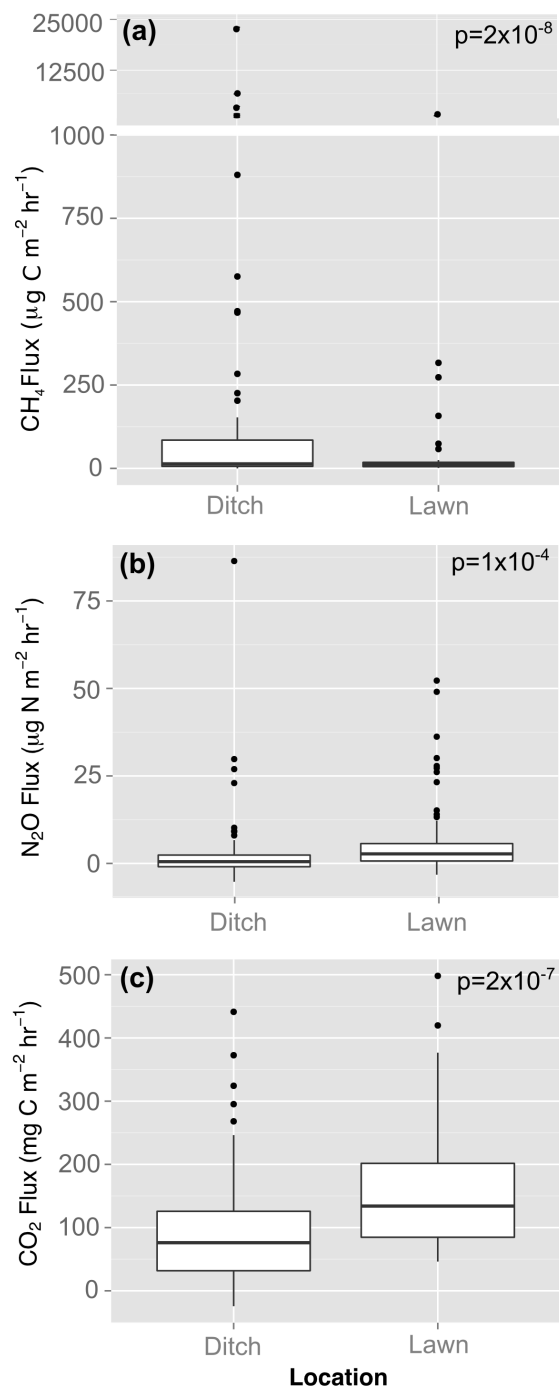


Figure 4.3. Boxplots of (a) CH_4 , (b) N_2O , and (c) CO_2 fluxes for all sites. Data include all twelve ditch or lawn locations for all six time-points. Horizontal black lines show the data median, the box boundaries mark the first and third quartiles, the whiskers indicate 1.5 times the interquartile range, and the points represent extreme values.

For the other two greenhouse gases of interest, the patterns were opposite. N₂O emissions were significantly higher at the lawn sites (mean= 6.4 $\mu\text{g N m}^{-2} \text{ hr}^{-1}$) compared to the ditches (mean= 3.0 $\mu\text{g N m}^{-2} \text{ hr}^{-1}$; Figure 4.3b). Overall, N₂O fluxes were low except for a few ‘hot moments’ of emissions at both the ditch and reference sites where emissions exceeded 50 $\mu\text{g N m}^{-2} \text{ hr}^{-1}$. These rates are similar to measurements made in lawns in Baltimore, Maryland which ranged from -0.07 to 63 $\mu\text{g N m}^{-2} \text{ hr}^{-1}$ (Groffman et al., 2009b; Raciti et al., 2011a) but are lower than fluxes measured in stormwater biofiltration cells in Australia (max= 1,100 $\mu\text{g N m}^{-2} \text{ hr}^{-1}$; (Grover et al., 2013)) and fertilized lawns in California (max= 720 $\mu\text{g N m}^{-2} \text{ hr}^{-1}$; (Townsend-Small and Czimczik, 2010).

Across all sites, average N₂O fluxes were significantly positively correlated with soil NO₃⁻ and negatively correlated with soil VWC (Table 4.1). This is in line with previous findings on N₂O controls, which note that availability of NO₃⁻ and oxygen promote production of N₂O during denitrification (Firestone et al., 1980). N₂O may also be produced by oxidation of NH₄⁺ to NO₃⁻ in nitrification, which can occur at higher rates in lawns due to NH₄⁺ availability and oxic soil conditions (Raciti et al., 2011b, 2008). N₂O fluxes were significantly higher in fertilized lawns compared to unfertilized lawns (Figure 4.4a). There were no differences in N₂O fluxes from ditches grouped by fertilizer application (Figure 4.4c). The combination of this lack of difference with the high denitrification potential and VWC in ditch soils indicates the possibility that denitrification is proceeding to N₂ in the wetter ditch sites. Additionally, ditches are experiencing influence from both the fertilization of the adjacent lawns as well as the runoff from the rest of the ditch’s watershed, confounding the influence of these factors.

