Greenhouse gas emissions from saturated riparian buffers and woodchip bioreactors

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Greenhouse gas emissions from saturated riparian buffers and woodchip bioreactors

by

Morgan P. Davis

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Environmental Science

Program of Study Committee:
Thomas M. Isenhart, Major Professor
Matthew J. Helmers
Kirsten S. Hofmockel
Dan B. Jaynes
Timothy B. Parkin

The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University
Ames, Iowa
2018

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ACKNOWLEDGMENTS

I would like to thank my major professor, Dr. Thomas M. Isenhart, and my committee members, Dr. Matthew J. Helmers, Dr. Kirsten S. Hoffmockel, Dr. Dan B Jaynes, and Dr. Timothy B. Parkin, for their funding, guidance, and support throughout the course of this research. I feel honored to have had the opportunity to learn from such outstanding scientists and academics. I would like to thank Dr. Richard Schultz for his encouragement and unwavering support as a mentor. Also, thank you to the Department of Natural Resource Ecology and Management staff, with a special thanks to Kelly Kyle, Janice Berhow, Tammy Porter, and Sue Jones. Research would be impossible without your help.

In addition, I would also like to thank my colleagues, undergraduate employees, and friends at Iowa State University. While it is impossible to mention all of the individuals who have contributed to this work, notable individuals include: Cameron Adams, Chelsea Ferrie, Jack Heikens, Kent Heikens, Tim King, Joe Klingelhutz, Hannah McBrearty, Corey McKinney, Shane Murphy, Mason Nafts, and Clay Rogers, Hillary Pierce. To Billy Beck and Tyler Groh, you are two of my best friends. Thank you for making everyday a work adventure.

I want to thank my parents, Jeff and Tammy Davis, and grandparents, Gary and Silvia Morgan. The support from my parents has been unmeasurable and I contribute all of my success to the values they have instilled in me. Thank you to my late grandfathers Dr. Edward Davis and Dennis Schmidt. Lastly, I want to thank my wife, Mary Davis. Mary, you are my balance in life. Thank you for your patience and open heart.
This material is based on work funded in part by the Foundational Program from the USDA National Institute of Food and Agriculture (Grant no. 2013-67019-2193/Project Accession no. 1001190) and the National Science Foundation (Grant no. EPSC-1101284).
Nitrogen (N) losses from the Mississippi River Basin contribute to the hypoxic zone in the Gulf of Mexico, and NO$_3^-$ concentrations in surface waters often exceed the USEPA’s drinking water standard of 10 mg-N L$^{-1}$. Nitrate from artificial subsurface drainage (tiles) underlying agricultural fields can be a major source of reactive N in surface waters. Reducing N flux from agroecosystems is complex and difficult to manage at the watershed scale, as N management alone will not significantly reduce N flux. One method for N removal is enhanced microbial denitrification in edge of field practices. Microbial denitrification is an anaerobic process that reduces NO$_3^-$ to N$_2$ gas. Nitrogen gas released to the atmosphere in a non-reactive state. However, incomplete denitrification can result in nitrous oxide (N$_2$O) production. Nitrous oxide is the third largest contributor to radiative forcing and global climate change. Furthermore, other forms of anaerobic respiration producing greenhouse gases, like methane, can occur in environments designed for denitrification. The studies presented in this dissertation improve greenhouse gas sampling methodology and advance understanding of the effects of enhanced denitrification technologies on greenhouse gas emissions. The Chamber Automated Sampling Equipment (FluxCASE) to measure soil gas flux was found to be accurate and precise compared to manual sampling and improved sampling efficiency. The FluxCASE system was utilized to maximize coverage of spatial variability associated with gas flux from soil surfaces of saturated riparian buffers (SRBs) and woodchip bioreactors. Nitrous oxide emissions from SRBs were compared to traditional buffers and corn (*Zea mays* L.) and soybean (*Glycine max* (L.) Merr.) agriculture. Nitrous oxide emissions from SRBs were similar to traditional buffers and lower than crop fields.
Nitrous oxide and CH$_4$ production was measured at three hydraulic retention times (HRTs) from pilot scale (5.8 × 1.0 × 1.1 m) woodchip bioreactors. Nitrous oxide production increased with decreasing HRT and CH$_4$ increased with increasing HRT. The lowest HRT had the greatest global warming potential. Edge of field practices designed to enhance microbial denitrification are integral strategies to reduce NO$_3$ loss to surface waters, and have the potential to also reduce greenhouse gas emissions from agricultural landscapes.
CHAPTER 1. INTRODUCTION

Anthropogenic activities have more than doubled the amount of reactive nitrogen (N) cycling across the globe (Vitousek et al., 1997). The majority of anthropogenic N is produced as fertilizer for conventional row crops (Galloway et al., 2008). The terrestrial-aquatic interface of agricultural watersheds is a hotspot for N transformations and particularly important for quantifying N losses to aquatic ecosystems (Groffman et al., 2000). Nitrogen losses are intensified by subsurface (tile) drainage of agricultural lands (Jaynes et al., 2001). Displaced N from agroecosystems has resulted in the eutrophication of surface waters and increase in atmospheric nitrous oxide (N$_2$O), a powerful greenhouse gas (Gruber and Galloway, 2008).

Nitrogen losses from the Upper Midwest of the United States (US) contribute to the hypoxic zone in the Gulf of Mexico and nitrate concentrations in surface waters exceeding the Environmental Protection Agency’s (EPA) drinking water standard (Schilling and Zhang, 2004; David et al., 2010). The US EPA convened a Hypoxia Task Force in 2008 to develop an action plan for states in the Mississippi River Basin (MRB) to reduce nutrients contributing to the hypoxic zone in the Gulf of Mexico. The first action item of the 2008 plan called for states to develop nutrient reduction strategies to reduce N losses by 45% (US EPA, 2008). Reduction strategies from Iowa and Illinois, two of the MRBs largest contributors of N to the Gulf of Mexico, identify non-point source pollution, particularly agricultural drainage, as a significant focus area for N loss reduction (IDALS et al., 2014; Illinois EPA, 2015). The Iowa nutrient reduction strategy utilizes N management, land retirement, and edge of field agronomic practices to reach a statewide 45% N reduction. Edge of field practices with the greatest N reduction potential include wetlands, woodchip bioreactors, and saturated riparian buffers (SRBs). These conservation practices remove nitrate (NO$_3$) from drainage water through microbial
denitrification, the reduction of NO$_3$ to N$_2$ gas. Complete denitrification returns reactive N to a non-reactive state in the atmosphere (Seitzinger et al., 2006). Incomplete denitrification can yield N$_2$O, the third largest greenhouse gas contributor to radiative forcing with 265 times (100-year adjustment without the inclusion of climate-carbon feedbacks) the global warming potential of carbon dioxide (Myhre et al., 2013). Furthermore, denitrifying technologies may create environments ideal for other forms of anaerobic respiration, including methane (CH$_4$) production through methanogenensis (Healy et al., 2012). Methane is the second largest contributor to radiative forcing and has 28 times (100-year adjustment without the inclusion of climate-carbon feedbacks) the global warming potential of carbon dioxide (Myhre et al., 2013). Concerns of trading NO$_3$ losses to surface waters with greenhouse gases in the atmosphere are addressed in this dissertation. The chapters include: i) a methodological study detailing automated greenhouse gas samplers used in subsequent chapters, ii) the first study of N$_2$O emissions from SRBs, iii) and a study advancing understandings of N$_2$O and CH$_4$ production in woodchip bioreactors.

Chapter 2, “Portable Automation of Static Chamber Sample Collection for Quantifying Soil Gas Flux”, presents a study published in The Journal of Environmental Quality. The objective was to test the precision and accuracy of an automated sampling system to improve the efficiency of greenhouse gas sample collection from soil gas flux. Manual sampling from static vented chambers is an inexpensive method to simultaneously collect multiple gas species from soil gas flux (Parkin and Ventera, 2010). However, the static chamber method is labor intensive, which often limits the number of chambers that can be deployed for a given sampling period. Automated samplers improve efficiency of static chamber sample collection, while maintaining the accuracy and precision of manual sampling. Accuracy and precision were tested in field and laboratory studies to examine a range of gas concentrations and fluxes. The automated samplers
developed were vital in sample collection from the surface of SRBs and bioreactors in subsequent chapters.

Chapters 3 and 4 investigate greenhouse gas flux from SRBs and woodchip bioreactors. In chapter 3, “Nitrous Oxide Emissions from Saturated Riparian Buffers: Are We Trading a Water Quality Problem for an Air Quality Problem?”, N\textsubscript{2}O measurements were made at two SRBs in central Iowa over three years. Saturated riparian buffers are a newly developed conservation practice that divert tile water into the soil of a vegetated buffer. Tile water is then allowed to seep through the buffer, where microbes in the carbon rich alluvial soil denitrify dissolved NO\textsubscript{3}. Despite only one published study quantifying nitrate removal from a tile drained field (Jaynes and Isenhart, 2014), the potential for efficient N removal has prompted rapid adoption of SRBs into nutrient reduction strategies. The USDA Natural Resource Conservation Service (NRCS) has developed a Conservation Practice Standard (cite 604) and SRB establishment is eligible for incentives in several state and federal programs, including the USDA Farm Services Agency Conservation Reserve Program. The study in Chapter 3 is the first to examine N\textsubscript{2}O emissions as a product of enhanced denitrification in SRBs. The objective was to compare direct and indirect N\textsubscript{2}O emissions from SRBs, traditional buffers, and crop fields in corn (\textit{Zea mays} \textit{L.}) and soybean [\textit{Glycine max} (\textit{L.}) Merr.] rotations. Chapter 3 results expand the limited body of work on SRBs, and highlight SRB potential to reduce N\textsubscript{2}O emissions from riparian zones in agroecosystems.

In Chapter 4, “Nitrous Oxide and Methane Production from Denitrifying Woodchip Bioreactors at Three Hydraulic Retention Times”, N\textsubscript{2}O and CH\textsubscript{4} production was measured within pilot scale (5.8 × 1.0 × 1.1 m) bioreactors across three different hydraulic retention times (HRTs). Unlike SRBs, several studies have measured greenhouse gas emissions from woodchip
bioreactors. Bioreactors have been shown to produce both N\textsubscript{2}O (Elgood et al., 2010; Greenan et al., 2009; Warneke et al., 2011) and CH\textsubscript{4} (Elgood et al., 2010; Healy et al., 2012). However, the effect of HRT on greenhouse gas production from bioreactors has previously only been studied at the laboratory scale (Greenan et al., 2009; Healy et al., 2012). Pilot scale reactors create similar conditions to field scale bioreactors but allow for replication and precise flow manipulation (Hoover et al., 2017). Our objective in chapter 4 was to examine the effect of hydraulic retention time (HRT) on the production of N\textsubscript{2}O and CH\textsubscript{4} through denitrifying woodchip bioreactors. Results from this study can be used for future bioreactor design to maximize NO\textsubscript{3} removal and minimize greenhouse gas production.

Pressures to reduce N losses from agroecosystems will continue to increase as environmental effects remain prevalent (Galloway et al., 2003; Galloway et al., 2008). Denitrification strategies to reduce N losses to aquatic ecosystems are ideal as the N is not stored but returned to a non-reactive state in the atmosphere. These studies were conducted to examine potential adverse effects of implementing denitrifying technologies to reduce nitrate flux to surface waters. Results will inform the potential for denitrifying conditions to increase greenhouse gas emissions from SRBs and woodchip bioreactors.

References


CHAPTER 2. PORTABLE AUTOMATION OF STATIC CHAMBER SAMPLE COLLECTION FOR QUANTIFYING SOIL GAS FLUX

A manuscript published in The Journal of Environmental Quality

Morgan P. Davis, Tyler A. Groh, Timothy B. Parkin, Ryan J. Williams, Thomas M. Isenhart, and Kirsten S. Hofmockel

Contributions
The study was designed by MPD, TBB, RJW, and KSH
MPD and TAG performed the analysis
MPD was the primary author with contributions from TAG, TBB, TMI, and KSH

Abstract

Quantification of soil gas flux using the static chamber method is labor-intensive. The number of chambers that can be sampled is limited by the spacing between chambers and the availability of trained research technicians. An automated system for collecting gas samples from chambers in the field would eliminate the need for personnel to return to the chamber during a flux measurement period and would allow a single technician to sample multiple chambers simultaneously. This study describes Chamber Automated Sampling Equipment (FluxCASE) to collect and store chamber headspace gas samples at assigned time points for the measurement of soil gas flux. The FluxCASE design and operation is described, and the accuracy and precision of the FluxCASE system is evaluated. In laboratory measurements of nitrous oxide (N$_2$O), carbon dioxide (CO$_2$), and methane (CH$_4$) concentrations of a standardized gas mixture, coefficients of variation associated with automated and manual sample collection were comparable, indicating no loss of precision. In the field, soil gas fluxes measured from FluxCASEs were in agreement with manual sampling for both N$_2$O and CO$_2$. Slopes of regression equations were 1.01 for CO$_2$ and 0.97 for N$_2$O. The 95% confidence limits of the slopes of the regression lines included the value of one, indicating no bias. Additionally, an
expense analysis found a cost recovery ranging from 0.6 to 2.2 yr. Implementing the FluxCASE system is an alternative to improve the efficiency of the static chamber method for measuring soil gas flux while maintaining the accuracy and precision of manual sampling.

**Introduction**

Soil greenhouse gas fluxes are commonly measured using the static chamber method (Rochette et al., 2012; Parkin and Venterea, 2010; de Klein et al., 2014; Maier and Schack-Kirchner 2014). Benefits to using static chambers for collecting soil gas flux include their low cost and allowance for the analysis of carbon dioxide (CO$_2$), nitrous oxide (N$_2$O), and methane (CH$_4$) from a single sample. Because of their relative simplicity and low cost, multiple chambers can be used to provide enhanced spatial coverage applicable to replicated plot studies (de Klein et al., 2014) or investigation of landscape effects (Denmead, 2008). However, the requirement for collection of multiple gas samples from the chamber headspace over the flux measurement period (Parkin and Venterea, 2010) presents logistical challenges, especially if many chambers are deployed and/or chamber spacing across the study area is great. To ensure precisely timed sample collection, the number of chambers that can be sampled by an individual is limited by the proximity of chambers to one another. Therefore, the number and spacing of chambers will be dictated by labor availability.

