Nitrous oxide and methane fluxes in riparian buffers and adjacent crop fields

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Nitrous oxide and methane fluxes in riparian buffers and adjacent crop fields

by

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ABSTRACT

Denitrification is recognized as the major mechanism for reducing nitrate (NO$_3^-$) in riparian buffers and thus diminishing non-point source pollution (NPS) of surface water bodies subject to high N loads. However, increasing denitrification rates in riparian buffers may be trading the problem of NPS pollution of surface waters for atmospheric deterioration and increased global warming potential because denitrification produces nitrous oxide (N$_2$O), a greenhouse gas also involved in stratospheric ozone depletion. Also N$_2$O produced in the denitrification process can be dissolved in groundwater and is eventually emitted into the air when groundwater flows into a stream or a river. Riparian buffers restored from cultivated crop fields may have significant capacities as sinks or sources of CH$_4$. It therefore is important to quantify the fluxes of N$_2$O, CH$_4$ and dissolved N$_2$O, identify the source of N$_2$O from different kinds of riparian buffer systems and evaluate the significance of N$_2$O and CH$_4$ sources. We measured N inputs, weather conditions and N$_2$O and CH$_4$ fluxes from soils in forested riparian buffers, warm-season and cool-season grass filters, and a crop field located in the Bear Creek watershed in central Iowa. We measured concentrations of NO$_3^-$, dissolved N$_2$O, and other chemical properties in groundwater under a multi-species riparian buffer, a cool-season grass filter, and the adjacent crop field. We sampled soils in the site and measured soil properties, and conducted incubation experiments with inhibitors (CH$_3$F, C$_2$H$_2$, and O$_2$) to determine sources of N$_2$O, the ratio of N$_2$O to N$_2$, and the production and consumption of CH$_4$ in vitro. The forest buffer and grass filter soils had significantly lower bulk density; and higher pH, total carbon (TC), total nitrogen (TN), and ammonium (NH$_4^+$) than those in the crop field. Nitrous oxide emissions from soils in all riparian buffers (1.8-4.5 kg N$_2$O-N ha$^{-1}$) were significantly less than those in the crop fields (7.2-16.8 kg N$_2$O-N ha$^{-1}$), but no differences among different kinds of riparian buffers were observed. Our results indicate that the emission factor (ratio of N$_2$O emission to N inputs) of soils in riparian buffers was smaller than the crop fields. While N$_2$O peak emissions followed by rewetting dry soils and thawing frozen soils significantly contributed to annual N$_2$O emissions from soils in the crop fields, soils in the riparian buffers were less sensitive to such events. Soil incubation with inhibitors indicated that the main sources of N$_2$O might be nitrifier denitrification and denitrification in the crop field soil and nitrifier denitrification in the riparian buffer soils. The ratio of N$_2$O to N$_2$ in riparian buffer soil (0.88-6.8) was less than that found in crop field soil (16.5). These results suggest that N$_2$O emissions from soils in all riparian buffers were significantly less than those in the crop field. In both a multi-species riparian buffer and a cool-season grass filter, NO$_3^-$ concentrations in groundwater were significantly decreased in comparison to those in the crop field, by 48-59 %. However, dissolved N$_2$O concentrations in groundwater did not differ among locations (6-14 µg L$^{-1}$). These results indicate
that the riparian buffers decreased NO$_3^-$ concentrations in near-surface groundwater, without increasing N$_2$O losses. Methane fluxes in crop field soil were not observed to be significantly different from those in the forest buffer and grass filter soils, and no significant difference in CH$_4$ flux was found between the forest buffer and grass filter soils. Annual CH$_4$ flux was -0.80 kg C ha$^{-1}$ yr$^{-1}$, -0.46 kg C ha$^{-1}$ yr$^{-1}$, and 0.04 kg C ha$^{-1}$ yr$^{-1}$ in the crop field, forest buffers and grass filters, respectively. The annual CH$_4$ flux in forest buffers and grass filters were not significantly different from zero and these three amounts were not significantly different from one another. These results suggest that 1) N$_2$O emissions from soils in all riparian buffers were significantly less than those in the crop field, 2) the riparian buffers decreased NO$_3^-$ concentrations in near-surface groundwater, without increasing N$_2$O losses, and 3) CH$_4$ flux in the crop field, forest buffers and grass filters were not different and CH$_4$ flux was not changed in the forest buffers and grass filters soils, despite that soil properties have changed significantly since the planting of the forest buffers and the grass filters.
GENERAL INTRODUCTION