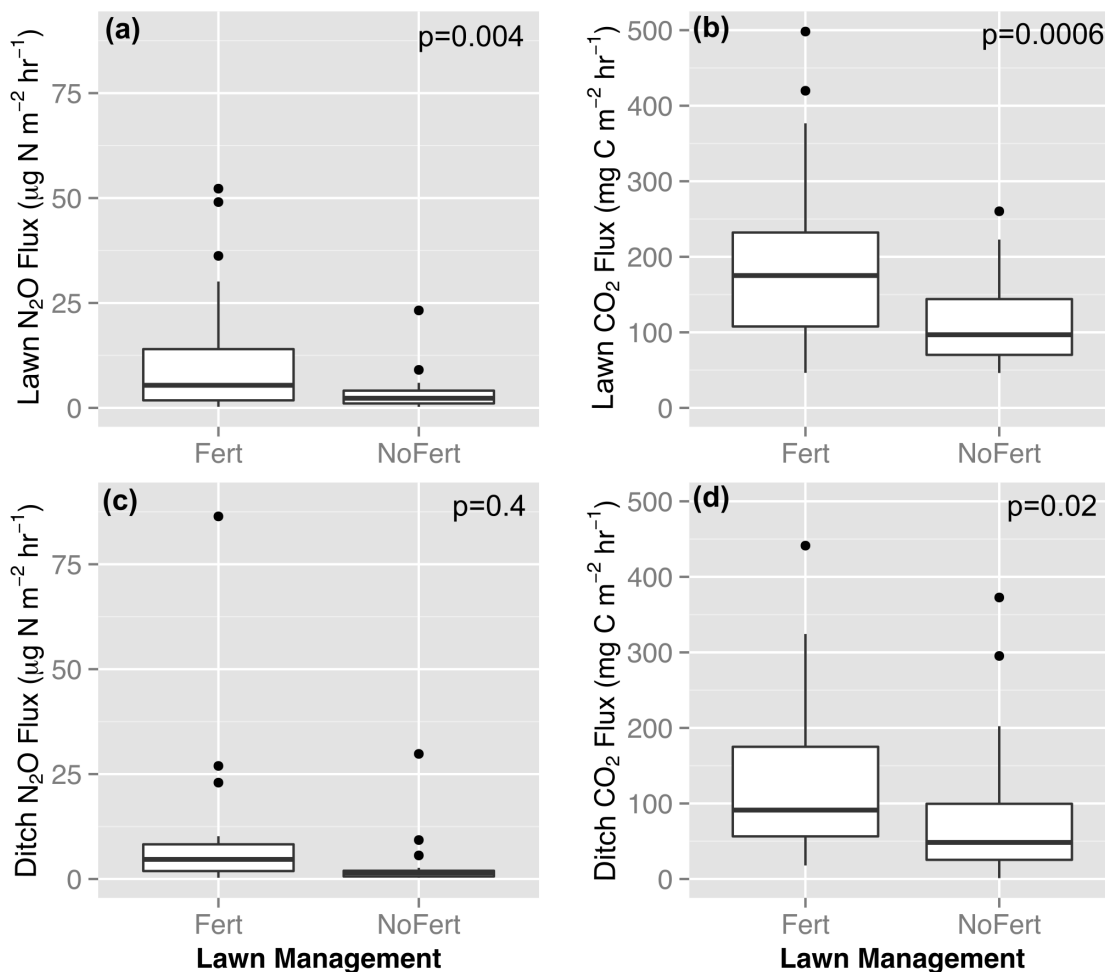


Figure 4.4. Boxplots of (a) N₂O and (b) CO₂ fluxes from fertilized or unfertilized lawns and (c) N₂O and (d) CO₂ fluxes from the ditches adjacent to these lawns for all six timepoints. Horizontal black lines show the data median, the box boundaries mark the first and third quartiles, the whiskers indicate 1.5 times the interquartile range, and the points represent extreme values.

CO₂ emissions were statistically significantly higher from lawn compared to ditch sites (Figure 4.3c). Average fluxes at all sites (lawn = 151 mg C m⁻² hr⁻¹, ditches= 98 mg C m⁻² hr⁻¹) were comparable to those measured from lawns in the similar climatic conditions of the Boston, Massachusetts region (mean= 194 mg C m⁻² hr⁻¹; Decina et al., 2016) and were lower than those reported for lawn sites under a range of management practices in the temperate coastal climate of Melbourne, Australia (>300 mg C m⁻² hr⁻¹; (Livesley et al., 2010)). Across all sites, average CO₂

fluxes were significantly positively correlated with soil NO_3^- and % soil C and N. CO_2 was also significantly negatively correlated with soil VWC (Table 4.1). Across all time points, the mixed effects model identified a significant positive correlation between CO_2 fluxes and soil temperature, which concurs with broadly observed relationships between temperature and soil respiration (Kirschbaum, 1995). As with N_2O , CO_2 fluxes were significantly higher in fertilized than in unfertilized lawns (Figure 4.4b), suggesting increased ecosystem respiration with increased N availability. CO_2 fluxes were also significantly higher in ditches located adjacent to fertilized lawns compared to unfertilized lawns (Figure 4.4d). Increased respiratory CO_2 production with fertilizer addition has been observed in other urban lawn and garden systems (Livesley et al., 2010) and may be driven by increased primary production from nutrient inputs (Kaye et al., 2005). Thus, despite the increase in CO_2 emissions from ecosystem respiration, there also may be a corresponding increase in primary production leading to net C sequestration in these fertilized lawns, but primary production was not quantified in this study.

Examining the total GHG fluxes from ditches and lawns in this study, emission rates from lawns are greater (Figure 4.5a). Despite higher rates of CH_4 emissions in ditches, the higher rate of N_2O and CO_2 emissions from lawns combined with the greater GWP of N_2O (298) relative to CH_4 (25) makes lawns the greater emitters. If only N_2O and CH_4 are considered, ditches do have a greater rate of GHG emissions per area (Figure 4.5a, inset).

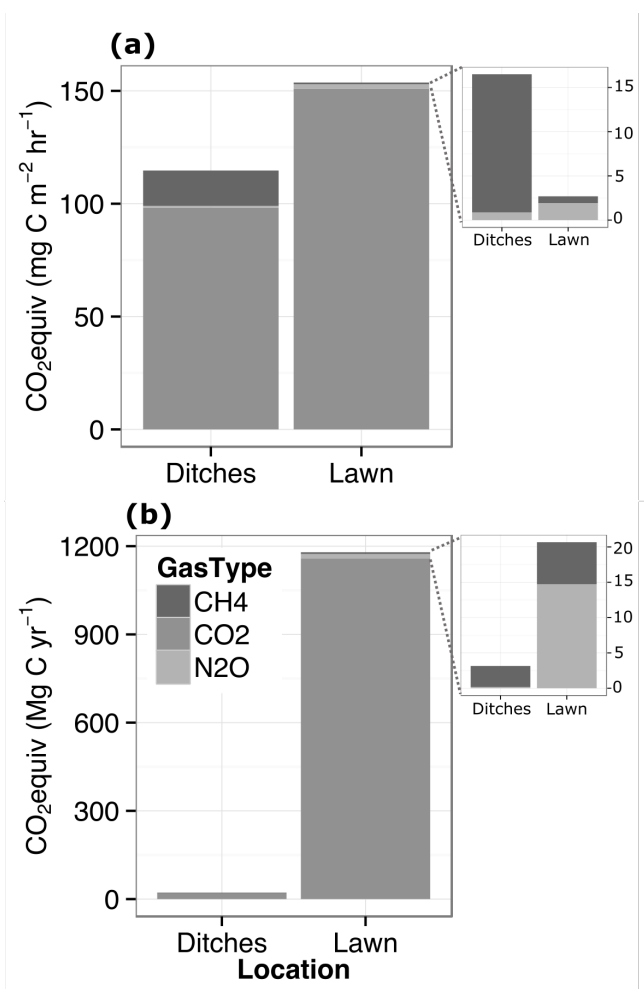


Figure 4.5. Average GHG fluxes for ditches and lawns on (a) a per area basis and (b) scaled by watershed area. Fluxes are represented in CO₂ equivalents according to their GWP. Inset graphs show N₂O and CH₄ data only.

4.3.3. Upscaling to the watershed

Within this study watershed, forest was the dominant land type, at 50.36% of total watershed area; lawns occupied 29.91% and ditches occupied 0.74% of total watershed area. Combining the total area with the averaged GHG fluxes, lawns in the watershed emitted 1,179 Mg CO₂Equiv yr⁻¹ compared with 22 Mg CO₂Equiv yr⁻¹ from ditches (Figure 4.5b). Thus, even though ditches had higher rates of CH₄ emissions, the greater total area occupied by lawns combined with their greater rates of N₂O and CO₂ emissions made them much greater overall

emitters of GHGs. Some of these emissions are likely offset by C sequestration in lawn and ditch soils. Previous work in lawns has identified substantial C sequestration (Townsend-Small and Czimeczik, 2010) and a study of vegetated swales along highways found increasing soil C density with age (Bouchard et al., 2013). Lawn fertilization strongly impacted the overall GHG footprint of lawns in this investigation. The estimate of 1,179 Mg CO₂Equiv yr⁻¹ used the average flux from all twelve sites, which is reasonable given that 43% of homeowner surveys in the watershed (n=28) indicated that they applied lawn fertilizer. If emissions were upscaled using only average fluxes from the fertilized or non-fertilized sites, lawns emitted 889 Mg CO₂Equiv yr⁻¹ if all were assumed to not be fertilized, while emissions increased 65% to 1470 Mg CO₂Equiv yr⁻¹ if all lawns were assumed to be fertilized.