Automated chambers have been used to measure soil gas flux (Shütz et al., 1989; Ambus and Robertson, 1998; Scott et al., 1999; Parkin and Kaspar, 2003; Savage and Davidson, 2003; Parkin, 2008; Rowlings et. al., 2012, Scheer et al., 2012; Barton et al., 2015), and have an advantage over static chamber methods with regard to enhanced temporal coverage. However, most systems are designed to be stationary in the field and have additional logistical requirements such as a power supply and instrument housing. Replication of these systems to
account for spatial variability can be costly. For example, new analytical equipment using near-infrared and tuneable diode lasers allows for simultaneous analysis of CO₂, N₂O, and CH₄ fluxes (Werle et al., 2002), but this equipment is expensive and can be cumbersome to transport in the field.

Here we describe a cost-effective portable automated instrument that interfaces with static chambers and allows for simultaneous collection and storage of samples from multiple locations while also significantly reducing time and associated labor costs of manual sampling. The Chamber Automated Sampling Equipment for measuring soil gas flux (FluxCASE) automatically collects samples at assigned time points into a syringe equipped with a stopcock for storage. Multiple FluxCASEs can be deployed simultaneously, eliminating the need for technicians to return to each chamber multiple times during the flux measurement period. The objectives of this study were to examine the viability and cost effectiveness of the FluxCASE system. We designed laboratory and field experiments to assess accuracy and precision, both among FluxCASEs and compared with manual sampling. Furthermore, we examined expense recovery through three scenarios.

**Material and Methods**

**FluxCASE Design**

The FluxCASE consists of four major components: (i) an Arduino Uno microcontroller interfaced to a relay board, (ii) a linear actuator attached to a sampling syringe, (iii) solenoid valves with attached collection syringes, and (iv) a battery (Fig. 2.1). A length of flexible tubing connects the chamber headspace to solenoid no. 1, and the sampling syringe is attached to the common port of solenoid no. 1 with a length of 0.32 cm copper tubing. All the solenoids are linked together with 0.32 cm copper tubing. Collection syringes are connected to their respective solenoids by a female Luer fitting. A detailed list of all components is provided in (Table 2.1).
All components are housed in a fluorescent orange storage box (Model 141250, Plano Storage Solutions), allowing for easy deployment and visibility in the field (Fig. 2.2).

**FluxCASE Operation**

The principle underlying the operation of FluxCASE is that at fixed time intervals (programmable by the user) the linear actuator is energized by the microcontroller and relay board, and the sampling syringe withdraws a volume of gas from the chamber headspace. Solenoid no. 1 is energized to bring the gas contained in the sampling syringe in line with solenoids 2 through 5. Depending on the energized states of solenoids 2 through 5, the gas in the sampling syringe can be directed to one of the four collection syringes. After the desired collection syringe is selected, the linear actuator is deenergized and the sample syringe injects the gas into the collection syringe. The solenoid attached to the filled collection syringe is then deenergized, isolating the gas in the collection syringe from the other solenoids in the chain. This process is then repeated at subsequent time points (programmable by the user) to collect subsequent gas samples in the remaining collection syringes. After the chamber deployment period, the stopcocks on the syringes are manually closed to prevent sample loss while the syringes are transported to the laboratory for gas analyses (detailed below).

Before the sampling time points, the internal tubing and solenoids are flushed with chamber headspace gas. The flushing operation is accomplished by actuating the sampling syringe to withdraw 40 mL of headspace gas. Solenoid no. 1 is then energized and the linear actuator is deenergized to expel the gas from the sampling syringe out the vent port on solenoid no. 5. It should be noted that although the sampling syringe has a 60-mL volume, the actual volume of gas withdrawn is controlled by the throw length of the linear actuator. For the system described here, the throw length of the linear actuator results is a 40-mL gas sample. Flushing the system with sample before collection in the syringe eliminates contamination from the previous sample.
remaining in the system tubing. The size of the sampling syringe can be modified but should not be less than the volume of the system tubing (6.29 mL) plus the size of sample injected into the collection syringe. It is also noted that the 40-mL flush event results in a slight dilution of chamber headspace gas, as outside air is drawn into the chamber through the vent line (in a vented chamber). The degree of dilution is dependent on chamber headspace volume. With the chambers used in this study (30-cm diam., 15-cm height), the chamber headspace volume is ~10.6 L, and the resulting error due to dilution is <0.4%.

**Laboratory Evaluations and Gas Analyses**

The precision and accuracy of FluxCASE was examined in the laboratory by evaluating samples taken from a 40-L gas bag filled with standard gas. Concentrations of the standard gas components (CH$_4$, CO$_2$, and N$_2$O) were certified by the National Institute of Standards and Technology (NIST). The gas bag was flushed with helium three times before being completely evacuated and filled with the NIST standard gas mixture. A FluxCASE was attached to the gas bag through the sampling tube. The gas bag was equipped with a stopcock and positive pressure was applied to the bag to flush the tube and stopcock before connection. The FluxCASE was then actuated and allowed to complete operation as described above. Three different FluxCASEs were used to sample the standard gas five times, for a total of 20 samples per FluxCASE (five repeated samplings across the four ports). Five samples were also collected manually from the gas bag using a 20-mL syringe before and after each of the three FluxCASE runs, totaling 20 manual samples. All samples were collected from a single gas bag that was filled once before the start of the experiment. Thirteen milliliters of each sample was transferred from the collection syringe to a 6-mL evacuated vial. All samples were analyzed for CO$_2$, N$_2$O, and CH$_4$ on a gas chromatograph (SRI Instruments, Model 8610) equipped with an electron capture detector and a flame ionization detector. Gas species separation took place in a stainless steel column (0.3175-
cm diam. × 74.54-cm length) packed with Haysep D. Nitrogen was used as a carrier gas (25 mL min$^{-1}$). An autosampler (Arnold et al., 2001) was used to introduce the gas samples into the sample valve on the gas chromatograph. Sample concentration was calculated using linear regression coefficients of analyzed certified gas standards (Air Liquide specialty gases). Coefficients of variation were calculated for all three gases on all three FluxCASEs. The FluxCASE samples were compared with manual samples using ANOVA. Furthermore, each sampling port from the five different FluxCASEs was compared with every other sampling port in an ANOVA with a Tukey’s honest significance post-hoc test (78 comparisons for each gas). All statistics were conducted in R version 3.1.2 (R Development Core Team, 2014).

**Field Evaluation**

Field samples were collected to compare soil gas fluxes from manual samples with those collected by FluxCASEs. The FluxCASE samples were collected in conjunction with a project designed to quantify greenhouse gas emissions from a switchgrass (*Panicum virgatum* L.) riparian buffer removed from agricultural production of corn (*Zea mays* L.) and soybean (*Glycine max* (L.) Merr.] in 1995 (Fig. 2.2). Sampling took place on a USDA National Resources Conservation Service-described Coland soil series (fine-loamy, mixed, supepractive, mesic Cumlic Endoaquoll). Circular polyvinyl chloride (PVC) anchors and chambers were used as described in Appendix IV of Parkin and Venterea (2010). Chamber tops were constructed from Section 40 PVC (30-cm diam. × 15-cm height) and were vented and covered with reflective tape to minimize temperature changes from solar radiation. Two 20-mm holes were drilled to house two 20-mL butyl rubber septa (Voigt Global). Two septa ports allowed for simultaneous manual and FluxCASE sample collection. Manual samples were collected from one septa while 5 cm of the sampling tube was inserted into the other septa. Needle and sampling tube depth were equal
to one another. Anchors were constructed from 30-cm-diam. PVC and were 15 cm in height. Ten centimeters of each anchor was inserted into the ground, leaving 5 cm exposed above the surface. Five FluxCASEs, including the three FluxCASEs used in the laboratory evaluation, were randomly assigned to a pool of 20 locations within the 0.6-ha riparian buffer. Samples were collected on five different dates from May through July of 2015, for a total of 25 flux measurements. Manual samples were collected simultaneously with 20-mL syringes equipped with stopcocks (identical to those used in the FluxCASEs) at each of the four sample time points (0, 15, 30, and 45 min) taken by the FluxCASEs.

Additionally, to sample across a range of flux intensities, six independent locations were sampled from a nearby site after treatment to enhance CO₂ and N₂O production (Christensen et al., 1990). The six treated sites were also described as a Coland soil series and were located in a riparian area of an Iowa State University farm 16 km downstream of the buffer site. The university farm site was the closest accessible location where fertilization did not conflict with any other ongoing experiments. Six static chamber anchors were installed and the soil surface was disturbed with a hand trowel, watered (2 L), and fertilized with ammonium nitrate at a rate 200 kg N ha⁻¹. Fertilized locations were sampled in the same manner as described above four times at 12 h after fertilization on 29 Sept. 2015.

Samples were placed in evacuated vials and analyzed on a gas chromatograph as described above. Fluxes were calculated using the HMR package in R version 3.1.2 (R Development Core Team, 2014), as described by Pedersen et al. (2010). If the HMR software failed to produce a flux using the HMR model, the HMR software used linear regression for flux calculation or assigned a “no flux” value of zero.
Expense Analysis

An expense analysis was conducted to determine the expense recovery from the design and construction of 20 FluxCASEs. We defined expense recovery as the number of sampling years needed to cover FluxCASE investment costs. Chamber quantity, chamber spacing, sampling events, and labor costs were evaluated to create expense recovery scenarios. Three scenarios were considered in the expense analysis. Scenario 1 adjusts the number of chambers to reflect chamber-intensive experiments. Scenario 2 calculates expenses for experiments with increased labor costs. Scenario 3 depicts experiments designed to sample frequently over a given year. Several assumptions were made in the expense analysis on the basis of personal field experiences and literature recommendations. Labor expense for greenhouse gas sampling was dependent on chamber spacing and the number of chambers deployed. At a sampling rate of 1.5 min chamber$^{-1}$ (60 s for walking, and 30 s for sampling) and a walking rate of 5 km h$^{-1}$ (or 83 m min$^{-1}$), 10 chambers could be manually sampled if the complete route to return to the starting chamber was <83 m. To cover a greater spatial variability, experimental designs may require greater chamber spacing than 83 m. A rate of US$10.00 h$^{-1}$ was used as the standard rate of pay. Finally, the expense analysis assumed 52 sampling events per year.

Results and Discussion

Precision

Precision (variability) was determined in the laboratory evaluation by comparing three FluxCASEs to manual samples taken from a gas bag filled with a NIST gas mixture. Coefficients of variation of FluxCASE samples for N$_2$O, CO$_2$, and CH$_4$ were all comparable with manual samples (Table 2.2). The FluxCASE coefficients of variation ranged from 11.0 to 15.3% for N$_2$O, 18.5 to 22.4% for CO$_2$, and 3.5 to 6.2% for CH$_4$, compared with manual sample variations
of 16.7% for N$_2$O, 16.3% for CO$_2$, and 3.2% for CH$_4$. The FluxCASE precision was comparable with manual sampling for N$_2$O and CH$_4$, but slightly lower for CO$_2$.

**Accuracy**

Accuracy (bias) was assessed from both laboratory and field evaluations. In the laboratory, gas concentrations of samples taken from the NIST standard bag were compared among each port across all three FluxCASEs. Mean concentrations of gases in samples collected with the FluxCASEs were not significantly different from samples collected manually ($P \geq 0.44$) for all three gas species (Table 2.2). Furthermore, no sampling port was significantly different ($P \geq 0.71$) from any other sampling port for all three gases analyzed (data not shown).

Accuracy was determined in the field by comparing N$_2$O and CO$_2$ flux rates from the FluxCASEs with those from manual sampling (Fig. 2.3). Methane fluxes were not observed from the soil surface and therefore were not included in the analysis. Nitrous oxide and CO$_2$ fluxes were greater in the fertilized sites compared with the unfertilized sites. Slopes of the regression equations comparing emissions determined by FluxCASE gas sampling vs. manual sampling were 1.01 for CO$_2$ and 0.97 N$_2$O. The 95% confidence intervals of the regression lines for both CO$_2$ and N$_2$O included the 1:1 line, indicating no significant bias in the FluxCASE samples compared with manual sampling.

**Expense Recovery**

The FluxCASEs designed in this study cost ~$337 per unit (Table 2.1). Labor expenses of assembly were not included in the cost estimation, as they are dependent on the source of assembly (e.g., student employee vs. professional engineer). Although assembly does not require an expertise in electrical engineering, some knowledge of electronic systems is needed.
We calculated manual labor expenses to be four times that of FluxCASE labor expenses, as our spacing is, on average, five chambers per 80.5 m (the maximum distance that can be covered through assumptions detailed in the method section). A technician equipped with 20 FluxCASEs could reasonably sample 20 sites in an hour. Manual sampling of the same 20 sites would take a technician 4 h, limited to deploying five chambers before the initial chamber needs to be sampled again. Therefore, expense recovery was shortest for chamber-intensive and event-intensive experiments (Table 2.3). The FluxCASE system was found to be less expensive than manual sampling in experiments lasting >1 yr, where researchers are sampling 80 chambers weekly or 200 events a year. Cost recovery was found within 2.2 yr in very labor-intensive situations, including experiments where study sites are in different locations and travel is required from one site to another. The FluxCASE system reduces labor expenses and narrows the sampling window to minimize diurnal variability observed in CO$_2$ and N$_2$O fluxes (Kaiser et al., 1998; Parkin and Kaspar, 2003; Parkin, 2008). Scenarios presented in Table 2.3 do not represent all scenarios where the FluxCASE system is cost effective. A single variable was adjusted in each scenario. If multiple variables were considered, there are scenarios in which the FluxCASE system would rapidly reach cost recovery. For example, if a study calls for 104 sampling events across 80 chambers, cost recovery would be obtained in 0.5 yr. Although there are many scenarios where the FluxCASE system is less expensive than manual sampling, an expense analysis should be calculated before investing.