Non-point source (NPS) pollutants such as sediment, nitrogen (N), phosphorus (P), and pesticides are the major causes of water quality problems worldwide (Duda, 1993; Tonderski, 1996; Carpenter et al., 1998). Shortly after the Waikato Valley Authority in New Zealand (1973) first discussed the use of riparian buffers for the prevention of water pollution, a number of research projects were initiated to quantify the ability of riparian buffers to control NPS pollution (e.g. Lowrance et al., 1983; Peterjohn and Correll, 1984). Based on these and other studies, riparian buffers have been recommended as one of the most effective tools for coping with NPS pollution (e.g. Mitsch et al., 2001; Sabater et al., 2003; Hubbard et al., 2004).

Some of the important functions of riparian buffers related to NPS pollution control are filtering and retaining sediment and immobilizing, storing, and transforming chemical inputs from uplands (Schultz et al., 2000). Many studies have shown that riparian buffers can reduce sediment erosion to surface waters by 70 to 95% (e.g. Lee et al., 2000, 2003), N fluxes by 5 to more than 90% (e.g. Kuusemets et al., 2001; Dukes et al., 2002) and P losses by 27 to 97% (e.g. Uusi-Kamppa et al., 2000; Kuusemets et al., 2001; Lee et al., 2003). Denitrification is recognized as the major mechanism for reducing nitrate, with removal generally ranging from 2–7 g N m⁻² y⁻¹ in riparian buffers (e.g. Lowrance et al., 1995; Groffman and Hanson, 1997; Watts et al., 2000).

It recently has been hypothesized that the increased denitrification that occurs in riparian areas may be trading a water quality problem for an atmospheric problem (Groffman et al., 1998) because nitrous oxide (N₂O), which is produced during nitrification and denitrification, adds to the greenhouse effect (Wang et al., 1976) and ozone depletion (Crutzen, 1970; Liu et al., 1977). The global warming potential of N₂O is 298 times that of carbon dioxide (CO₂) and 25 times that of methane (CH₄) in a 100-year time horizon (Forster, 2007). Some studies (Groffman et al., 1998, 2000; Hefting et al., 2003, 2006; Dhondt et al., 2004) conclude that N transformation by nitrate-loaded buffer zones results in a significant increase of greenhouse gas emission. In contrast, because riparian buffers efficiently decrease NO₃⁻, a source of indirect N₂O emissions, riparian buffers could provide an opportunity to decrease indirect N₂O emissions if we can develop reliable strategies for decreasing N₂O production during denitrification (Groffman, 2000). Besides denitrification, N₂O can be produced from nitrification (e.g. Firestone and Davidson, 1989), nitrifier denitrification (Webster and Hopkins, 1996; Wrage et al., 2001, 2004, 2005; Ma et al., 2007) and non-biological processes such as chemodenitrification (e.g. Daum and Schenk, 1998; Mørkved et al., 2007). It has been suggested that N₂O flux is a complex and that the source cannot be easily distinguished between nitrification and
denitrification (e.g. Wolf and Russow, 2000; Wrage et al., 2001, and 2004). Several authors have recently suggested that additional studies should be conducted to quantify N₂O emissions and identify source mechanisms within various regions, in different landscape settings, and under different vegetation communities. It is well known than that forest soils are the most active sink of CH₄, followed by grass lands and cultivated soils, and that the uptake potential of upland soils is reduced by cultivation, and especially by ammonium-N fertilizer application (e.g. Le Mer and Roger, 2001; Dutaur and Verchot, 2007). Therefore, riparian forest buffers and grass filters restored from cultivated crop fields for diminishing non-point source pollution may have benefits as a sink of CH₄. Riparian buffers are often flooded and also sustain relatively high soil moisture conditions caused by high water tables, long residence time and slow discharge (Schultz et al. 2000). These conditions may be favorable for CH₄ production. Therefore, the benefits of reduced non-point source pollution from riparian buffers may be offset by increased greenhouse gas emissions.