For denitrification, upscaling of potential denitrification rates to the full watershed network of ditches yielded an N removal potential of 42,805 kg N yr⁻¹. This can be compared to the ditch NO_x load, which was calculated as 118 kg N yr⁻¹. While this is a coarse estimate of NO_x load based on a relatively small number of water samples and a simple model of ditch flow, the much greater magnitude of potential denitrification demonstrates that the ditches could provide more than enough removal of N loads in ditch stormwater. However, increases in average NO_x from 0.27 to 0.38 mg N L⁻¹ (Table B3) between upstream and outlet stream sites indicate that the developed, ditch-drained portion of the watershed continued to contribute some N. There are several key assumptions in the calculations of denitrification N removal that are important to consider. This rate is representative of maximum denitrification under optimal conditions (e.g. anaerobic, ample nutrients). The actual *in situ* rate likely varies throughout the year based on temperature, wetness, etc. (Groffman et al., 2009a). Additionally, N removal was calculated for a ditch soil depth of 5 cm. With the high velocity of water movement during storms in these

ditches, much of the incoming N may not have an opportunity to interact with ditch soils beyond the sediment surface. Streams provide an interesting comparison though, where measurement of potential denitrification using the DEA method on shallow sediment samples and *in situ* denitrification using a ^{15}N tracer in 65 streams across the U.S. found that *in situ* rates were similar in magnitude to potential N removal (Findlay et al., 2010).

4.3.4. *Management implications*

These findings have several implications for management of suburban landscapes. For lawns, it is clear that nutrient availability is a driver of GHG emissions, particularly N_2O and CO_2 , and this nutrient availability is linked to fertilizer application. Thus, working with homeowners to better optimize fertilizer application to lawns in terms of amount and timing could help reduce excess nutrients available for transformation into GHGs or runoff into ditches.

In managing ditches, goals should include optimizing water quality services like denitrification while reducing emissions of CH_4 . CH_4 emissions were highest from wettest ditches, particularly those with standing water. From observations, standing water occurred when metal culverts under driveways were blocked by debris or were not flush with the ditch. Thus maintenance practices such as using PVC culverts in place of metal could prevent warping that might back up water, and grates or screens over culvert ends could prevent debris that causes blockages.

We found that grassed ditches were hotspots for potential denitrification, which can prevent excess NO_3^- from reaching downstream water bodies. While it was not clear which environmental factors most strongly promoted potential denitrification at these sites, it is clear that grassed ditches overall are hotspots for this process relative to lawns, which dominate suburban landscapes. Additionally, upscaled estimates of denitrification indicated that there is

potential for these grassed ditches to remove all incoming NO_x in stormwater. One key limitation to reaching this potential N removal is residence time of N in ditches, since observations during storms indicate that most stormwater is moving at high velocity and may not have an opportunity to infiltrate or interact sufficiently with soils and associated microbial communities. Research in stream sediments has found that residence time of water and associated substrates in the subsurface hyporheic zone is a key positive influence on denitrification occurrence (Zarnetske et al., 2011). Future research should investigate ditch denitrification rates *in situ* and quantify ditch water residence time and exchange with ditch soils.

Managers of suburban watersheds should consider how to modify ditch design to increase interaction of stormwater with ditch soils to promote biogeochemical processing, in ways that wouldn't simply back up water for extended periods and promote CH_4 emissions. One existing management practice that inherently reduces interactions with soils is the practice of scraping ditches every few years in order to reduce risk of ditches overflowing into the road during large storm events (Johnson, 2015). While this practice did not occur at our study sites and, thus, was not directly evaluated, we predict that the removal of soil and vegetation would reduce the beneficial NO_3^- removal potential observed in our grassed ditches, and so stopping scraping could improve water quality benefits. Previous work in grassed highway swales in Maryland found that adding check dams reduced NO_3^- loads in runoff, likely due to infiltration and denitrification (Stagge et al., 2012). In agricultural settings, modification of ditches to be 'two-stage', which means adding a secondary floodplain to allow increased soil contact during high flows, enhanced overall nitrogen removal (Roley et al., 2011). For suburban road ditches, this approach could be modified such that ditches could overflow laterally onto a portion of the adjacent lawn. Other management options to increase opportunities for water quality

improvement include strategically placed bioretention basins (e.g. where there is available space to route ditch water into a basin for longer detention) or subsurface woodchip bioreactors in ditches.

4.4. Conclusions

This study provides the first known data on GHG emissions and potential denitrification in grassed roadside ditches in a suburban landscape. With their pulses of stormflow and associated solutes and particulates, these ubiquitous features have the potential to be important biogeochemical hotspots in developed landscapes. Comparing these features to adjacent lawns in the study watershed, we found that ditches were hotspots for CH₄ emissions due to higher wetness but that lawns had greater rates of N₂O and CO₂ emissions. Fertilization and nutrient availability influenced N₂O and CO₂ emissions, driving greater emissions for both gases from fertilized versus unfertilized lawns and greater CO₂ fluxes in ditches adjacent to fertilized lawns. Scaling GHG emissions up to the watershed, the much greater area of lawns relative to ditches made lawns the overall greater emitter of GHGs. Potential denitrification rates were greater in ditches, demonstrating that ditches can provide important N removal services. Future research should focus on identifying design and management strategies to minimize CH₄ emissions in grassed roadside ditches while also promoting beneficial processes like denitrification.

Supplementary Material

Appendix B contains summary information on soil properties, sampling dates, greenhouse gas and denitrification fluxes, and water quality data for all sites.

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APPENDIX A

Supplementary material for Chapter 3

Table A1. Compost chemical analysis results (Bassuk, 2014)

Parameter	Quantity	Units
pH	8.20	NA
Total N	1.77	%
Total C	25.24	%
C:N	14.27	NA
NH ₄ ⁺ -N	30.04	mg kg ⁻¹
NO ₃ ⁻ -N	767.99	mg kg ⁻¹
P ₂ O ₅	0.52	%

Table A2. Vegetation planted in bioretention basin in April 2014

Botanical Name	Quantity
Amorpha fruticosa	1
Callicarpa dichotoma 'Early Amethyst'	10
Caryopteris clandonensis 'Sterling Silver'	20
Ceanothus americanus	14
Cornus mas	1
Diervilla sessilifolia 'Cool Splash'	5
Eleutherococcus sieboldianus 'Variegatus'	11
Forsythia 'Goldtide'	64
Hypericum prolificum	21
Morella pennsylvanica	9
Rhus coppalina 'Prairie Flame'	10
Rosa rugosa 'alba'	50
Salix acutifolia 'Blue Streak'	3
Salix arenaria	1
Salix candide	8
Salix eleagnos	9
Salix integra 'Hakuro Nishiki'	1
Salix irrorata	1
Salix koriyanagi	3
Salix myricodes	11
Salix purpurea 'Nana'	5
Spiraea japonica 'Goldmound'	24
Syringa meyeri	5
Viburnum burkwoodii	13
Viburnum prunifolium	13
Weigela florida 'Spilled Wine'	20

Table A3. Summary of greenhouse gas fluxes for the bioretention and grassed stormwater basins. Reported values indicate mean of site replicates for a given date, except for 'All Dates', where values represent overall mean \pm standard error. No values are reported for CO₂ for 2014 since data was not collected for that analyte.