**Conclusions**

Recent research has highlighted the importance of high sampling intensity of static chambers to incorporate more spatial and temporal variability, specifically with N$_2$O emissions (Parkin, 2008; Jeuffroy et al., 2013; Rees et al., 2013; Barton et al., 2015). Sufficient manual sampling to include a greater coverage of spatial and temporal variability is labor intensive. The FluxCASE
is an alternative to intensive manual sampling that can increase efficiency and eliminate human-induced sampling error. Manual sampling requires a technician to sample at known time points to ensure accurate flux modeling. The FluxCASE eliminates potential sampling time errors. It could also help improve flux estimates if future designs collected samples at more than four time points, improving fit in linear, Hutchinson–Mosier, and quadratic flux models. The FluxCASE was found to be both accurate and precise when compared with manual sampling. Implementing the FluxCASE system is an alternative to improve the efficiency of the chamber method for measuring soil gas flux.

Acknowledgments
This material is based on work supported in part by the National Science Foundation (Grant no. EPSC-1101284) and the Foundational Program from the USDA National Institute of Food and Agriculture (Grant no. 2013-67019-2193/Project Accession no. 1001190).

References


doi:10.1029/JD094iD13p16405

doi:10.2134/jeq1999.00472425002800050030x

doi:10.1016/S0143-8166(01)00092-6
**Tables and Figures**

*Table 2.1 List of components and cost of a single FluxCASE (chamber automated sampling equipment for measuring soil gas flux, cost of assembly not included).*

<table>
<thead>
<tr>
<th>Part</th>
<th>Manufacturer</th>
<th>Model</th>
<th>Website</th>
<th>Cost US$</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solenoid valves</td>
<td>Humphrey</td>
<td>315</td>
<td><a href="http://www.humphrey-products.com">www.humphrey-products.com</a></td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>Linear actuator</td>
<td>Frigelli Automations</td>
<td>FA-35-S-12-3</td>
<td><a href="http://www.firgelliauto.com">www.firgelliauto.com</a></td>
<td>80</td>
<td>1</td>
</tr>
<tr>
<td>Relay board</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Microcontroller board</td>
<td>Arduino</td>
<td>Uno</td>
<td><a href="http://www.arduino.com">www.arduino.com</a></td>
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<td>1</td>
</tr>
<tr>
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<td>Power Sonic</td>
<td>PS-1250 F1 1412-50</td>
<td><a href="http://www.power-sonic.com">www.power-sonic.com</a></td>
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<td>1</td>
</tr>
<tr>
<td>Case</td>
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<td></td>
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<td>1</td>
</tr>
<tr>
<td>Male connector tube fitting (0.32 cm)</td>
<td>Swagelok</td>
<td>B-200-1-2</td>
<td><a href="http://www.swagelok.com">www.swagelok.com</a></td>
<td>2</td>
<td>7</td>
</tr>
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<td>Male connector tube fitting (0.64 cm)</td>
<td>Swagelok</td>
<td>B-400-1-2</td>
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<td>3</td>
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<tr>
<td>Ferrules and insert (6.4 mm)</td>
<td>Swagelok</td>
<td>PFA-423-1, PFA-424-2, B-405-2 D02050</td>
<td><a href="http://www.swagelok.com">www.swagelok.com</a></td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>Copper tubing (0.32 cm)</td>
<td>Mueller Industries</td>
<td></td>
<td>muellerindustries.com</td>
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<tr>
<td>Plastic tubing (0.64 cm)</td>
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<td>B-5</td>
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<td>2</td>
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<td>Plastic tubing (0.32 cm)</td>
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<td>Female luer fitting</td>
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<td>coleparmer.com</td>
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<td>60-mL sampling syringe</td>
<td>Dickinson Company</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td></td>
<td>~337</td>
<td></td>
</tr>
</tbody>
</table>
Table 2.2 FluxCASE (chamber automated sampling equipment for measuring soil gas flux) comparison with manual sampling from a gas bag filled with National Institute of Standards and Technology gas mixture, including SD. FluxCASE coefficients of variation (CVs) were similar to CVs of manual samples. Listed P-values were calculated through an ANOVA to compare mean concentrations of gas species from FluxCASEs to manual samples.

<table>
<thead>
<tr>
<th>Method</th>
<th>Nitrous oxide</th>
<th>Carbon dioxide</th>
<th>Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean concentration</td>
<td>SD</td>
<td>CV</td>
</tr>
<tr>
<td>FluxCASE 1</td>
<td>0.69</td>
<td>0.11</td>
<td>0.15</td>
</tr>
<tr>
<td>FluxCASE 2</td>
<td>0.68</td>
<td>0.10</td>
<td>0.15</td>
</tr>
<tr>
<td>FluxCASE 3</td>
<td>0.68</td>
<td>0.07</td>
<td>0.11</td>
</tr>
<tr>
<td>Manual</td>
<td>0.66</td>
<td>0.11</td>
<td>0.17</td>
</tr>
<tr>
<td>P-value</td>
<td>0.44</td>
<td>0.48</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Table 2.3 Expense recovery was calculated for three different scenarios: chamber-intensive, labor-intensive, and event-intensive sampling. In this study, expense recovery is defined as the number of sampling years needed to cover the investment costs of the FluxCASE (chamber automated sampling equipment for measuring soil gas flux) system. Scenarios were analyzed for the utilization of 20 FluxCASEs for a minimum of 52 sampling events per year. Manual sampling labor was assumed to be four times the cost of FluxCASE labor. Labor expenses were assumed to be US$10 h⁻¹.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Scenario 1: Chamber intensive</th>
<th>Scenario 2: Labor intensive</th>
<th>Scenario 3: Event intensive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chambers</td>
<td>60</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>Sampling events (yr⁻¹)</td>
<td>52</td>
<td>52</td>
<td>52</td>
</tr>
<tr>
<td>Manual labor expense (US$)</td>
<td>120</td>
<td>160</td>
<td>200</td>
</tr>
<tr>
<td>FluxCASE labor expense (US$)</td>
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<tr>
<td>Expense recovery (yr)</td>
<td>1.4</td>
<td>1.1</td>
<td>0.9</td>
</tr>
</tbody>
</table>


Fig. 2.1 FluxCASE (chamber automated sampling equipment for measuring soil gas flux) schematic in the vented pathway position. Dotted lines represent alternative pathways. VDC, volts direct current.

Fig. 2.2 Deployed FluxCASE (chamber automated sampling equipment for measuring soil gas flux).
Fig. 2.3 Regression models for CO$_2$ and N$_2$O of FluxCASE (chamber automated sampling equipment for measuring soil gas flux) fluxes compared with manual fluxes during infield experiments. Slopes of CO$_2$ and N$_2$O were 1.01 and 0.97, respectively. A regression model with a slope of 1 was within the 95% confidence interval for both CO$_2$ and N$_2$O models.
CHAPTER 3. NITROUS OXIDE EMISSIONS FROM SATURATED RIPARIAN BUFFERS: ARE WE TRADING A WATER QUALITY PROBLEM FOR AN AIR QUALITY PROBLEM?

A manuscript in preparation The Journal of Environmental Quality

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Contributions
The study was designed by MPD, TMI, DBJ, and TBP
MPD and TAG preformed the analysis
MPD was the primary author with contributions from TAG, TMI, DBJ, and TBP

Abstract
Reestablishing perennial vegetation along riparian areas in agroecosystems reduces nutrient and sediment losses from agricultural runoff. However, Subsurface (tile) drains route the majority of shallow groundwater through traditional buffers, limiting their nutrient removal capabilities. Saturated riparian buffers (SRBs) reconnect subsurface drainage water with the soil profile to remove nitrate in tile water through microbial denitrification. One concern of enhancing denitrification on agricultural landscapes is the increase in nitrous oxide (N\textsubscript{2}O) emissions from incomplete denitrification. Our study objective was to compare N\textsubscript{2}O emissions from SRBs to traditional buffers and bordering crop fields, at two sites, Bear Creek Site-1 (BC-1) and Iowa Site-1 (IA-1), in Central Iowa. We measured N\textsubscript{2}O emissions directly from the soil surface and dissolved in shallow groundwater, and estimated indirect emissions from downstream denitrification. Nitrous oxide emissions from soil surfaces were greatest from fertilized corn, and SRBs were only significantly greater ($P < 0.05$) than traditional buffers in one site-year. Dissolved N\textsubscript{2}O in shallow groundwater seeping from SRBs was not significantly greater ($P < 0.05$) than dissolved N\textsubscript{2}O from the tile outlet among site years. Indirect emissions from rivers and estuaries were significantly less at both sites. Overall, total N\textsubscript{2}O emissions from SRBs were similar to traditional buffers and less than fertilized corn-soybean agriculture.
Introduction

Perennial vegetation along riparian areas within agricultural landscapes increases ecosystem diversity, provides wildlife corridors, and reduces sediment and nutrient losses from overland flow (Lee et al., 2000, 2003; Berges et al., 2010; McCracken et al., 2012). Multifunctional benefits of vegetated riparian areas have been promoted by the United States Department of Agriculture (USDA) through the establishment of filter strips and riparian forest buffers on 647,162 ha of privately owned land (FSA, 2017). While riparian buffers reduce nutrient losses from overland flow (Lee et al., 2003), traditional buffers are ineffective at removing nutrients routed through artificial subsurface (tile) drains. Nitrogen (N) flux via tile drainage is a primary source of nitrate (NO$_3^-$) in surface waters in the Mississippi River Basin (David et al., 2010). Nitrate concentrations in surface water of the United States (US) corn belt often exceed the US Environmental Protection Agency’s drinking water standard of 10 mg L$^{-1}$ (Cambardella et al., 1999; Schilling and Zhang, 2004), and N loading impacts the size of the hypoxic zone in the Gulf of Mexico (Scavia et al., 2003).

Nutrient reduction strategies have been developed by many states in the Mississippi River Basin to reduce N flux to the Gulf of Mexico through N management and edge of field conservation practices (IDALS et al., 2014; Illinois EPA, 2015). Edge of field practices are designed to remove NO$_3^-$ primarily through microbial denitrification and have included wetlands, bioreactors, and drainage water management. Wetlands are efficient at removing NO$_3^-$ from large drainage areas (Kovacic et al., 2000; Tomer et al., 2013; Groh et al., 2015), but wetland design often requires removing large areas of land from production and can be expensive to implement. Woodchip bioreactors can also be a costly practice with some maintenance required in the eventual replacement of woodchips (Christianson et al., 2013; Addy et al., 2016). Drainage water management requires regular monitoring and management with differing reports on nitrate
removal efficiency (Drury et al., 1996; Lavaire et al., 2017). Saturated riparian buffers (SRBs) are a newly developed conservation practice that are less expensive than wetlands and woodchip bioreactors, and improve NO₃ removal capabilities of traditional conservation buffers to include the treatment of tile drainage (Jaynes and Isenhart, 2014).

Saturated riparian buffers function by intercepting tile water within a distribution box located just inside the buffer near the field edge. From the distribution box, drainage water is routed into lateral distribution tiles that are installed perpendicular to the field tile and extend along the buffer. Lateral distribution tiles re-introduce drainage water as shallow ground water into riparian buffer soils (Fig. 3.1). As drainage water seeps through organic matter rich alluvial soil, NO₃ is removed through microbial denitrification or stored through microbial immobilization and plant uptake (Jaynes and Isenhart, 2014). Measurements made in conjunction with this study have found denitrification to be the primary mechanism for NO₃ removal in saturated buffers (Groh et al. 2018). These findings support other studies that found NO₃ removal in traditional riparian buffers with high water tables was primarily through denitrification (Simmons et al., 1992; Ranalli and Macalady, 2010). Complete denitrification is ideal for NO₃ removal, converting NO₃ to N₂ gas. However, incomplete denitrification can result in the production of nitrous oxide (N₂O), a powerful greenhouse gas. Nitrous oxide is the third largest greenhouse gas contributor to global radiative forcing, and has a global warming potential 282 times (50-year lifetime adjustment) that of carbon dioxide (Myhre et al., 2013). Nitrous oxide is 5.5% of the total greenhouse gas inventory in the US and agricultural soils are responsible for 75.1% of the total N₂O inventory (Desai and Harvey, 2017). Direct N₂O emissions from the surface of crop fields and perennial riparian areas have been well studied (Kim et al., 2009), with greatest annual N₂O emissions from fertilized corn (Parkin and Kaspar, 2006; Kim et al., 2009;
Fisher et al., 2014a; Iqbal et al., 2015a). Implementation of edge of field conservation practices to remove NO$_3$ from agricultural drainage could result in increased N$_2$O production. Nitrous oxide production from wetlands and bioreactors has been found to be 0.003 to 4.5% of the total N removed (Greenan et al., 2009; Woli et al., 2010; Groh et al., 2015). While some studies have found direct emission rates equal to agricultural fields on a per ha basis, these rates are greatly reduced if emissions are considered on a per ha of drained land basis (Groh et al., 2015). Furthermore, most studies do not include dissolved N$_2$O production or the potential for reduction in indirect N$_2$O emissions from NO$_3$ flux to rivers and estuaries through NO$_3$ removal. Indirect N$_2$O emissions from fertilizer application are more difficult to quantify and often not included in N$_2$O loss estimations from agricultural areas (Reay et al., 2009).

Research reported here represents the first study of N$_2$O emissions from saturated riparian buffers. We monitored two SRBs for three years to begin answering the question, are SRBs trading a water quality problem for an air quality problem? Our study objective was to compare N$_2$O emissions from SRBs, traditional buffers, and crop fields in corn (Zea mays L.) and soybean (Glycine max (L.) Merr.) rotations. Specific objectives were to: i) quantify annual N$_2$O emissions from the soil surface of SRBs, traditional buffers, and crop fields ii) quantify dissolved N$_2$O in shallow groundwater flow iii) estimate indirect N$_2$O emissions from SRBs and drainage tiles iv) and compare total N$_2$O emissions from SRBs, traditional buffers, and crop fields for a two year rotation.