The overarching objective of this study was 1) to quantify the emissions of N₂O from different kinds of vegetated riparian buffer systems, 2) to quantify dissolved N₂O in groundwater moving from intensively row-cropped fields through riparian buffers of two vegetation types, 3) to distinguish the sources of produced N₂O in riparian buffers and crop fields and assess the differences in N₂O and N₂ among cropped fields and riparian buffers of three vegetation types, 4) to quantify the emission and consumption of CH₄ from different kinds of vegetated riparian buffer systems.

The study was intended to address 1) Are riparian buffers a more significant source of N₂O than adjacent crop fields? 2) Is groundwater exported to the stream from riparian buffers a significant source of N₂O emissions? 3) What are the main sources of produced N₂O in riparian buffers and crop fields? 4) Are riparian buffers a more significant source of CH₄ than adjacent crop fields?

This dissertation consists of four chapters which addressed each of above four questions. The first chapter entitled “Emission of the greenhouse gas nitrous oxide (N₂O) from riparian forest buffers, warm-season and cool-season grass filters, and crop fields”. The second chapter entitled “Transport and fate of nitrate and dissolved nitrous oxide in groundwater under riparian buffers adjacent to crop fields”. The third chapter entitled “Distinguishing sources of N₂O in riparian forest buffers, warm-season and cool-season grass filters, and crop fields”. The firth chapter entitled “Production and consumption of the greenhouse gas methane in riparian forest buffers, warm-season and cool-season
grass filters and adjacent crop fields soils” The four chapter are followed by a general conclusion section.
References


Emission of the greenhouse gas nitrous oxide from riparian forest buffers, warm-season and cool-season grass filters, and an adjacent crop field

A paper to be submitted to Biogeosciences

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Abstract
Denitrification is recognized as a major mechanism for reducing nitrate in riparian buffers and thus diminishing non-point source (NPS) pollution of surface water bodies subject to high N loads. However, increasing denitrification rates in riparian buffers may be trading the problem of NPS pollution of surface waters for atmospheric deterioration and increased global warming potential because denitrification produces nitrous oxide (N$_2$O), a greenhouse gas also involved in stratospheric ozone depletion. It therefore is important to quantify the emissions of N$_2$O from different kinds of riparian buffer systems and adjacent crop fields, and evaluate if N$_2$O emission from riparian buffer systems is larger than one from adjacent crop fields. We measured soil properties, N inputs, weather conditions and N$_2$O fluxes from soils in forested riparian buffers, warm-season and cool-season grass filters, and a crop field located in the Bear Creek watershed in central Iowa, USA. Annual N$_2$O emissions from soils in all riparian buffers (1.8 kg N$_2$O-N ha$^{-1}$ in 2006 and 3.4 - 4.5 kg N$_2$O-N ha$^{-1}$ in 2007) were significantly less than those in the crop field (7.2 kg N$_2$O-N ha$^{-1}$ in 2006 and 16.8 kg N$_2$O-N ha$^{-1}$ in 2007), but no differences among different kinds of riparian buffers were observed. Our results indicate that the emission factor (ratio of N$_2$O emission to N inputs, 0.02) of soils in riparian buffers was smaller than the crop field (0.07). While N$_2$O peak emissions (up to 70-fold increase) followed by rewetting dry soils and thawing frozen soils significantly contributed (46 - 70%) to annual N$_2$O emissions from soils in the crop field, soils in the riparian buffers were less sensitive to such events (3 to 10-fold increase). These results suggest that N$_2$O emissions from soils in all riparian buffers were significantly less than those in the crop field. In addition, this study suggests that more studies of N$_2$O peak emissions and negative N$_2$O fluxes are needed to better understand factors influencing N2O fluxes and to predict the impacts of land use on future climate change.

1 Introduction
Non-point source (NPS) pollutants such as sediment, nitrogen (N), phosphorus (P), and pesticides are major causes of water quality problems worldwide (Duda, 1993; Tonderski, 1996; Carpenter et al.,
Shortly after the Waikato Valley Authority in New Zealand (1973) first discussed the use of riparian buffers for the prevention of water pollution, a number of research projects were initiated to quantify the ability of riparian buffers to control NPS pollution (e.g. Lowrance et al., 1983; Peterjohn and Correll, 1984). Based on these and other studies, riparian buffers have been recommended as one of the most effective tools for coping with NPS pollution (e.g. Mitsch et al., 2001; Sabater et al., 2003; Hubbard et al., 2004).