Date	Site	Sampling Location	N ₂ O Flux μg N m ⁻² hr ⁻¹	CO ₂ Flux mg C m ⁻² hr ⁻¹	CH ₄ Flux μg C m ⁻² hr ⁻¹
29 May 2014	Bio	Basin	2.4	--	165.0
		Reference	9.0	--	-26.9
	Grassed	Basin	3.3	--	-57.1
		Reference	75.7	--	699.6
27 Jun 2014	Bio	Basin	28.3	--	139.9
		Reference	42.9	--	87.5
	Grassed	Basin	-2.2	--	126.6
		Reference	17.9	--	6.5
21 Jul 2014	Bio	Basin	15.7	--	48.2
		Reference	1.2	--	-17.1
	Grassed	Basin	8.9	--	27.2
		Reference	9.1	--	36.0
28 Aug 2014	Bio	Basin	27.8	--	-9.5
		Reference	-0.7	--	82.3
	Grassed	Basin	13.8	--	119.6
		Reference	-1.2	--	75.3
30 Sept 2014	Bio	Basin	47.7	--	26.7
		Reference	-0.5	--	8.0
	Grassed	Basin	8.6	--	15.7
		Reference	10.8	--	53.7
14 May 2015	Bio	Basin	64.5	655.5	-5.4
		Reference	15.3	329.2	-3.4
	Grassed	Basin	53.9	321.6	-9.4
		Reference	22.4	178.4	-4.0
11 Jun 2015	Bio	Basin	24.4	583.6	13.2
		Reference	-5.1	424.4	20.4
	Grassed	Basin	43.5	444.8	-40.7
		Reference	15.1	305.5	-34.6
15 Jul 2015	Bio	Basin	26.8	229.5	-1.2
		Reference	3.3	244.4	-9.5
	Grassed	Basin	-10.1	30.8	-0.9
		Reference	7.3	8.8	2.6
25 Aug 2015	Bio	Basin	-2.6	226.7	22.9
		Reference	3.4	111.2	117.1
	Grassed	Basin	7.3	80.0	2.5
		Reference	13.6	25.1	-25.9
22 Sept 2015	Bio	Basin	-1.1	144.3	54.6
		Reference	-3.4	148.0	82.4
	Grassed	Basin	4.2	115.0	5.8
		Reference	33.9	134.6	42.5
All Dates	Bio	Basin	23.4 ± 5.8	367.9 ± 66.7	45.4 ± 22.8
		Reference	6.5 ± 3.5	251.4 ± 48.4	34.1 ± 15.0
	Grassed	Basin	13.1 ± 5.8	198.4 ± 43.5	18.9 ± 14.0
		Reference	20.5 ± 7.8	130.5 ± 36.9	85.1 ± 71.2

Table A4. Summary of water quality data for the bioretention and grassed stormwater basins. Reported values indicate mean of sample replicates for a given date, except for ‘All Dates’, where values represent overall mean \pm standard error.

Date	Site	Sampling Location	NO _x mg N L ⁻¹	NH ₄ mg N L ⁻¹	DOC mg C L ⁻¹	SRP mg P L ⁻¹	CI mg Cl L ⁻¹
16 May 2014	Bio	Inlet	0.11	0.03	1.0	0.05	1.65
		Outlet	4.46	0.08	35.5	1.96	56.09
	Grassed	Inlet	0.36	0.07	1.6	0.35	23.05
		Outlet	0.14	0.03	5.8	0.10	77.24
25 Jun 2014	Bio	Inlet	0.28	0.01	8.1	0.02	1.02
		Outlet	1.04	0.03	12.4	0.82	2.89
	Grassed	Inlet	0.17	0.19	6.4	0.03	0.99
		Outlet	0.65	0.01	7.5	0.08	33.44
5 Aug 2014	Bio	Inlet	0.22	0.17	1.6	0.03	0.69
		Outlet	1.00	0.04	9.1	1.26	3.84
	Grassed	Inlet	0.21	0.14	2.6	0.07	0.52
		Outlet	0.74	0.09	3.8	0.20	46.94
20 Aug 2014	Bio	Inlet	0.21	0.11	1.5	0.02	0.26
		Outlet	1.17	0.01	9.9	1.28	0.74
	Grassed	Inlet	0.23	0.03	3.1	0.05	0.16
		Outlet	1.31	0.02	5.2	0.24	34.93
8 Apr 2015	Bio	Inlet	0.18	0.01	2.5	0.02	35.14
		Outlet	0.98	0.01	15.5	3.46	103.91
	Grassed	Inlet	0.65	0.01	5.8	0.22	338.01
		Outlet	2.83	0.01	7.5	0.53	914.15
8 Jun 2015	Bio	Inlet	0.39	0.01	1.4	0.02	1.61
		Outlet	1.14	0.01	11.5	1.25	1.97
	Grassed	Inlet	0.26	0.02	3.2	0.03	0.67
		Outlet	0.83	0.01	7.3	0.35	93.92
14 Jul 2015	Bio	Inlet	0.24	0.21	2.6	0.02	1.14
		Outlet	0.84	0.10	8.00	0.65	2.80
	Grassed	Inlet	0.44	0.20	3.24	0.02	2.23
		Outlet	0.98	0.15	6.97	0.05	75.10
All Dates	Bio	Inlet	0.23 \pm 0.03	0.07 \pm 0.03	2.7 \pm 0.9	0.03 \pm 0.00	5.93 \pm 4.87
			1.52 \pm 0.49	0.04 \pm 0.01	14.5 \pm 3.6	1.53 \pm 0.36	24.61 \pm 15.23
		Outlet	0.33 \pm 0.06	0.09 \pm 0.03	4.0 \pm 0.7	0.11 \pm 0.05	52.23 \pm 47.73
			1.07 \pm 0.32	0.04 \pm 0.02	6.3 \pm 0.5	0.22 \pm 0.07	182.25 \pm 122.30
	Grassed	Inlet	0.23 \pm 0.03	0.07 \pm 0.03	2.7 \pm 0.9	0.03 \pm 0.00	5.93 \pm 4.87
			1.52 \pm 0.49	0.04 \pm 0.01	14.5 \pm 3.6	1.53 \pm 0.36	24.61 \pm 15.23
		Outlet	0.33 \pm 0.06	0.09 \pm 0.03	4.0 \pm 0.7	0.11 \pm 0.05	52.23 \pm 47.73
			1.07 \pm 0.32	0.04 \pm 0.02	6.3 \pm 0.5	0.22 \pm 0.07	182.25 \pm 122.30

APPENDIX B

Supplementary material for Chapter 4



Figure B1. Photograph of example study ditch and adjacent road and lawn

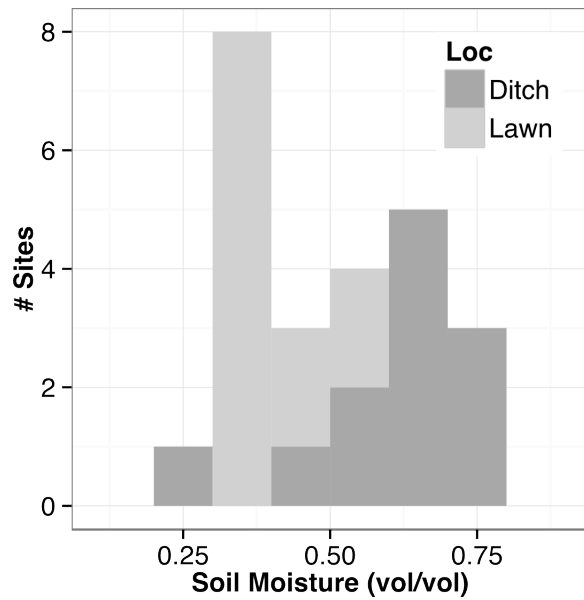


Figure B2. Distribution of average soil moisture (n= 6 sampling dates) across the twelve ditch and lawn research sites