**Methods and Materials**

**Site Descriptions**

Nitrous oxide was measured at two SRBs, Bear Creek Site-1 (BC-1) and Iowa Site-1 (IA-1), in Hamilton County in Central Iowa, USA. Bear Creek Site-1 was studied in Jaynes and Isenhart (2014), and both site abbreviations are consistent with nomenclature in Jaynes et al.
Both SRBs are privately owned and located within the headwaters of the South Skunk River Watershed. Hamilton County is located in the prairie pothole region of the Des Moines Lobe, formed by the Wisconsin Glacial Episode at the end of the Pleistocene era (10,000 YBP). Today 93% of the county is in cropland and a majority of depressional wetlands in the region have been drained through tile drainage for increased agricultural production (Thessen et al., 2017). Mean annual precipitation is 912 mm and mean annual temperature 9.7°C.

Three chambered distribution boxes were installed with calibrated v-notch weirs at both sites. Distribution box chambers were equipped with pressure transducers to measure the height of water above the v-notch weir. Flow from the field tile was measured as water passing over the first chamber’s v-notch into the middle chamber. Flow leaving the middle chamber was measured as overflow discharged directly to the stream. Diverted flow was calculated as the difference of flow from the field tile and overflow to the stream. Details of v-notch calibration and flow calculations can be found in Jaynes and Isenhart (2014) and Jaynes et al. (2018).

Bear Creek Site-1 was installed in October of 2010 into a riparian forest buffer alongside Bear Creek, a second order stream. The field tile diverting flow into BC-1 drains 5.9 ha of cropland (Jaynes et al., 2018). The distribution tile is 305 m in length and diverted water seeps through 21 m of buffer soil (0.64 ha) before entering Bear Creek. Water level was set to 32 cm below ground surface for the duration of the study. The riparian forest buffer was established in 1995 and consisted of 6 m of sugar maple (Acer saccharinum L.), 6 m of mixed shrub-grass, and 8 m of switchgrass (Panicum virgatum L.). Additional details on shrub species can be found in Shultz et al. (1995). Soils across the buffer and at the field edge are described as poorly drained Coland series (fine-loamy, mixed, superactive, mesic Cumulic Endoaquolls) (USDA NRCS).
The agricultural field adjacent to BC-1 was planted to soybeans in 2015, corn in 2016, and soybeans in 2017. Anhydrous ammonia was injected into the crop field at a rate of 120 kg N ha\(^{-1}\) on April 19, 2016.

Iowa Site-1 was installed in June of 2013 into a filter strip seeded to switchgrass (*Panicum virgatum* L.) in 2000. The distribution tile is 308 m in length and 24 m from the stream (0.74 ha). The water level was set to 28 cm below the ground surface for the duration of the study. The distribution box at IA-1 receives subsurface drainage water from 4.7 ha of cropland draining into a small tributary of the South Skunk River. Soils at IA-1 are described as a Coland-Terrill (Fine-loamy, mixed, superactive, mesic, Cumulic Hapludolls) complex. The agricultural field adjacent to the IA-1 SRB was planted to the same rotation as BC-1, soybeans in 2015, corn in 2016, and soybeans in 2017. Anhydrous ammonia was injected into the crop field at a rate of 120 kg N ha\(^{-1}\) on April 25, 2016.

**Nitrate removal**

Nitrate removal was calculated from NO\(_3\) concentrations and flow into the buffer. Nitrate samples were collected from the distribution box and at sampling wells (2.3 m deep and fully screened) on the stream edge of the buffer (Fig. 3.1). Water samples were collected from the distribution box and each well on a weekly basis while each SRB was flowing. Samples were stored at 4°C until analyzed for NO\(_3\) using a Lachat 8000 (Zellweger Analytics, Lachat Instrument Division). Mass NO\(_3\) removal was calculated by subtracting the diverted load from the shallow groundwater load of NO\(_3\) flowing from the SRB. Annual mass NO\(_3\) loads were calculated by multiplying NO\(_3\) concentration by the volume of water between sampling dates and summing over the calendar year.
**Surface Nitrous Oxide Emissions**

Surface $\text{N}_2\text{O}$ emissions from buffer soils were measured using static vented chambers equipped with automated sample collection equipment (Davis et al., 2018). Nitrous oxide fluxes from SRBs and traditional buffers were measured from January 2015 through December 2017. Crop field soil $\text{N}_2\text{O}$ fluxes were collected from January 2016 through December 2017. Circular schedule 40 PVC anchors (30 cm diameter, 15 cm tall) were pushed into the soil leaving 5 cm of exposed anchor above the soil surface. Nine anchors were evenly spaced across both SRBs and six anchors were installed on traditional buffer counterparts (Fig. 3.1). Traditional buffers were adjacent to SRBs but not affected by flow diverted into the SRBs. Anchors in the SRBs and traditional buffers were left in place for the duration of the study. Six anchors were installed approximately 3 m from the buffer edge within the crop field. Field anchors were placed to reduce the potential of edge effects, but remained in a poorly drained soil classification for treatment comparison. Anchors were installed in pairs with one anchor over a planting row and the other in the interrow. Each pair was spaced evenly over the length of the SRB (Fig. 3.1). Crop field anchors were only removed for planting, harvest, tilling, and fertilizer application. After fertilizer application, the in-row anchors were placed to include a single fertilizer injection line.

Flux measurements were collected weekly from April through September, twice per month in October, November, and March, and monthly from December through February. Sample were collected between 8:00 am and 12:00 pm to limit diurnal biases (Parkin, 2008). Weekly sampling intervals have been calculated to have a 90% probability of estimating the average $\text{N}_2\text{O}$ flux with ± 20% accuracy (Parkin, 2008). We estimate from Kim et al. (2009) that 85% of annual $\text{N}_2\text{O}$ emissions from traditional buffers and cropland in the Bear Creek Watershed occur between March and October, with soil thawing events and fertilization producing the
largest fluxes. Sampling campaigns were also conducted to collect N\textsubscript{2}O emissions from thawing events through return to baseline emissions after events.

Circular PVC static chambers were used as described in Parkin and Venterea (2010). Chamber tops were constructed from 30 cm schedule 40 PVC pipe to a height of 15 cm. Chambers were vented and covered with reflective tape to minimize temperature change from solar radiation. Samples were collected from a butyl rubber stopper (Voigt Global) sampling port in the top of each chamber. Gas samples were collected from the chamber headspace at 0, 15, 30, and 45 minutes following chamber placement onto the anchor. Automated samplers collected headspace gas through a sampling tube inserted into the sampling port. Samples were stored in the automated sampler in 20 ml syringes equipped with stopcocks until laboratory analysis (Davis et al., 2018). In the laboratory, 13 ml of sample was injected into evacuated 6 ml glass vials sealed with butyl rubber stoppers (Voigt Global). Gas samples were analyzed on a gas chromatograph (GC) (SRI Instruments, model 8610) equipped with an automated sampler to introduce gas samples into the sample valve of the GC (Arnold et al., 2001). Gas samples traveled through a stainless steel column (0.3175 cm diameter × 74.54 cm long) packed with Haysep D to a $^{63}$Ni electron capture detector. Nitrous oxide standards (Air Liquide Specialty gases) were analyzed to calculate sample concentration using linear regression coefficients.

Fluxes were calculated using the HMR package in R v3.1.2 (The R Foundation, 2014). If the HMR model failed to calculate a flux, the software used linear regression or assigned a “no flux” value of zero (Pedersen et al., 2010). Based on linear regression coefficients from Parkin et al. (2012) minimum detectable fluxes were 0.00031 g m\textsuperscript{-2} day\textsuperscript{-1} for linear regression and 0.00185 g m\textsuperscript{-2} day\textsuperscript{-1} for the HMR method. Annual cumulative fluxes were calculated using linear interpolation between daily fluxes and summing daily fluxes for the calendar year. Saturated and
traditional buffer annual N\textsubscript{2}O emissions were compared within site-years using Welch’s t-test. Annual emissions from SRBs and traditional buffers were also compared among site-years using a paired t-test.

**Nitrous Oxide Emissions from Groundwater and Tile Drainage**

Within tile-drained landscapes, “groundwater” flux to receiving waters can be via shallow groundwater flux through the riparian zone or within tile drainage water. In this study, we directly measured dissolved N\textsubscript{2}O load from tile drainage and shallow groundwater within the SRB. Dissolved N\textsubscript{2}O samples were collected monthly (2015 - 2017) from the distribution box and sampling wells at each SRB (Fig. 3.1). Samples were collected using a peristaltic pump. The sampling tube was gently lowered into the well or distribution box to approximately 15 cm above the bottom surface. Sample water was pumped into a 10 ml sampling syringe held onto the end of the sampling tube. Triplicate samples were injected into evacuated 20 ml glass vials sealed with rubber butyl stoppers (Voigt Global) and treated with 0.3 ml of 80% zinc chloride solution for sample preservation. Samples were stored on ice in the field and vial headspace pressure adjusted to atmospheric pressure in the laboratory. Vials were overfilled with 7 ml of helium to utilize the automated sampler design to introduce samples to the GC (described above). Vials were shaken for 15 min on a reciprocal shaker to equilibrate dissolved N\textsubscript{2}O with the headspace. Total dissolved N\textsubscript{2}O was calculated using Henry’s law and Bunsen absorption coefficients. Nitrous oxide standards were prepared in a similar manner, including atmospheric pressure adjustment and helium dilution. Nitrous oxide concentrations (calculations described above) were linearly interpolated between sampling points and multiplied by daily water volumes to calculate dissolved N\textsubscript{2}O loads. The volume of seepage water through the buffer was assumed to be equal to the volume of water diverted into the SRBs. Annual N\textsubscript{2}O loads were calculated for water leaving crop fields, diverted into the SRBs, leaching out of the SRBs, and
leaving as overflow discharge. Total indirect N$_2$O load from SRB groundwater was calculated by summing overflow loads to seepage water loads.

**Indirect Nitrous Oxide Emissions from Rivers and Streams**

Indirect N$_2$O emissions within rivers and estuaries from NO$_3$ flux from shallow groundwater and tile drainage were calculated using the Tier 1 IPCC protocol for estimating indirect N$_2$O emissions (IPCC, 2006). The mass of NO$_3$-N leached was multiplied by 0.005 kg N$_2$O-N kg$^{-1}$ NO$_3$-N, the sum of the default emission factors for rivers (EF$_{5r} = 0.0025$ kg N$_2$O-N kg$^{-1}$ NO$_3$-N) and estuaries (EF$_{5e} = 0.0025$ kg N$_2$O-N kg$^{-1}$ NO$_3$-N). Paired t tests were used to examine differences in means of annual indirect N$_2$O emissions from SRBs compared to the field tiles.

**Nitrous oxide loads from two year agricultural rotation**

Cumulative N$_2$O loads for traditional buffers and SRBs were calculated for a two year corn-soybean crop rotation, 2016-2017. Soil surface N$_2$O loads (kg-N) were calculated by multiplying 2016-2017 cumulative emission rates (kg-N ha$^{-1}$) by the surface area (ha$^{-1}$) of the respective SRB. Surface N$_2$O loads from traditional buffers and crop fields represent the potential N$_2$O loads for the given SRB area. Total N$_2$O emissions were calculated by adding direct and indirect loads. Statistical analyses could not be conducted on only two total emission budgets for each treatment. However, we believe presenting total load data over a corn-soybean rotation best represents N$_2$O emissions for treatment comparison.

**Results**

**Tile flow and nitrate removal**

Tile flow from crop fields ranged from 8,279 m$^3$ yr$^{-1}$ to 28,772 m$^3$ yr$^{-1}$ across SRB sites (Table 3.1). On average, 40% of total annual flow was diverted into BC-1; whereas, an average of 95% of annual flow was diverted into IA-1. The discrepancy in percentage of diverted flow
between sites is attributed to the difference between SRB area to drainage area ratios. Bear Creek-1 drains a larger area (5.9 ha) into a smaller buffer (0.64 ha) compared to IA-1 (4.7 ha draining to 0.74 ha of buffer). Diverted NO₃ load ranged from 51 to 85 kg-N at BC-1 and from 36 to 70 kg-N at IA-1. Flow weighted mean concentration of diverted NO₃ ranged from 8.2 to 13.0 mg N L⁻¹ at BC-1 and from 3.8 to 7.6 mg N L⁻¹ at IA-1. Nitrate removal in the SRBs ranged from 47 to 80 kg N at BC-1 and from 33 to 70 kg N at IA-1 (Table 3.1). Average removal rates from diverted NO₃ loads were 94% for BC-1 and 95% for IA-1. However, total NO₃ load removal rates were lower at BC-1 (38%) compared to IA-1 (88%) due to limited tile water diversion capacity at BC-1.

**Annual surface nitrous oxide losses**

Nitrous oxide flux ranged from -1.3 to 533.1 g N ha⁻¹ day⁻¹, and flux was greatest after corn fertilization in late spring and early summer months of 2016 (Fig. 3.2). Fluxes were less than 40 g N ha⁻¹ day⁻¹ for 95% of the measured events. Snow accumulation deeper than the anchor height prevented measurements in February of 2016. Measurements collected in June of 2015 were lost through a malfunction in sample analysis. Annual N₂O emissions from soil surfaces ranged from 0.87 to 16.20 kg N ha⁻¹ (Fig. 3.3). Nitrous oxide emissions from fertilized corn were more than twice the greatest annual emission from SRBs and tradition buffers. Field measurements were excluded from annual N₂O comparisons to focus attention on the treatment effect of saturating a traditional buffer. Field soil surface emissions were expected to be greater than any perennial system without nitrogen fertilizer application (Parkin and Kaspar, 2006; Kim et al., 2009; Fisher et al., 2014b). Comparing SRBs to traditional buffers is a more conservative approach for evaluating significant changes in N₂O emissions from the effect of SRB installation. Annual N₂O emissions from saturated buffers ranged from 1.12 to 5.83 kg N ha⁻¹. The greatest annual emission at both sites was in 2015. Saturated riparian buffer emissions were
only significantly greater \((P = 0.045)\) than traditional buffers for one site-year, BC-1 in 2015 (Fig. 3.3). Comparing among site-years, annual surface N\(_2\)O emissions from SRBs were not significantly different \((P = 0.17)\) from traditional buffers.