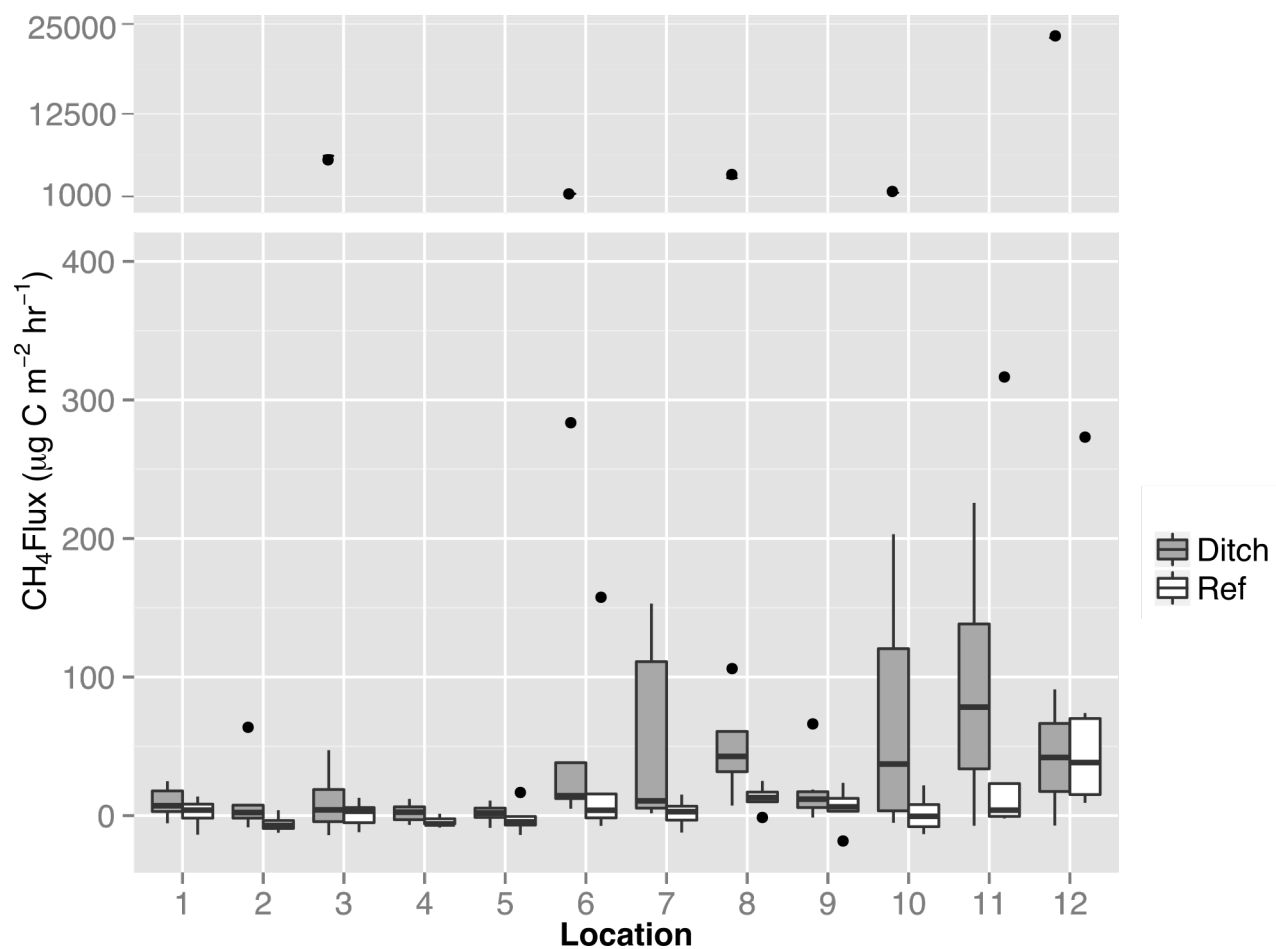


Figure B3. Boxplots of CH₄ for all sites. Data include all six time-points. Horizontal black lines show the data median, the box boundaries mark the first and third quartiles, the whiskers indicate 1.5 times the interquartile range, and the points represent extreme values.

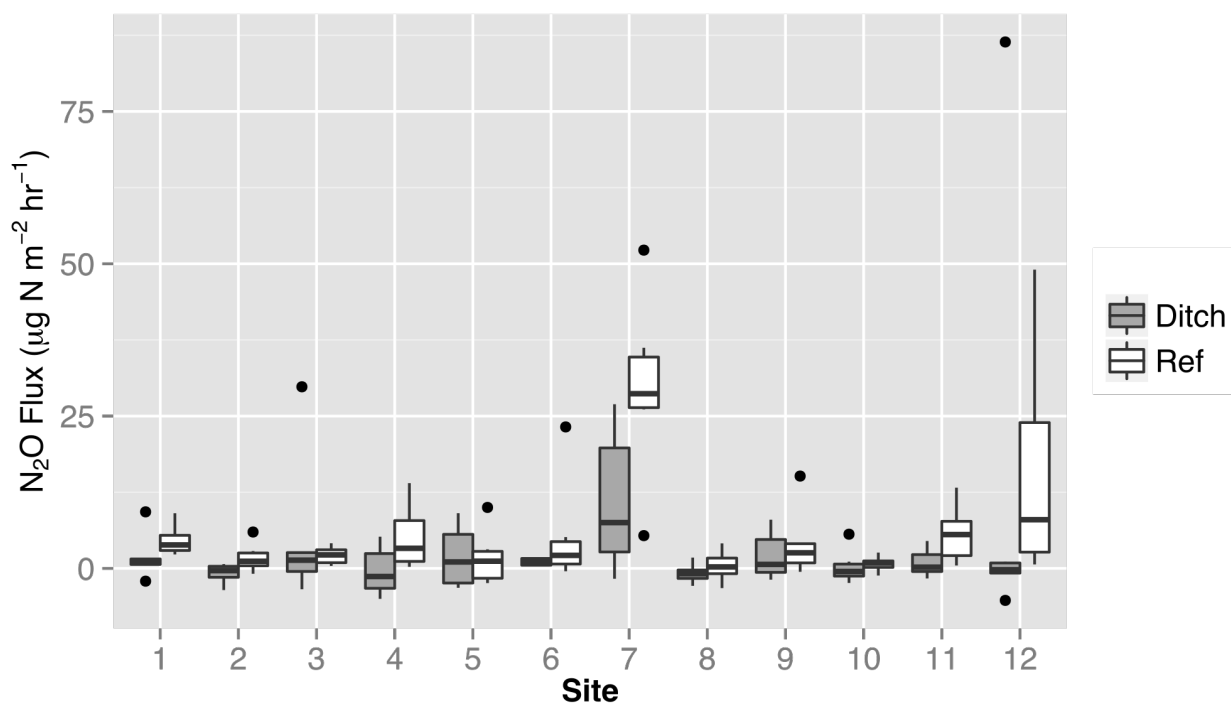


Figure B4. Boxplots of N₂O for all sites. Data include all six time-points. Horizontal black lines show the data median, the box boundaries mark the first and third quartiles, the whiskers indicate 1.5 times the interquartile range, and the points represent extreme values.

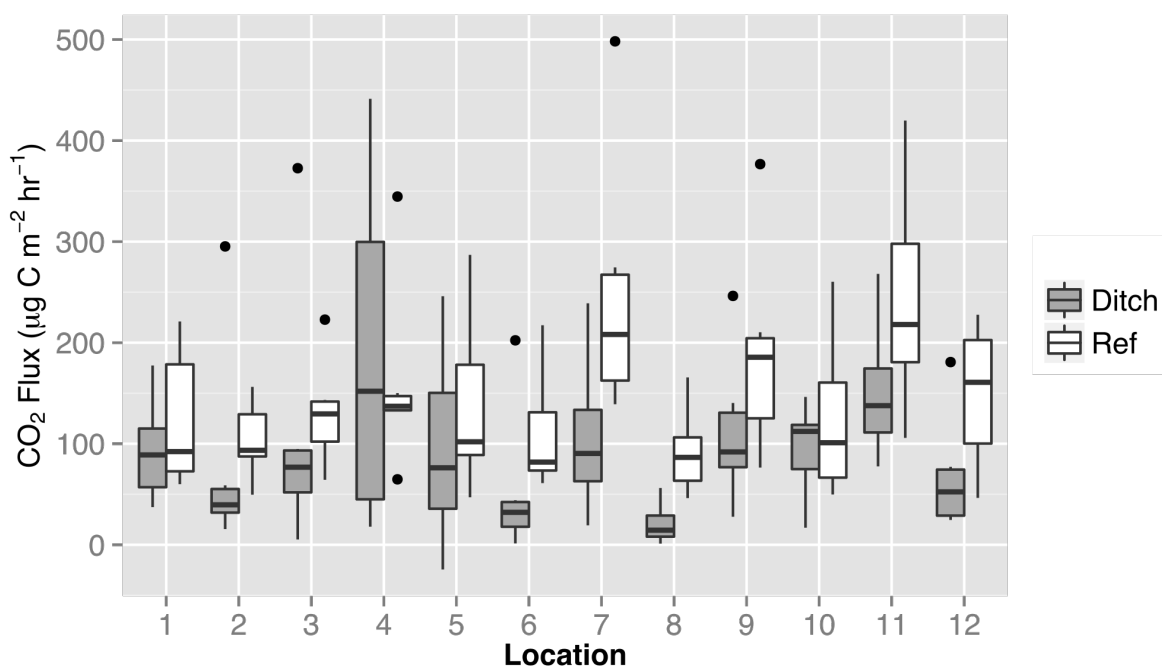


Figure B5. Boxplots of CO₂ for all sites. Data include all six time-points. Horizontal black lines show the data median, the box boundaries mark the first and third quartiles, the whiskers indicate 1.5 times the interquartile range, and the points represent extreme values.

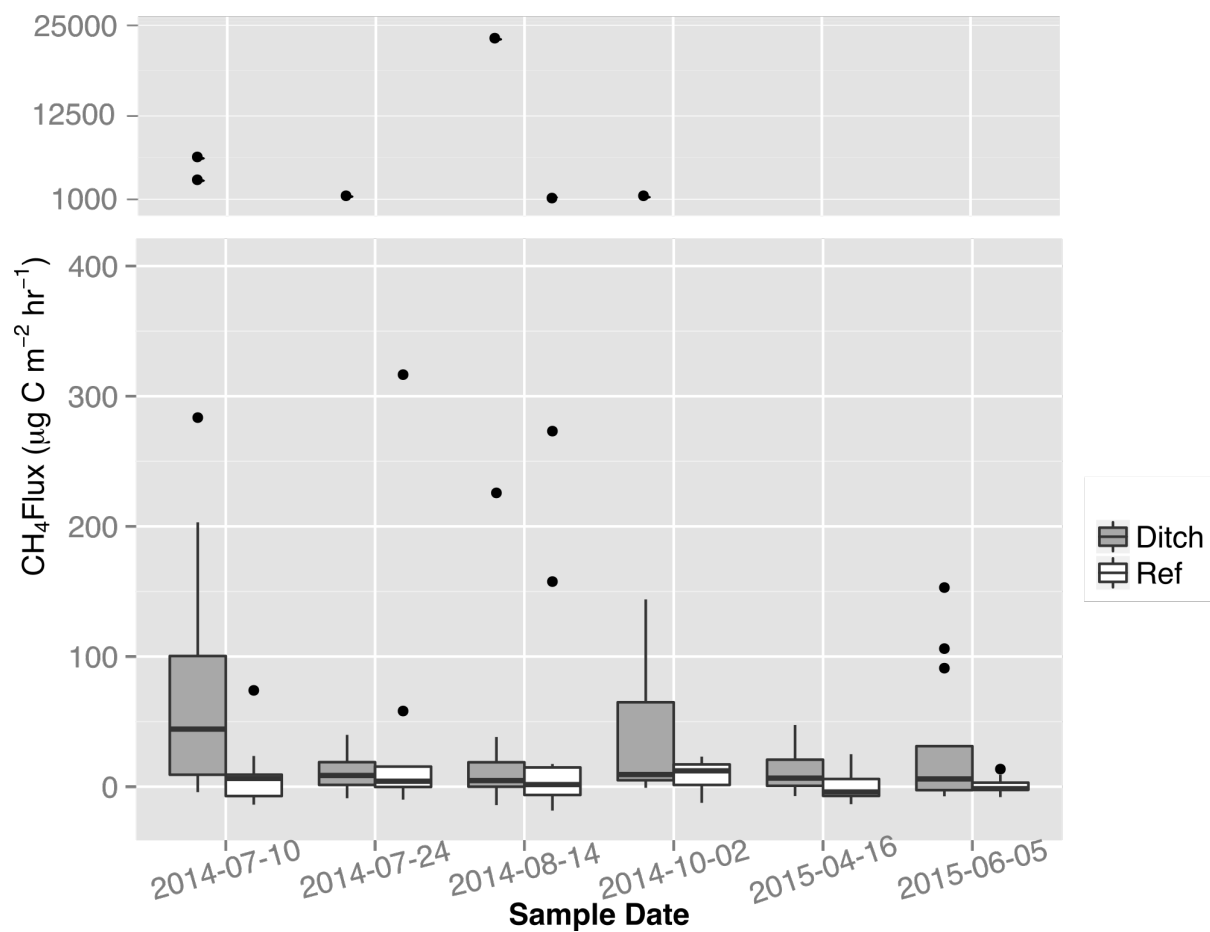


Figure B6. Boxplots of CH₄ for all six time-points. Data include all twelve research sites. Horizontal black lines show the data median, the box boundaries mark the first and third quartiles, the whiskers indicate 1.5 times the interquartile range, and the points represent extreme values.