**Dissolved nitrous oxide and indirect losses**

Annual load of dissolved N\(_2\)O leaving crop fields in tile drains ranged from 0.31 to 1.28 kg N. Dissolved N\(_2\)O load diverted into SRBs ranged from 0.19 to 0.67 kg-N (Table 3.2). Nitrous oxide production was observed at BC-1, where dissolved N\(_2\)O load in seepage water leaving the SRB was greater than the diverted N\(_2\)O load into the SRB. Dissolved N\(_2\)O consumption was observed at IA-1. Seepage N\(_2\)O load from IA-1 was less than the N\(_2\)O load diverted into the SRB. Total dissolved N\(_2\)O loads from SRB groundwater (0.06-1.69 kg N) were not significantly different \((P = 0.41)\) than tile N\(_2\)O loads (0.31-1.28 kg N) among all site-years. Estimated indirect emissions of tile NO\(_3\) discharged to rivers and estuaries ranged from 0.205 to 1.165 kg N. Saturated riparian buffers removed NO\(_3\) reducing indirect emissions from rivers and estuaries significantly \((P = 0.007)\) to a range from 0.030 to 0.765 kg N. Saturated riparian buffer contribution to total indirect N\(_2\)O emissions (groundwater, rivers, and estuaries) were significantly less \((P > 0.02)\) than contributions from tile drains (Table 3.3).

**Discussion**

Saturated riparian buffers have shown early promise as a conservation practice to remove NO\(_3\) from tile drainage (Jaynes and Isenhart, 2014; Jaynes et al., 2018). Denitrification is a primary mechanism of NO\(_3\) removal (data not shown), and incomplete denitrification can result in the production of N\(_2\)O. Concerns of trading water quality problems for air quality problems prompted the measurement of direct and indirect N\(_2\)O emissions from two SRBs in central Iowa. Specific objectives included measuring direct and indirect N\(_2\)O emissions from SRBs, traditional buffers, and crop field.
Annual direct N\textsubscript{2}O emissions from the soil surface were greatest in the crop field of 2016 at both sites. Annual surface N\textsubscript{2}O fluxes in corn years were 16.2 for BC-1 and 15.3 kg N ha\textsuperscript{-1} for IA-1. Observed emissions from fertilized corn in central Iowa average around 10 kg N ha\textsuperscript{-1} yr\textsuperscript{-1} (Parkin and Kaspar, 2006; Kim et al., 2009; Iqbal et al., 2015). Greater than average annual N\textsubscript{2}O emissions from fertilized corn in our study are likely attributed to measurements focused on poorly-drained soils within the crop field over a wet year. Nitrous oxide emissions from poorly-drained soils are often greater than well-drained counterparts (Davidson et al., 2000; Iqbal et al., 2015). Crop field measurements for this study were taken on soils that were representative of soils on SRBs to emphasize the magnitude of N\textsubscript{2}O emissions from cultivated riparian areas.

Surface N\textsubscript{2}O emissions from SRBs and traditional buffers were less than crop fields, and similar to other measurements of riparian areas under perennial vegetation in central Iowa (Kim et al., 2009; Iqbal et al., 2015). Annual surface N\textsubscript{2}O emissions from SRBs were only significantly greater ($P = 0.045$) than traditional riparian buffers at BC-1 in 2015 (Fig. 3.3). In 2015, BC-1 observed the greatest tile flow (28,772 m\textsuperscript{3}), number of tile flow days (212), and diverted NO\textsubscript{3} load (85 kg) (table 3.1). Increased flow and NO\textsubscript{3} load through BC-1 in 2015 provided the longest period of diverted flow for the potential to increase denitrification compared to other years. Over all three years and at both sites, N\textsubscript{2}O emissions from SRBs were not significantly different ($P = 0.165$) from traditional buffers.

Nitrous oxide emissions from groundwater and tile drainage were measured and emissions from rivers and estuaries were estimated to provide a complete assessment of N\textsubscript{2}O losses from SRBs. Few studies have quantified dissolved N\textsubscript{2}O in tile drainage or in riparian groundwater (Groffman, et al., 1998; Sawamoto et al., 2005). Dissolved loads from groundwater were measured as dissolved N\textsubscript{2}O load in field tile, diverted, overflow, and seepage water.
Dissolved N\textsubscript{2}O concentrations in our study were wide ranging, from 0.1 to 981.1 µg L\textsuperscript{-1}. A large range of dissolved N\textsubscript{2}O concentrations has also been reported in other studies measuring dissolved N\textsubscript{2}O in drainage water (Reay et al., 2003; Sawamoto et al., 2003; Parkin et al., 2016). Dissolved samples in this study were collected with greater frequency than other studies. High N\textsubscript{2}O concentrations in both tile drainage and SRB seepage water highlight the data gap of dissolved N\textsubscript{2}O concentration measurements and accurate emission estimates from subsurface drainage.

The fate of diverted N\textsubscript{2}O differed between sites. Nitrous oxide in diverted water was consumed or lost through surface emissions as it seeped through soil at IA-1, but was produced at BC-1. Apparent nitrous oxide consumption resulted in a reduction of dissolved losses from groundwater at IA-1; whereas, N\textsubscript{2}O production at BC-1 resulted in an increase in dissolved losses from groundwater diverted into the SRB. Nitrous oxide production was primarily found in one of the five sampling wells at BC-1. Nitrate concentrations were greatest in this sampling well during times of N\textsubscript{2}O production. Nitrous oxide reductase, the enzyme catalyzing N\textsubscript{2}O reduction to N\textsubscript{2}, has shown sensitivity to environmental factors including oxygen concentration, carbon to NO\textsubscript{3} ratios, and pH (Cavigelli and Robertson, 2001). Preferential flow may have played a role in greater NO\textsubscript{3} concentrations and controlled environmental factors reducing N reductase.

Discrepancies in dissolved NO\textsubscript{3} and N\textsubscript{2}O concentrations highlight the potential for improving experimental designs in future SRB studies. Improved designs could include a greater number of sampling wells at the buffer edge to capture a greater spatial variability. Tracer studies could also be used to attribute specific flow proportions to each sampling well (Czapar et al., 1994; Jaynes et al., 2001). However, production at BC-1 was less than 0.07 kg yr\textsuperscript{-1} and indirect groundwater emissions from SRBs were not significantly different ($P = 0.41$) than the crop field tile (Table
Indirect N\textsubscript{2}O emissions from rivers and estuaries were estimated using the IPCC Tier 1 protocol by multiplying NO\textsubscript{3} leached in groundwater and lost in tile drainage by default emission factors (EF\textsubscript{5r} = 0.0025 and EF\textsubscript{5e} = 0.0025). Estimated indirect N\textsubscript{2}O emissions from rivers and estuaries were significantly less ($P = 0.0007$) from SRBs compared to the crop field due to lower NO\textsubscript{3} discharge to streams after diversion into the SRB (Table 3.3). Nitrate loads from crop field tiles were reduced by 34 to 92%, subsequently reducing indirect N\textsubscript{2}O emissions from rivers and estuaries. Recent studies have proposed an increase in the default EF\textsubscript{5r} to 0.0075 kg N\textsubscript{2}O-N kg\textsuperscript{-1} N (Beaulieu et al., 2011), and a proposed regional EF\textsubscript{5r} of 0.015 kg N\textsubscript{2}O-N kg\textsuperscript{-1} N for the Upper-Midwest United States (Turner et al., 2015). This change in the default value of EF\textsubscript{5r} would magnify the effect of lower indirect N\textsubscript{2}O emissions from rivers and stream resulting from NO\textsubscript{3} diversion through SRBs. However, these studies do not propose changes to the emission factor for groundwater (EF\textsubscript{5g}) or estuaries (EF\textsubscript{5e}) and the proposed increases in EF\textsubscript{5r} would be within the combined EF\textsubscript{5} uncertainty range ($0.0005$–$0.025$ kg N\textsubscript{2}O-N kg\textsuperscript{-1} N). Reduction in indirect emissions from water diverted into SRBs resulted in a significant ($P = 0.02$) reduction in total dissolved emissions. While no reduction in the measured groundwater N\textsubscript{2}O was observed, the estimated reduction of N\textsubscript{2}O emissions from rivers and estuaries was significant ($P = 0.007$) and the driver of the reduction in total indirect N\textsubscript{2}O emissions from SRBs.

Total N\textsubscript{2}O loads (direct + indirect) from SRBs were found to be comparable to traditional buffers and less than cropped land for a corn-soybean rotation (Fig. 3.4). Annual SRB loads were not significantly different ($P = 0.37$) from traditional buffers (Table 3.4). Nitrous oxide loads from corn-soybean rotations were approximately 10 kg N greater than SRB and traditional buffers at both sites. Fertilized corn was the single greatest contributor to N\textsubscript{2}O loads across the
three treatments. Nitrous oxide fluxes in summer months after corn fertilization (Fig. 3.2) represented over 90% of total emissions from cropland in 2016. Nitrous oxide production per kg N removed in SRBs ranged from 3.2 to 9.3%, greater than other edge of field practices (Kovacic et al., 2000; Christianson et al., 2013; Groh et al., 2015). The largest percentage of N₂O production per kg N removed was at BC-1 in 2015, all other site years were below 4%. However, comparison studies did not include indirect emissions. Direct N₂O production per kg N removed in our study ranged from 2.6 to 7.2%, similar to production from constructed wetlands and woodchip bioreactors (Christianson et al., 2013; Groh et al., 2015). We encourage future studies to include both surface and dissolved N₂O emissions for more accurate estimates.

Conclusions

Saturated riparian buffers are designed to remove NO₃ from tile drainage through denitrification. Incomplete denitrification results in N₂O production, potentially trading a water quality problem for an air quality problem. To examine changes in N₂O emissions from SRB implementation, we measured direct and indirect N₂O emissions from SRBs, traditional buffers, and crop fields. Direct emissions from fertilized corn were an order of magnitude greater than emissions from SRBs and traditional buffers. Nitrous oxide production from the soil surface within saturated riparian buffers were only significantly greater than traditional buffers in one site-year (Fig. 3.3). Reduction in indirect emissions from water diverted into SRBs resulted in a significant \( P = 0.02 \) reduction in total indirect emissions. Total N₂O loads from direct and indirect sources were greatest in the crop field for corn-soybean rotations (Fig. 3.4), and total N₂O loads from SRBs were not significantly greater \( P = 0.37 \) than traditional buffers (Table 3.4). Our data suggest installing a SRB into an established traditional buffer will not increase N₂O emissions. Furthermore, replacing cultivated riparian areas with a SRB could reduce N₂O emissions, simultaneously reducing losses of NO₃ to surface water and N₂O to the atmosphere.
References


Tables and Figures

Figure 3.1. Sampling layout for Bear Creek Site-1 and Iowa Site-1. Open circles are surface greenhouse gas sampling locations. Closed circles are sampling well locations. Water travels from the field tile into the distribution box where it is diverted into the distribution tile.
Figure 3.2. Nitrous oxide fluxes from the soil surface and diverted flow volumes at Bear Creek Site-1 and Iowa Site-1. Largest fluxes were observed under corn fertilization years.
Figure 3.3. Annual N2O from saturated riparian buffers, traditional buffers, and crop field (corn in 2016 and soybean 2017) at Bear Creek Site-1 (BC-1) and Iowa Site-1 (IA-1). P-values (P) indicate significance levels between saturated riparian buffers and traditional buffers. * indicates significant difference in means at P = 0.05.
Figure 4. Average nitrous oxide emissions from Bear Creek Site-1 and Iowa Site-1. Average emissions are for 2016 through 2017. Total emissions are the summation of direct and indirect emissions.
Table 3.1. Flow, nitrate concentration, and nitrate load from the field tiles and saturated riparian buffers. Days of flow are reported as the number of days that flow occurred.

<table>
<thead>
<tr>
<th>Site</th>
<th>Year</th>
<th>Flow</th>
<th>Nitrate Concentration</th>
<th>Load</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>d</td>
<td>mg·N·L⁻¹</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>m³</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BC-1</td>
<td>2015</td>
<td>212</td>
<td>28,772</td>
<td>10,339</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.2</td>
<td>233</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>2016</td>
<td>161</td>
<td>12,111</td>
<td>5,878</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.4</td>
<td>111</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>2017</td>
<td>97</td>
<td>11,153</td>
<td>3,922</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13.0</td>
<td>151</td>
<td>51</td>
</tr>
<tr>
<td>IA-1</td>
<td>2015</td>
<td>179</td>
<td>12,519</td>
<td>11,453</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.1</td>
<td>76</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>2016</td>
<td>185</td>
<td>8,279</td>
<td>8,056</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.6</td>
<td>62</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>2017</td>
<td>133</td>
<td>9,838</td>
<td>9,575</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.8</td>
<td>41</td>
<td>36</td>
</tr>
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</table>

Table 3.2. Dissolved nitrous oxide (N₂O) loads from the field tiles and saturated riparian buffers with standard deviations reported in parentheses. Dissolved N₂O loads are reported for water diverted into the saturated riparian buffer, leaving through the overflow pipe, and seeping as shallow groundwater.