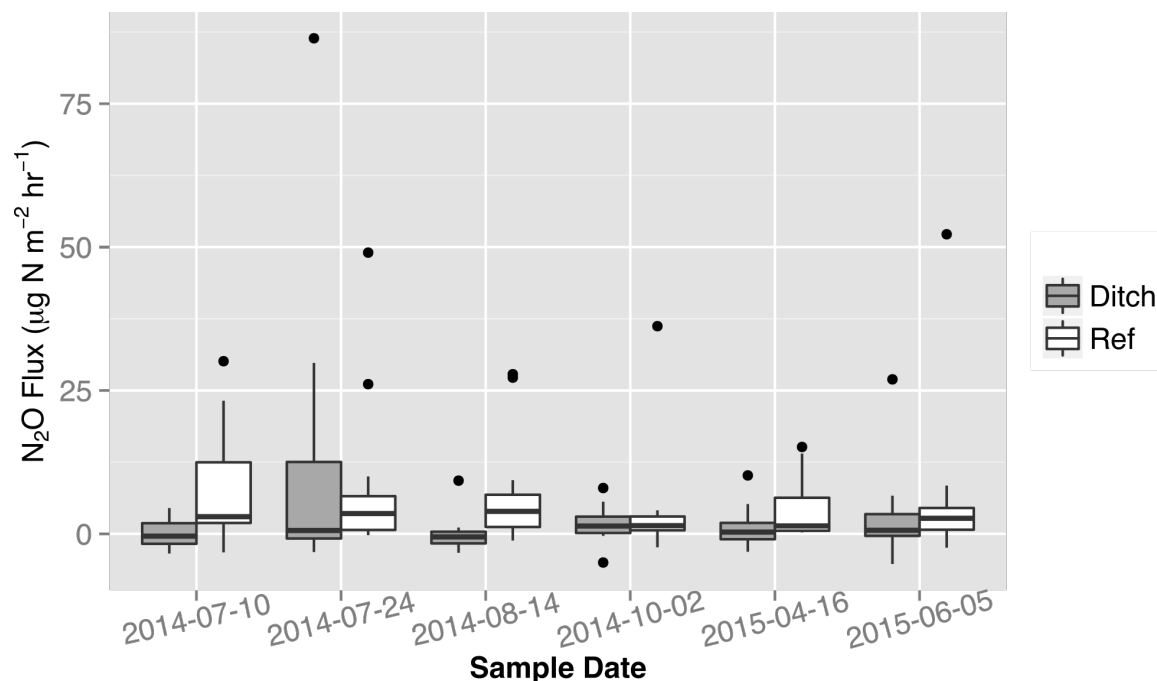


Figure B7. Boxplots of N₂O for all six time-points. Data include all twelve research sites. Horizontal black lines show the data median, the box boundaries mark the first and third quartiles, the whiskers indicate 1.5 times the interquartile range, and the points represent extreme values.

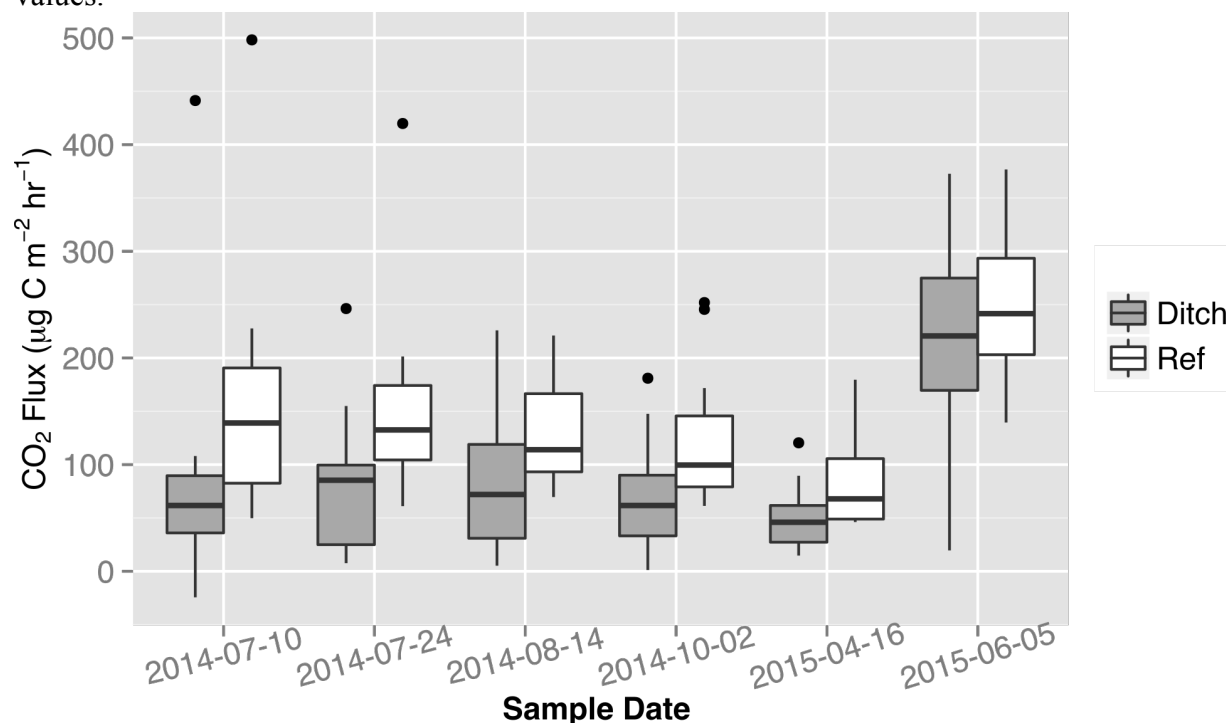


Figure B8. Boxplots of CO₂ for all six time-points. Data include all twelve research sites. Horizontal black lines show the data median, the box boundaries mark the first and third quartiles, the whiskers indicate 1.5 times the interquartile range, and the points represent extreme values.

Table B1. Summary of soil conditions. Reported values indicate mean \pm standard error.

Site	Sampling Location	VWC vol vol ⁻¹	OM %	C %	N %	NO ₃ ⁻ μg g ⁻¹	pH	Lawn Fertilized?
1	Ditch	0.30 ± 0.04	6.4 ± 0.0	5.86 ± 2.14	0.30 ± 0.02	5.9 ± 3.8	7.80 ± 0.01	
	Ref	0.38 ± 0.05	6.5 ± 0.1	5.05 ± 0.75	0.37 ± 0.04	1.5 ± 1.2	7.95 ± 0.37	No
2	Ditch	0.63 ± 0.05	5.3 ± 0.7	6.04 ± 0.09	0.40 ± 0.00	6.8 ± 3.3	7.87 ± 0.26	
	Ref	0.44 ± 0.06	6.6 ± 1.2	7.10 ± 3.52	0.44 ± 0.19	2.5 ± 2.0	7.63 ± 0.01	No
3	Ditch	0.77 ± 0.07	8.5 ± 0.2	6.87 ± 1.01	0.43 ± 0.08	3.5 ± 0.1	8.07 ± 0.33	
	Ref	0.38 ± 0.06	7.7 ± 0.5	6.19 ± 2.70	0.34 ± 0.12	2.7 ± 1.7	7.74 ± 0.11	No
4	Ditch	0.51 ± 0.05	7.7 ± 0.1	8.83 ± 0.88	0.58 ± 0.05	7.8 ± 0.9	7.88 ± 0.38	
	Ref	0.35 ± 0.05	5.4 ± 0.9	5.32 ± 2.70	0.29 ± 0.06	4.5 ± 0.5	7.58 ± 0.04	Yes
5	Ditch	0.48 ± 0.05	8.4 ± 0.0	7.83 ± 0.48	0.50 ± 0.04	19.5 ± 8.8	7.98 ± 0.12	
	Ref	0.36 ± 0.05	4.8 ± 0.4	5.50 ± 0.16	0.33 ± 0.07	3.3 ± 2.7	8.33 ± 0.05	Yes
6	Ditch	0.67 ± 0.05	9.8 ± 2.2	2.62 ± 0.30	0.13 ± 0.00	5.7 ± 1.9	7.75 ± 0.08	
	Ref	0.49 ± 0.06	6.2 ± 0.0	7.02 ± 2.27	0.35 ± 0.04	3.2 ± 2.5	7.92 ± 0.03	No
7	Ditch	0.54 ± 0.04	3.5 ± 0.1	5.88 ± 0.49	0.48 ± 0.04	1.4 ± 1.1	7.72 ± 0.00	
	Ref	0.32 ± 0.03	4.6 ± 0.6	8.35 ± 4.63	0.58 ± 0.28	0.3 ± 0.1	7.89 ± 0.01	Yes
8	Ditch	0.71 ± 0.05	7.1 ± 0.9	5.32 ± 0.40	0.26 ± 0.02	7.9 ± 4.8	7.76 ± 0.00	
	Ref	0.56 ± 0.05	5.3 ± 0.1	4.69 ± 0.64	0.34 ± 0.02	4.4 ± 1.3	8.21 ± 0.17	No
9	Ditch	0.63 ± 0.03	5.9 ± 2.1	9.25 ± 1.75	0.72 ± 0.00	5.0 ± 0.2	8.17 ± 0.14	
	Ref	0.37 ± 0.04	3.0 ± 0.8	7.07 ± 0.34	0.42 ± 0.02	6.2 ± 0.1	8.39 ± 0.02	Yes
10	Ditch	0.63 ± 0.02	5.9 ± 0.4	5.00 ± 0.85	0.17 ± 0.05	3.2 ± 0.8	7.70 ± 0.43	
	Ref	0.36 ± 0.04	5.6 ± 1.4	4.70 ± 0.16	0.26 ± 0.02	4.0 ± 1.1	8.10 ± 0.02	No
11	Ditch	0.70 ± 0.04	5.5 ± 0.3	8.51 ± 0.88	0.58 ± 0.07	2.0 ± 1.7	7.83 ± 0.09	
	Ref	0.54 ± 0.03	3.5 ± 0.8	8.28 ± 2.95	0.60 ± 0.20	0.3 ± 0.2	7.49 ± 0.02	Yes