<table>
<thead>
<tr>
<th>Site</th>
<th>Year</th>
<th>Tile</th>
<th>Diverted</th>
<th>Overflow</th>
<th>Seepage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>kg-N</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BC-1</td>
<td>2015</td>
<td>1.279 (0.065)</td>
<td>0.456 (0.035)</td>
<td>0.822 (0.030)</td>
<td>0.868 (1.556)</td>
</tr>
<tr>
<td></td>
<td>2016</td>
<td>0.366 (0.008)</td>
<td>0.178 (0.004)</td>
<td>0.183 (0.004)</td>
<td>0.253 (0.537)</td>
</tr>
<tr>
<td></td>
<td>2017</td>
<td>0.731 (0.065)</td>
<td>0.251 (0.022)</td>
<td>0.296 (0.026)</td>
<td>0.344 (0.757)</td>
</tr>
<tr>
<td>IA-1</td>
<td>2015</td>
<td>0.325 (0.014)</td>
<td>0.308 (0.013)</td>
<td>0.016 (0.001)</td>
<td>0.058 (0.047)</td>
</tr>
<tr>
<td></td>
<td>2016</td>
<td>0.311 (0.001)</td>
<td>0.304 (0.001)</td>
<td>0.007 (&lt;0.001)</td>
<td>0.030 (0.020)</td>
</tr>
<tr>
<td></td>
<td>2017</td>
<td>0.694 (0.003)</td>
<td>0.673 (0.003)</td>
<td>0.019 (&lt;0.001)</td>
<td>0.044 (0.017)</td>
</tr>
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</table>
Table 3.3. Measured (groundwater and tile) and estimated indirect (rivers and estuaries) $\text{N}_2\text{O}$ emission loads from saturated riparian buffers. Groundwater load standard deviations in parentheses. Indirect river and estuary emissions were estimated using the IPCC Tier 1 protocol.

<table>
<thead>
<tr>
<th>Site</th>
<th>Year</th>
<th>Dissolved $\text{N}_2\text{O}$ Emissions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Groundwater</td>
<td>Rivers and Estuaries</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SRB Tile</td>
<td>SRB Tile</td>
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<tr>
<td></td>
<td></td>
<td>kg-N</td>
<td>kg ha$^{-1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SRB Tile</td>
<td>SRB Tile</td>
</tr>
<tr>
<td></td>
<td></td>
<td>kg-N</td>
<td>kg ha$^{-1}$</td>
</tr>
<tr>
<td>BC-1</td>
<td>2015</td>
<td>1.690 (1.556) 1.279 (0.065)</td>
<td>0.765 1.165</td>
</tr>
<tr>
<td></td>
<td>2016</td>
<td>0.436 (0.537) 0.366 (0.008)</td>
<td>0.300 0.555</td>
</tr>
<tr>
<td></td>
<td>2017</td>
<td>0.639 (0.757) 0.731 (0.065)</td>
<td>0.540 0.755</td>
</tr>
<tr>
<td>IA-1</td>
<td>2015</td>
<td>0.074 (0.047) 0.325 (0.014)</td>
<td>0.030 0.380</td>
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<td>2016</td>
<td>0.036 (0.020) 0.311 (0.001)</td>
<td>0.045 0.310</td>
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<td>2017</td>
<td>0.063 (0.017) 0.694 (0.003)</td>
<td>0.055 0.205</td>
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<tr>
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<td>0.0007195</td>
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Table 4. Total $\text{N}_2\text{O}$ loads from saturated and traditional riparian buffers. Direct loads were calculated from surface emissions and measured groundwater and tile loads. Indirect loads were calculated through river and estuary emission estimations. Total emissions were calculated by summing direct and indirect emissions. $p$-values ($P$) indicated level of significance for saturated riparian buffer v. traditional buffer comparison.

<table>
<thead>
<tr>
<th>Site</th>
<th>Year</th>
<th>Surface SRB</th>
<th>Surface Traditional</th>
<th>Groundwater and Indirect SRB</th>
<th>Groundwater and Indirect Traditional</th>
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<th>Total Traditional</th>
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<tr>
<td></td>
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<td>2.42</td>
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<td>0.81</td>
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<td>0.705</td>
<td>2.27</td>
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<td>0.081</td>
<td>0.621</td>
<td>1.96</td>
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<td>0.118</td>
<td>0.899</td>
<td>1.73</td>
<td>1.77</td>
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<td>0.3665</td>
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CHAPTER 4. NITROUS OXIDE AND METHANE PRODUCTION FROM DENITRIFYING WOODCHIP BIOREACTORS AT THREE HYDRAULIC RETENTION TIMES

A manuscript in preparation for Ecological Engineering

Morgan P. Davis, Emily A. Martin, Thomas B. Moorman, Thomas M. Isenhart, and Michelle L. Soupir

Contributions
The study was designed by MPD, TMI, TBM, and MLS
MPD and EAM preformed the analysis
MPD was the primary author with contributions from EAM, TMI, TBM, and MLS

Abstract
Denitrifying bioreactors remove nitrate (NO₃⁻) from agricultural drainage and are slated to be an integral part of nitrogen reduction strategies in the Mississippi River Basin. However, incomplete denitrification can result in nitrous oxide (N₂O) production and anaerobic conditions conducive to methane (CH₄) production via methanogenisis. Greenhouse gas production has the potential to trade excess NO₃⁻ in surface water with excess greenhouses gases in the atmosphere. Our study examined N₂O and CH₄ production from pilot scale (5.8 × 1.0 × 1.1 m) bioreactors across three hydraulic retention times (HRTs), 2, 8, and 16 hours. Production was measured from both the surface of the bioreactors and dissolved in the outlets. Nitrous oxide and CH₄ was produced across all HRTs, with the majority dissolved in the tile outlet. Nitrous oxide production was significantly greater (P < 0.05) from 2 hour HRTs (501.5 mg N₂O m⁻³ day⁻¹) than from 8 (30.4 mg N₂O m⁻³ day⁻¹) and 16 (38.4 mg N₂O m⁻³ day⁻¹) hour HRTs. Methane production was significantly less (P < 0.05) from 2 hour HRTs (0.51 g C m3 day) compared to 8 (1.50 g C m3 day) and 16 (1.69 g C m3 day) hour HRTs. The 2 hour HRTs had significantly greater (P = 0.05) global warming potential compared to 8 and 16 hour HRTs. Results suggest managing for longer HRTs in field
bioreactors to reduce greenhouse gas production from woodchip bioreactors.

**Keywords**

Woodchip bioreactor
Greenhouse gases
Denitrification
Nitrous oxide
Methane
Hydraulic retention time

1. Introduction

Nitrate (NO$_3$) losses from agriculture in the upper Midwest of the United States contribute to the extent of the hypoxic zone in the Gulf of Mexico (David et al., 2010) and lead to high NO$_3$ concentrations in surface drinking water sources (Schilling and Zhang, 2004). Midwestern states have responded to environmental concerns of nitrogen (N) loss through the implementation of nutrient reduction strategies. Nutrient reduction strategies utilize both in-field and edge of field practices to reduce NO$_3$ losses from predominantly corn ([*Zea mays* L]) and soybean ([*Glycine max* (L.) Merr.] agriculture (IDALS et al., 2014; Illinois EPA, 2015). Edge of field practices including wetlands, saturated buffers, and bioreactors have shown promise to reduce NO$_3$ losses from artificial subsurface, tile, drainage (Addy et al., 2016; Groh et al., 2015; Jaynes and Isenhart, 2014; Tomer et al., 2013). Bioreactors are an integral part of nutrient strategies and comprise up to 18% of planned reductions within some scenarios of the Iowa Nutrient Reduction Strategy. Bioreactor removal efficiency is highly dependent on design, including the hydraulic retention time (HRT) of tile water being treated in the bioreactor. Addy et al. (2016) conducted a meta-analysis and found significantly less mass nitrate removal in bioreactors with HRTs less than 6 hours. For
maximum nitrate removal, HRT should be included in bioreactor design to optimize NO$_3$ removal.

Bioreactors create anaerobic environments ideal for denitrification and other forms of anaerobic respiration (Christianson et al., 2009; Jaynes et al., 2008; Schipper et al., 2010). Incomplete denitrification in bioreactors can result in nitrous oxide (N$_2$O) production (Elgood et al., 2010; Greenan et al., 2009; Warneke et al., 2011). Furthermore, bioreactors can be sources of methane (CH$_4$) production via methanogenesis (Elgood et al., 2010; Healy et al., 2012). Nitrous oxide and CH$_4$ are the second and third largest contributors to global radiative forcing respectively. Furthermore, N$_2$O and CH$_4$ have respectively 265 and 28 times (100-year adjustment) the global warming potential of carbon dioxide, without the inclusion of climate-carbon feedbacks (Myhre et al., 2013). Nitrous oxide and CH$_4$ production have been observed from bioreactors, but measurements do not always include both emissions dissolved in treated water and from bioreactor surfaces (David et al., 2016; Woli et al., 2010). Laboratory studies have examined N$_2$O and CH$_4$ production at different HRTs (Greenan et al., 2009; Healy et al., 2012), but these studies were conducted on relatively small columns. If significant, N$_2$O and CH$_4$ production from bioreactors represents the potential for pollution swapping of NO$_3$ in surface waters with increased greenhouse gas emissions.

This study utilized nine pilot scale (5.8 × 1.0 × 1.1 m) bioreactors to maintain tile water HRTs of 2, 8, and 16 hours. Our study objectives were (i) to determine the effect of HRTs on of N$_2$O and CH$_4$ production, (ii) to examine potential environmental parameters influencing N$_2$O and CH$_4$ production (iii) to determine the effect of HRT on total global warming potential from bioreactors.
2. Materials and Methods

2.1. Bioreactor Design and Operation

Greenhouse gas and water chemistry measurements were taken from nine pilot scale (5.8 × 1.0 × 1.1 m) bioreactors designed specifically for research at Iowa State University’s Agronomy and Agricultural Engineering Research Farm located west of Ames, IA (42°01’01’’N, 93°46’48’’W). Specifics on the design and operation of the pilot-scale bioreactors can be found in Hoover et al. (2017). Bioreactors were installed in September 2014 and only active for three weeks in 2015 prior to this study. Local hardwood woodchips, supplier details in Christianson et al. (2010), were housed in concrete trenches capped with 20 cm of excavated soil. The site was seeded to a Midwestern wildflower mix in fall of 2015. Bioreactor influent water was sourced from a 30.5 cm tile that passes through the University farm. An underground cistern (11 m³) intercepts the tile line and from there water is pumped to three temporary above ground storage tanks (11 m³ each). Each of the three storage tanks distributes water to three bioreactors through 5.1 cm polyvinyl chloride (PVC) pipes. A brass gate-valve controls inlet flows into each bioreactor, and an in-line ball valve is used to redirect influent for sample collection and flow calibration. Water control structures (Agri Drain, Adair, IA) at the outlet of each bioreactor control the height of water within the bioreactors. Water was held to 1 m above the bottom of each bioreactor for a total saturated volume of 6.08 m³ per bioreactor. Each bioreactor is equipped with two sampling wells (10.2 cm diameter) located 1.42 m and 4.26 m from the inlet (Fig. 4.1). Sampling wells were fully screened (1 m) to the height of the water in the bioreactors.

Flow rates were calculated for three HRTs, 2, 8, and 16 hours, using saturated volume and media porosity. A potassium bromide tracer study was conducted to determine media porosity (Hoover et al., 2017). Hydraulic retention times were assigned in a randomized
complete block design. Bioreactors were blocked by temporary water storage tanks (3), and HRT treatments (3) were randomly assigned within each block, for a total of nine bioreactors (Fig. 4.1). As part of a companion study examining nitrate removal and flow dynamics, flow rates were found to be significantly different from one another (data not shown).

2.2. Sample Collection

Greenhouse gas and water chemistry samples were collected simultaneously on a weekly basis from August 15 through October 26 in 2016 and from June 1 through July 6 in 2017. Bioreactors were not drained and allowed to freeze throughout 2016-2017 winter months. Flow was returned to the bioreactors in late May of 2017 and one week of flow was allowed before collection began on Jun 1, 2017. Water that over-winters in bioreactors has the potential to contain elevated concentrations of dissolved N$_2$O and CH$_4$ and could confound our objective to determine the effects of HRTs on greenhouse gas production. Measurements were limited in 2017 due to abnormally low precipitation in the region. The source tile supplying drainage water to the bioreactors stopped flowing, inhibiting our ability to maintain desired HRTs. Therefore, sample collection took place for 78 days in 2016 and 36 days in 2017.

Samples were collected between 10:00 am to 2:00 pm to limit potential diurnal variation in greenhouse gas emissions from the soil surfaces (Parkin and Ventera, 2010). A typical sample collection day consisted of aqueous sample collection from the inlet, sampling wells, and outlet of each bioreactor. Sampling wells were evacuated using a peristaltic pump prior to sample collection. Wells were considered evacuated after water equivalent to the volume of the well (8.2 L) passed through the pump. A 125 ml sample was then collected for NO$_3$ and ammonium analysis. Samples were stored on ice in the field, acidified, and stored at 4$^\circ$ C in the laboratory until analysis. Next, dissolved greenhouse gas samples were collected
into 10 ml syringes. A syringe was held onto the end of the sampling house of the pump and filled, limiting gas loss through atmospheric exposure. Samples (10 ml) were then injected into evacuated 20 ml glass vials sealed with butyl rubber stoppers (Voigt Global). Glass vials contained 0.3 ml of 80% zinc chloride to preserve dissolved gas concentrations until analysis. Duplicate samples were taken from each sampling point. After aqueous sample collection, dissolved oxygen (O₂) and temperature were measured using a YSI Pro ODO field probe (YSI Inc.). The dissolved O₂ probe was carefully lowered into each sampling structure and allowed to equilibrate before measurements were recorded.

Greenhouse gas samples from bioreactor surfaces were collected concurrently with aqueous sampling from circular static vented chambers equipped with automated sampling equipment (Davis et al., 2018). Schedule 40 PVC anchors (30 cm diameter, 15 cm tall) were installed 2.03 and 4.86 m from the inlet of each bioreactor (Fig. 4.1). Chamber tops were constructed from 30 cm sections of schedule 40 PVC to a height of 15 cm and are described in Parkin and Ventera (2010). Chamber tops were vented and covered with reflective tape to limit solar radiation absorbance. Chambers were placed on anchors and automated samplers attached to a butyl rubber stopper sampling port located on the top of each chamber. Automated samplers collected gas samples at time 0, 15, 30, and 45 minutes. Samples were collected into 20 ml syringes equipped with stopcocks. After sample collection stopcocks were closed until laboratory analysis. Air temperature was measured inside each static chamber using a HOBO temperature pendant (Onset Computer Corp.).

2.3. Sample analysis

Nitrate was analyzed on a Seal Analytical (Mequon, WI) AQ2 discrete autoanalyzer (AQ2 method EPA-114-A, Rev. 7). Samples are measured as NO₃-N+NO₂-N. Nitrate is reduced by copperized cadmium to NO₂ and measured spectrophotometrically at 520 nm.
The method detection limit is 0.03 mg N L\(^{-1}\).

Surface gas samples were prepared for analysis in the laboratory by injecting 13 ml of sample into 6 ml vials sealed with butyl rubber stoppers. Dissolved gas samples were also prepared for analysis in the laboratory. Samples were adjusted to atmospheric pressure and then overfilled with 7 ml of helium. Samples were shaken for 15 minutes on a reciprocal shaker to equilibrate N\(_2\)O and CH\(_4\) concentration with the vial headspace.

Greenhouse gas concentrations were measured on a gas chromatograph (GC) (SRI instruments, model 8610). An automated sampler (Arnold et al., 2001) introduced gas samples into the inlet valve of the GC where they traveled through a stainless steel column (0.3175 cm diameter \(\times\) 74.54 cm long) packed with Haysep D to a \(^{63}\)Ni electron capture detector (N\(_2\)O) and then a flame ionization detector (CH\(_4\)). Sample concentrations were calculated using linear regression coefficients of N\(_2\)O and CH\(_4\) standards (Air Liquide Specialty Gases) and the universal gas law. Total gas content in dissolved samples was calculated using Henry’s law and Bunsen absorption coefficients.

Greenhouse gas surface fluxes were calculated using the HMR package in R v3.1.2 (The R Foundation, 2014). The HMR model was attempted first for each set of time series samples. If the HMR model failed to produce a flux, the software used linear regression or assigned a “no flux” value of zero (Pedersen et al., 2010). Cumulative emissions were calculated by linearly interpolating between sampling dates and summing daily emission rates for the study period.

2.4. Greenhouse gas production

Mass N\(_2\)O and CH\(_4\) production was calculated for each bioreactor by subtracting inlet mass load from surface and dissolved outlet mass loads. Cumulative surface emissions were calculated by multiplying cumulative emissions for the study period by the surface area (6.38
m²) of each reactor. Dissolved concentrations and flow rates were used to calculate mass loads of dissolved gases for each reactor. Production rates (g m⁻³ day⁻¹) were calculated within the bioreactors at well sampling points and the outlet. Statistical analyses were conducted in R v3.1.2. Loads and production rates were compared using a repeated measures two-factor analysis of variance with a Tukey’s honest significance post-hoc test. Dissolved gas concentrations were compared to water chemistry parameters using linear regression models.

2.4. Indirect Nitrous Oxide Emissions

Indirect N₂O emissions occurring from downstream denitrification from nitrate leaching was calculated using the Tier 1 IPCC protocol for estimating indirect N₂O emissions (IPCC, 2006). The mass of NO₃-N leached was multiplied by 0.005 kg N₂O-N kg⁻¹ NO₃-N, the sum of the default emission factors for rivers (EF₅ᵣ = 0.0025 kg N₂O-N kg⁻¹ NO₃-N) and estuaries (EF₅ₑ = 0.0025 kg N₂O-N kg⁻¹ NO₃-N). Paired t tests were used to examine differences in means of annual indirect N₂O emissions from SRBs compared to the field tiles.

2.4. Global Warming Potential

To compare the radiative forcing potential from each bioreactor gas production rates were converted to carbon dioxide equivalents (CO₂e). Global warming potentials (GWP) of CH₄ and N₂O are 28 and 265 times the potential of CO₂, respectively, for a 100 year adjustment not including climate carbon feedbacks (Myhre et al., 2013). Carbon dioxide equivalents were calculated by multiplying production rates by respective GWP values.
3. Results and Discussion

3.1. Nitrate Removal

Nitrate was removed from all nine bioreactors. Nitrate concentrations were reduced significantly \((P = 0.05)\) from the inlet to the outlet at all three HRTs. Mass \(\text{NO}_3\) load removal increased significantly \((P = 0.05)\) with decreasing HRT, 6.70 kg-N (2 hour), 5.97 kg-N (8 hour), and 5.14 kg-N (16 hour) (Table 4.1). Details on Nitrate removal and dissimilatory nitrate reduction to ammonium (DNRA) can be found in Martin et al. (2018).

3.2. Nitrous Oxide Production

Cumulative \(\text{N}_2\text{O}\) emissions from the surface and outlet were greater than inlet contributions across all nine bioreactors, resulting in net production of \(\text{N}_2\text{O}\) (Table 4.1). Inlet tile \(\text{N}_2\text{O}\) concentrations showed little variation over the study period and ranged from 12.0 to 36.2 \(\mu\)g \(\text{N}_2\text{O}-\text{N} \text{ L}^{-1}\). See supplemental material for time series data on dissolved \(\text{N}_2\text{O}\) concentrations. Dissolved inlet concentrations were similar to other tile samples collected within Central Iowa (Parkin et al., 2016). Tile inlet loads were 1.06 (2hr HRT), 0.27 (8hr HRT), and 0.17 (16 hr HRT) g \(\text{N}_2\text{O}-\text{N} \text{ day}\) respectively. Dissolved \(\text{N}_2\text{O}\) loads leaving the bioreactor outlets were 4.17 (2hr HRT), 0.46 (4hr HRT), and 0.41 (16 hr HRT) g \(\text{N}_2\text{O}-\text{N} \text{ day}\). Nitrous oxide loads from the surface of the bioreactors were much lower than dissolved counterparts emitting 0.004 (2hr HRT), 0.005 (8hr HRT), and 0.002 (16hr HRT) g \(\text{N}_2\text{O}-\text{N} \text{ day}\). Surface \(\text{N}_2\text{O}\) emissions were not significantly different from one another \((P = 0.40)\) across the three HRTs (Table 4.1). However, dissolved \(\text{N}_2\text{O}\) loads from the 2 hour HRT treatment were significantly greater \((P < 0.05)\) than both 8 and 16 hour HRTs.

Nitrous oxide production did not change significantly over time \((P < 0.05)\) (Fig. 4.2). The 2 hour HRT bioreactor produced the most \(\text{N}_2\text{O}\) on average, 478.43 mg \(\text{N}_2\text{O}-\text{N} \text{ m}^3 \text{ day}^{-1}\). Nitrous oxide production from the 2 hour HRT was significantly greater \((P < 0.04)\) than 8
hour HRT (28.95 mg N$_2$O m$^{-3}$ day$^{-1}$) and 16 hour HRT (36.61 mg N$_2$O m$^{-3}$ day$^{-1}$) N$_2$O production. Production from the 8 hour HRT and 16 hour HRT were not significantly different ($P = 0.98$) from one another or from respective inlets ($P < 0.05$). Our results differ from the laboratory study by Greenan et al. (2011), who found no significant difference in N$_2$O production between varied flow rates. Nitrous oxide emissions within 2 hour HRTs were similar to Warneke et al. (2011), who found emissions of 380 mg N$_2$O-N m$^{-3}$ day$^{-1}$ over summer months. Waraneke

Surface fluxes represented 0.1 (2hr HRT), 2.6 (8hr HRT), and 0.8% (16hr HRT) of total N$_2$O production. Surface N$_2$O fluxes were similar to other studies measuring emissions from static chambers (David et al., 2016; Warneke et al., 2011; Woli et al., 2010). These studies were conducted on bioreactors without a soil cap and anchors were placed directly into the woodchips. Nitrous oxide emissions from the bioreactor surface could include N$_2$O from denitrification within the soil cap. Christianson et al. (2013) suggested N$_2$O emissions could be mitigated through soil cap implementation. However, surface emissions from our study with a soil cap were similar to emissions found in Warneke et al. (2011) and greater than emissions found in David et al. (2016) and Woli et al. (2010) without soil caps. Surface N$_2$O fluxes from the bioreactors were less than fluxes associated with N fertilized corn in summer months and similar to fluxes from perennial plant systems in the area (Iqbal et al., 2015; Parkin and Kaspar, 2006). The majority of N$_2$O produced exited the bioreactors through the outlet as dissolved N$_2$O.

Dissolved N$_2$O production within bioreactors was greatest from the inlet to well A across HRTs (Fig. 4.3), indicating the greatest rate of N$_2$O production was in the first 1.42 m of treatment. Production continued in the 2 hour HRT from well A to B, but was not
observed in 8 and 16 hour HRTs. Total N$_2$O load increased significantly ($P < 0.05$) from the inlet to the outlet within the 2 hour HRT, but not within the 8 or 16 hour HRTs. Overall nitrous oxide concentrations were not correlated with NO$_3$ concentrations ($r^2 = 0.003$) or dissolved oxygen ($r^2 = 0.002$) (Data not shown). However, when comparing average dissolved O$_2$ and N$_2$O concentrations by bioreactor position, we observed a correlation between decreasing average N$_2$O concentration with decreasing dissolved O$_2$ concentrations below 2 mg O$_2$ L$^{-1}$ ($r^2 = 0.77$) (Fig. 4.3). The inlet and well A of the 2 hour HRT averaged above 2 mg O$_2$ L$^{-1}$ and did not follow a similar trend. In this case N$_2$O production was the highest observed, despite dissolved O$_2$ concentrations typically above 2 mg O$_2$ L$^{-1}$. This could be explained by the fact that dissolved O$_2$ measurements were taken from water flowing through the woodchips in the reactor, while N$_2$O production likely took place at locally anaerobic sites on and within woodchips (Moorman et al., 2010).

While all nine bioreactors produced N$_2$O, mass loads from bioreactors were only significantly greater ($P = 0.05$) than inlet concentrations within the 2 hour HRT bioreactors. Nitrous oxide emissions were 5.19% of the total NO$_3$ removed at 2 hour HRT and only 0.38 for the 8 hour HRT and 0.50 for the 16 hour HRT. The 2 hour HRT percentage was greater than the range observed in the literature of <1 to 4.7% (Christianson, 2013; David et al., 2016; Warneke et al., 2011; Woli et al., 2010). However, N$_2$O production at the 2 hour HRT (0.00038 kg N$_2$O-N kg$^{-1}$ NO$_3$-N leached) was less than the Intergovernmental Panel on Climate Change’s (IPCC) estimation for indirect emissions from groundwater (EF$_{sg} = 0.0025$ kg N$_2$O-N kg$^{-1}$ NO$_3$-N leached) (IPCC, 2006). The 8 and 16 hour HRTs were closer to the IPCC estimations at 0.0017 and 0.0045 kg N$_2$O-N kg$^{-1}$ NO$_3$-N leached, respectively. The 2 hour HRT produced the greatest mass of N$_2$O and the greatest percentage of N$_2$O
produced kg\(^{-1}\) NO\(_3\)-N removed, yet 2 hour HRT bioreactors had the lowest estimation of emissions from groundwater production. Our results support discussions in Groffman et al. (2000) and Greenan et al. (2009) that controls of N\(_2\)O production and consumption are not reflected in N\(_2\)O/NO\(_3\) ratios and do not accurately reflect mass N\(_2\)O production.

### 3.3. Methane Production

The bioreactors were a source of methane production across all HRTs, significantly greater \((P < 0.05)\) than inlet loads at all three HRTs. Unlike N\(_2\)O production, CH\(_4\) production was greatest at the 8 and 16 hour HRTs. Methane production was significantly less \((P < 0.05)\) from 2 hour HRT \((0.51 \text{ g C m}^3 \text{ day})\) compared to 8 \((1.50 \text{ g C m}^3 \text{ day})\) and 16 \((1.69 \text{ g C m}^3 \text{ day})\) hour HRTs (Table 4.3). Methane production changed through time \((P < 0.05)\), appearing to reduce from the beginning of the study. Methane production may continue to be reduced as the woodchips of the bioreactor age loosing labile carbon and microbial activity. Dissolved methane represented between 84 and 99% of total CH\(_4\) load from the bioreactors, but surface fluxes were measurable and contributed to total mass loads.

Surface fluxes of methane are not typical from Midwestern soils but may occur in wet years (Chan and Parkin, 2001; Venterea et al., 2005). The majority of contribution of methane from agriculture is from livestock operations (Smith et al., 2014). However, CH\(_4\) fluxes from bioreactor surfaces averaged 0.18 (2hr HRT), 0.31 (8hr HRT), and 0.86 (16hr HRT) g CH\(_4\)-C day (Table 4.3). Cumulative CH\(_4\) surface emissions between HRT treatments were not significantly different from one another \((P = 0.23)\). Methane fluxes from our study were greater than emissions measured from the surface of an uncovered bioreactor in Warneke et al. (2009). The majority of bioreactor greenhouse gas emission studies have focused on nitrous oxide emissions. Our results highlight the importance of including methane measurements from bioreactor surfaces in future studies.
Dissolved mass loads were greatest in the 8 (9.83 g CH$_4$-C day) and 16 (10.43 g CH$_4$-C day) hour HRTs. Mass loads from 8 and 16 hour HRTs were significantly greater ($P < 0.05$) than 2 hour HRT (4.60 g CH$_4$-C day). Methane production rates were greatest between well A and well B (Fig. 4.3). Dissolved CH$_4$ concentrations were not correlated with NO$_3$ ($r^2 = 0.02$) or dissolved O$_2$ concentrations ($r^2 = 0.01$). However, averaging concentrations by bioreactor position resulted in an inverse linear relationship between CH$_4$ and NO$_3$ ($r^2 = 0.83$) (Fig. 4.4). Methane production occurred without the complete consumption of NO$_3$ at all three HRTs, but greatly increased below 10 mg NO$_3$-N L$^{-1}$. Unlike other field studies (Warneke et al., 2011), we found methane production from the surface and dissolved in water passing through bioreactors at all three HRTs. Other studies have found CH$_4$ emissions from woodchip bioreactors, but typically at NO$_3$ concentrations less than 1 mg NO$_3$-N L$^{-1}$(Elgood et al., 2010; Healy et al., 2012). Methane production from our bioreactors was likely from microsites within woodchips where NO$_3$ concentrations were depleted or from areas within the bioreactors where flow is not uniform.