Table B1 (continued)

12	Ditch	0.77 ± 0.06	6.9 ± 1.9	7.46 ± 0.98	0.54 ± 0.08	2.5 ± 2.2	7.72 ± 0.36	
	Ref	0.39 ± 0.05	4.2 ± 1.3	6.16 ± 0.61	0.27 ± 0.12	2.6 ± 2.2	7.63 ± 0.01	Yes
All Sites	Ditch	0.61 ± 0.02	6.7 ± 0.4	6.62 ± 0.02	0.42 ± 0.13	2.9 ± 0.5	7.90 ± 0.07	
	Ref	0.41 ± 0.01	5.3 ± 0.3	6.29 ± 0.06	0.38 ± 0.08	5.7 ± 1.2	7.85 ± 0.20	

Table B2. List of GHG sampling dates with average air and soil temperature, 1 day antecedent precipitation, and 3 day antecedent precipitation (NRCC, 2016)

Date	Air Temp °C	Soil Temp °C	1 Day Precip cm	3 Day Precip cm
10-11 Jul 2014	17.4	22.8	0.15	2.49
24-25 Jul 2014	18.2	22.7	0.66	0.66
13-14 Aug 2014	17.2	21.5	3.25	3.81
1-2 Oct 2014	16.1	18.0	0.33	0.33
14-15 Apr 2015	10.4	10.9	1.63	1.63
4-5 Jun 2015	16.8	19.2	0	0.28

Table B3. Summary of water quality data. Reported values indicate mean ± standard error.

Sampling Location	NO _x mg N L ⁻¹	DOC mg C L ⁻¹
Ditch 1	NA	NA
2	0.21 ± 0.13	16.91 ± 3.55
3	0.15 ± 0.09	17.84 ± 2.83
4	0.48 ± 0.23	18.37 ± 4.17
5	0.39 ± 0.17	12.86 ± 2.50
6	0.46 ± 0.13	9.94 ± 2.20
7	0.91 ± 0.85	27.69 ± 7.48
8	0.38 ± 0.17	10.53 ± 1.73
9	0.85 ± 0.28	14.33 ± 5.02
10	0.43 ± 0.14	19.52 ± 7.76
11	0.27 ± 0.14	23.10 ± 7.51
12	0.68 ± 0.46	17.97 ± 3.37
All Ditches	0.47 ± 0.10	17.19 ± 1.46
Stream- Up	0.27 ± 0.10	10.69 ± 3.03
Stream- Outlet	0.38 ± 0.09	4.73 ± 0.06

Table B4. Summary of denitrification and greenhouse gas fluxes. Reported values indicate mean \pm standard error.

Site	Sampling Location	Denit. Potential mg N kg ⁻¹ hr ⁻¹	N ₂ O Flux μg N m ⁻² hr ⁻¹	CO ₂ Flux mg C m ⁻² hr ⁻¹	CH ₄ Flux μg C m ⁻² hr ⁻¹
1	Ditch	2.05 \pm 0.19	2.0 \pm 1.1	93.8 \pm 19.9	9.4 \pm 4.0
	Ref	1.03 \pm 0.38	4.6 \pm 2.0	123.2 \pm 22.5	2.3 \pm 3.3
2	Ditch	0.94 \pm 0.42	-0.8 \pm 0.5	80.0 \pm 30.4	11.0 \pm 10.5
	Ref	0.54 \pm 0.09	1.8 \pm 1.0	103.2 \pm 19.4	-5.9 \pm 2.8
3	Ditch	0.40 \pm 0.09	5.2 \pm 5.1	112.3 \pm 38.5	1192.5 \pm 880.6
	Ref	0.19 \pm 0.12	2.1 \pm 1.0	130.8 \pm 21.1	1.0 \pm 2.9
4	Ditch	1.75 \pm 0.26	-0.4 \pm 1.2	186.9 \pm 75.2	2.2 \pm 2.7
	Ref	0.53 \pm 0.12	5.1 \pm 2.2	161.0 \pm 30.6	-7.6 \pm 4.1
5	Ditch	4.44 \pm 0.72	1.9 \pm 1.9	95.2 \pm 38.6	1.7 \pm 4.1
	Ref	1.33 \pm 0.40	1.8 \pm 1.5	137.7 \pm 28.3	-2.2 \pm 4.2
6	Ditch	3.14 \pm 0.69	1.1 \pm 0.7	54.5 \pm 21.4	288.0 \pm 228.3
	Ref	0.98 \pm 0.32	5.4 \pm 3.8	110.0 \pm 17.1	24.1 \pm 26.0
7	Ditch	9.45 \pm 7.52	10.9 \pm 3.9	106.8 \pm 24.1	54.0 \pm 31.4
	Ref	1.39 \pm 0.40	29.5 \pm 7.8	248.0 \pm 39.7	1.9 \pm 3.8
8	Ditch	1.93 \pm 1.90	-0.8 \pm 0.6	21.0 \pm 7.9	920.5 \pm 471.5
	Ref	0.54 \pm 0.25	0.4 \pm 1.1	92.3 \pm 15.4	12.8 \pm 3.3
9	Ditch	1.72 \pm 0.41	1.5 \pm 1.3	112.2 \pm 26.6	19.9 \pm 10.3
	Ref	0.96 \pm 0.08	4.1 \pm 2.6	190.0 \pm 32.6	5.8 \pm 4.7
10	Ditch	2.79 \pm 0.94	0.3 \pm 1.3	95.2 \pm 14.2	313.9 \pm 247.5
	Ref	0.83 \pm 0.17	0.8 \pm 0.8	124.6 \pm 26.9	212.8 \pm 204.0
11	Ditch	9.26 \pm 3.32	0.9 \pm 0.7	151.7 \pm 21.2	305.1 \pm 152.6
	Ref	1.84 \pm 0.91	5.7 \pm 2.5	242.4 \pm 34.1	51.8 \pm 40.7
12	Ditch	3.55 \pm 0.87	13.5 \pm 9.9	68.9 \pm 19.1	4328.6 \pm 3765.1
	Ref	1.57 \pm 0.18	16.0 \pm 8.3	148.7 \pm 25.0	74.5 \pm 30.2
All Sites	Ditch	3.45 \pm 0.79	2.9 \pm 1.1	98.2 \pm 9.7	624.8 \pm 330.7
	Ref	0.98 \pm 0.12	6.4 \pm 1.2	151.0 \pm 8.5	30.9 \pm 17.7