3.5. Global Warming Potential

Nitrous oxide production within 2 hour HRT bioreactors was the greatest contributor to global warming potential, 261 g CO$_2$equivalents day$^{-1}$ (Fig. 4.5). Methane emissions represented over 80% of total global warming potential from 8 and 16 hour HRTs and only 10% for the 2 hour HRT. Healy et al. (2012) found CH$_4$ to be the greatest contributor, greater than both N$_2$O and CO$_2$, across a number of bioreactor fill materials with HRTs more than 1 day. The CH$_4$ contributions highlight the importance of monitoring both N$_2$O and CH$_4$ from bioreactors for accurate global warming potential estimations. Nitrous oxide produced from incomplete denitrification at 2 hour HRTs could greatly increase dissolved N$_2$O from bioreactors and should be considered in bioreactor design.
4. Conclusions and Management Implications

The 2 hour HRT was the greatest contributor to N₂O emissions, resulting in the greatest global warming potential. While more CH₄ was produced in 8 and 16 hour HRTs, loads did not equate to a greater global warming potential compared to 2 hour HRTs. Our results support Healy et al. (2012) and Warneke et al. (2011), concluding bioreactors are producers of both N₂O and CH₄ and HRT can be used in management strategies to limit greenhouse gas production from woodchip bioreactors. Higher HRTs resulted in more complete denitrification and less impact on a CO₂ equivalent basis. To meet the USDA-NRCS conservation practice standard criteria, denitrifying bioreactors are designed to treat at least 15 percent of peak flow from the drainage system and have a minimum HRT of 3 hours at peak flow (NRCS, 2015). The greatest NO₃ load removal was observed in 2 hour HRT bioreactors, but many studies have shown increased cumulative mass NO₃ removal from bioreactors with greater HRTs (Addy et al., 2016). The 2 hour HRT was the least efficient at NO₃ removal, but removed the greatest mass of NO₃ because it received the most flow. Our results suggest increasing bioreactor flow to remove a greater mass of NO₃ also increases N₂O production and global warming potential. However, other environmental trades should be considered including methyl mercury production in bioreactors exhibiting sulfate reducing conditions (Shih et al., 2011).

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Tables and Figures

Figure 4.1. (a) Bioreactor layout with sampling locations and distances from the inlet. (b) Randomized complete block design for hydraulic retention times (HRTs) of pilot scale bioreactors.
Figure 4.2. Nitrous oxide ($N_2O$) and methane ($CH_4$) production over 114 days from both 2016 and 2017.
Figure 4.3. Nitrous oxide \((N_2O)\) and methane \((CH_4)\) loads, including dissolved and surface emissions at sampling points through the bioreactors. Production are positive slopes between points. Losses were negative slopes between points. Losses were not significant at any hydraulic retention times (HRTs) for both gases. Nitrous oxide production was greatest between the bioreactor inlet \((0 \text{ m})\) and well A \((1.42 \text{ m})\). Methane production was greatest between the bioreactor well A \((1.42 \text{ m})\) and well b \((4.26 \text{ m})\).
Figure 4.3. (a) Average dissolved nitrous oxide (N$_2$O) concentrations and average dissolved oxygen (O$_2$) for all reactors and positions. (b) Average dissolved nitrous oxide (N$_2$O) concentrations and average dissolved oxygen (O$_2$) below 2 mg O$_2$ L$^{-1}$ with linear regression analysis.
Figure 4.4. Average dissolved methane (CH$_4$) concentrations and average dissolved nitrate (NO$_3$) for all reactors and positions.

Figure 4.5. Global warming potential in carbon dioxide equivalents (CO$_2$e) of three hydraulic retention times (HRT). Letters denote significant differences at p-values < 0.05.
Table 4.1. Nitrate (NO$_3$) removal and nitrous oxide (N$_2$O) production from bioreactors at three different hydraulic retention times (HRTs). Nitrate removal is presented in load (kg-N) for the study period. Lowercase letters indicate significant differences among dissolved loads. Loads with different letters denote significant difference at $p$-values < 0.05. Uppercase letters indicate differences among HRT production rates, different letters denoting significance as $p$-value < 0.05. Surface fluxes were not significantly different among HRTs. Nitrous oxide production loads were used to calculate percentages of kg N$_2$O-N produced per kg NO$_3$-N removed.

<table>
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<th>HRT</th>
<th>Nitrate mass removal</th>
<th>N$_2$O mass loads</th>
<th>N$_2$O production</th>
<th>kg N$_2$O-N kg$^{-1}$ NO$_3$-N removed</th>
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<td></td>
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<td></td>
<td>kg-N</td>
<td>g N$_2$O-N day$^{-1}$</td>
<td>mg N$_2$O-N m$^{-3}$ day$^{-1}$</td>
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<td>0.457 c</td>
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<tr>
<td>16 hour</td>
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Table 4.2. Methane (CH$_4$) mass loads and production. Lowercase letters indicate significant differences among dissolved loads. Loads with different letters denote significant difference at $p$-values < 0.05. Uppercase letters indicate differences among HRT production rates, different letters denoting significance as $p$-value < 0.05. Surface fluxes were not significantly different among HRTs.

<table>
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<th>CH$_4$ production</th>
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<td></td>
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<td>Dissolved</td>
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<td></td>
<td>g CH$_4$-C day$^{-1}$</td>
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<td>2 hour</td>
<td>0.18</td>
<td>1.43 c</td>
</tr>
<tr>
<td>8 hour</td>
<td>0.31</td>
<td>0.36 c</td>
</tr>
<tr>
<td>16 hour</td>
<td>0.86</td>
<td>0.26 c</td>
</tr>
</tbody>
</table>
CHAPTER 5. GENERAL CONCLUSIONS

Strategies to remove nitrate (NO$_3$) from agricultural drainage are recommended as a primary mechanism to reduce nitrogen (N) losses to the Gulf of Mexico (IDALS et al., 2014; Illinois EPA, 2015). Edge of field strategies enhance microbial denitrification to return reactive N to the atmosphere as non-reactive N. Removal scenarios from states yielding the greatest N losses recommend widespread implementation of wetlands, bioreactors, and saturated riparian buffers (SRBs) to achieve N removal goals. However, conditions that are ideal for denitrification may also be ideal for greenhouse gases production. Here we presented three studies, one study improving sampling efficiency and two advancing understanding of greenhouse gas production from edge of field conservation practices.

In chapter 2, we presented a design to improve the efficiency of manual static chamber sampling of gas flux from soil surfaces. The chamber automated sampling equipment to measure soil gas flux (FluxCASE) was designed to minimize labor expenses, eliminate human-induced sampling error, and increase sample numbers to address spatial and temporal variability. We conducted laboratory and field studies to confirm FluxCASEs maintained similar precision and accuracy to manual sampling. In the laboratory study, FluxCASEs were precise when compared to manual sampling of a gas mixture standard. Coefficients of variation (CVs) sampled via FluxCASEs were similar to manual sampling across all three gas species sampled, nitrous oxide (N$_2$O), carbon dioxide (CO$_2$), and methane (CH$_4$). Soil gas fluxes measured using FluxCASEs were similar to manual sampling. Slopes of regression models with 95% confidence intervals from fluxes measured with FluxCASEs compared to fluxes measured manually were 1.01 for CO$_2$ and 0.97 for N$_2$O. Confidence intervals also included a regression model with a slope of 1. Finally, expense recovery for the
construction of 20 FluxCASEs was less than one year for a majority of sampling assumptions. We concluded FluxCASEs were both precise and accurate, and that the cost of construction can be recovered within the first year of use. The FluxCASE system was utilized in the collection of soil gas flux in the subsequent studies.

Chapter 3 compared N₂O emissions from SRBs and traditional riparian buffers and conventional agriculture fields within the same landscape position. This study is the first to measure N₂O emissions from SRBs. Nitrous oxide samples were collected as direct emissions from the soil surface and dissolved in shallow groundwater flow. We also estimated indirect emissions from denitrification in rivers and estuaries of NO₃ flux via tile drainage. Direct emissions from SRBs were only significantly greater ($P < 0.05$) in one sampling year (2015) compared to traditional riparian buffers. Saturated riparian buffers resulted in a decrease of indirect emissions from groundwater, rivers, and estuaries. Overall, SRB installation reduced N₂O emissions compared to conventional agriculture and emissions are similar to traditional riparian buffers. Nitrous oxide production per kg NO₃-N removed in SRBs ranged from 3.2 to 9.3%. Production rates were greater than other edge of field practices (Kovacic et al., 2000; Christianson et al., 2013b; Groh et al., 2015), but these studies did not include indirect emissions. The largest percentage of N₂O production per kg N removed was at BC-1 in 2015. All other site years were below 4%, similar to comparison studies. These results are encouraging for future success of SRBs as a conservation practice and highlight a potential for reduction of N₂O emissions from agroecosystems.

In Chapter 4, we examined N₂O and CH₄ production from bioreactors at three different hydraulic retention times (HRTs). Pilot scale bioreactors were used to maintain 2, 8, and 16 hour HRTs for summers in 2015 and 2016. Net production of N₂O and CH₄ was
observed across all HRTs, with the majority of production leaving as dissolved gas in the tile outlet. Nitrous oxide production was significantly greater ($P < 0.05$) from 2 hour than from 8 and 16 hour HRTs. Methane production was significantly less ($P < 0.05$) from 2 hour HRTs ($0.51 \text{ g C m}^{-3} \text{ day}^{-1}$) compared to 8 ($1.50 \text{ g C m}^{-3} \text{ day}^{-1}$) and 16 ($1.69 \text{ g C m}^{-3} \text{ day}^{-1}$) hour HRTs. Nitrous oxide has a greater global warming potential compared to CH$_4$. Nitrous oxide has 265 times the global warming potential of carbon dioxide; whereas, CH$_4$ has 28 times the global warming potential of carbon dioxide (100-yr adjustment, without the inclusion of climate-carbon feedbacks) (Myhre et al., 2013). Therefore, the greater N$_2$O production from the 2 hour HRTs had significantly greater ($P = 0.05$) global warming potential compared to 8 and 16 hour HRTs. These results suggest longer HRTs may reduce global warming potential of bioreactors. Bioreactors installed onto tiles for N removal should maximize HRTs to both increase NO$_3$ removal efficiency and reduce greenhouse gas emissions. However, more work should be done to examine HRT and methyl mercury production in bioreactors under sulfate reducing conditions (Shih et al., 2011).

Results from the studies presented here improve greenhouse gas sampling methodology and advance understanding of greenhouse gas emissions from edge of field conservation practices treating NO$_3$ from tile drainage. Furthermore, these studies highlight the uncertainty associated with indirect emissions of N$_2$O from fertilizer application. The Intergovernmental panel on Climate Change estimates N$_2$O emissions from managed lands are responsible for two-thirds of the uncertainty associated with the global N$_2$O budget (IPCC, 2006). In Chapter 3, we measured direct N$_2$O emissions from groundwater and estimated indirect emissions from rivers and estuaries of NO$_3$ flux via tile drainage using emissions factors (EF) established by IPCC.
The latest revision of the Intergovernmental Panel on Climate Change (IPCC) Guidelines for National Greenhouse Gas Inventories (2006) lowered the emissions factor of riverine systems (EF_{5r}) from 0.0075 to 0.0025 and the emissions factor of groundwater and surface drainage (EF_{5g}) from 0.015 to 0.0025. Justification for the reductions was supported by several studies (Reay et al., 2003; Dong et al., 2004; Clough et al., 2006) where researchers cited an overestimation of indirect emissions estimations compared to direct measurements collected from stream surfaces. However, recent measurements have argued the EF_{5r} is now underestimating N\textsubscript{2}O production from streams (Turner et al., 2015; Audet et al., 2017). A consensus in the literature has not been achieved due to the complex coupling of EF_{5r} and EF_{5g}. Studies reporting measurements as only EF_{5r} from floating chambers methods or gas transfer velocity models may provide inaccurate estimates, as N\textsubscript{2}O dissolved in groundwater or tile drains can also be released via the stream surface. Measurements of EF_{5r} emissions should only include N\textsubscript{2}O produced through in-stream denitrification from the water column and benthic sediments.

Emission factors are also difficult to estimate because of the potential environmental controls on N\textsubscript{2}O fluxes, including land use, geomorphology, streambed composition, water chemistry, and climate (Beaulieu et al., 2008). Nitrate is often cited as a strong predictor of N\textsubscript{2}O emissions from streams and rivers (Harrison and Matson, 2003; Reay et al., 2003; Stow et al., 2005; Beaulieu et al., 2008; Baulch et al., 2011). However, studies reporting surface waters with low NO\textsubscript{3} concentrations variation have found no relationship between NO\textsubscript{3} concentrations and N\textsubscript{2}O emissions (Clough et al., 2006; Beaulieu et al., 2010; Rosamond et al., 2011). These conflicting results highlight a growing concern with the linear relationship assumed by N\textsubscript{2}O emission factors in the IPCC’s greenhouse gas inventory guidelines. Future
studies to improve estimations in agricultural watersheds should focus attention on accurately defining the source of N$_2$O from chamber measurements, including better estimations of N$_2$O losses from tile drains.
References