Important functions of riparian buffers related to NPS pollution control are filtering and retaining sediment, and immobilizing, storing, and transforming chemical inputs from uplands (Schultz et al., 2000). Many studies have shown that riparian buffers can reduce sediment erosion to surface waters by 70 to 95% (e.g. Lee et al., 2000, 2003), N fluxes by 5 to more than 90% (e.g. Kuusemets et al., 2001; Dukes et al., 2002) and P losses by 27 to 97% (e.g. Uusi-Kamppa et al., 2000; Kuusemets et al., 2001). Denitrification is recognized as the major mechanism for reducing nitrate within riparian systems, with removal generally ranging from 2–7 g N m⁻² y⁻¹ (e.g.; Groffman and Hanson, 1997; Watts and Seitzinger, 2000).

It recently has been hypothesized that increased denitrification within riparian areas may trade a water quality problem for an atmospheric problem (Groffman et al., 1998; Xiong et al., 2006) resulting from the greenhouse effect of nitrous oxide (N₂O) produced during nitrification and denitrification (Wang et al., 1976) and ozone depletion (Crutzen, 1970; Liu et al., 1977). The global warming potential of N₂O is 298 times that of carbon dioxide (CO₂) and 25 times that of methane (CH₄) in a 100-year time horizon (Forster et al., 2007). Some studies (Groffman et al., 1998, 2000; Hefting et al., 2003, 2006; Dhondt et al., 2004) conclude that N transformation by buffer zones with high nitrate loads results in a significant increase of greenhouse gas emission. Groffman et al. (2002) suggested that the Intergovernmental Panel on Climate Change (IPCC) inventory might be improved by including more measurements of riparian N₂O fluxes.

Generally, the effectiveness of riparian buffers depends on the age and condition of the vegetation, soil characteristics such as porosity, aeration, and organic matter content, the depth to shallow groundwater, and the rate with which surface and subsurface waters move through the buffer (Groffman et al., 1992; Lowrance, 1992). Numerous studies have emphasized the role of vegetation in soil processes within riparian buffers. However, there are conflicting results regarding the relationship between vegetation type and denitrification rate in riparian buffers. While some studies (e.g. Hubbard and Lowrance, 1997; Verchot et al., 1997) found higher groundwater nitrate removal or
denitrification rates in forested riparian zones, other studies (Groffman et al., 1991; Schnabel et al. 1996) found higher removal in grass dominated riparian sites. Some studies (e.g. Hefting et al., 2003; Dhondt et al., 2004) found no significant difference in groundwater nitrate removal or denitrification rate between forested and grass dominated riparian sites. This variability suggests that there are still questions about the relationship between vegetation type of riparian buffers and N$_2$O emission from soils in riparian buffers and illustrates the need for additional studies in various regions of the country, in different landscape settings, and under different vegetation communities to quantify the emission of N$_2$O from soils in riparian buffers (Walker et al., 2002). The overarching objective of this study was to quantify the emissions of N$_2$O from riparian buffer systems comprised of forest, warm season grasses, and cool season grasses and to compare these emissions with those of adjacent crop fields. In addition, to evaluate current IPCC protocol estimating N$_2$O emissions, this study compared measured N$_2$O emissions in crop field with emissions estimated using the IPCC protocol.

2 Materials and Methods

2.1 Study Site

The study area consisted of three forest buffers, three warm-season grass filters, one cool-season grass filter, and one crop field, located in the Bear Creek watershed, Story County and Hamilton County, Iowa, United States (42° 11’ N, 93° 30’ W). The watershed drains 6,810 ha of farmland, with nearly 90 percent of these acres in a corn-soybean rotation. Located within the Des Moines Lobe subregion of the Western Corn Belt Plains ecoregion (Griffiths et al., 1994), the study area was once a tallgrass prairie ecosystem containing wet prairie marshes and pothole wetlands in topographically low areas and forests along higher order streams. An ongoing objective of the Bear Creek watershed project has been to establish riparian buffers along the upper portions of the watershed as willing landowners and cost-share are identified. This has provided a variety of sites of different streamside vegetation and buffer age to utilize in assessing the spatial and temporal variability of riparian buffers in reducing NPS pollution. Forest buffers and warm-season grass filters were previously under row-crop cultivation and a cool-season grass filters was previously under livestock grazing. Tree species included silver maple (Acer saccharinum L.), green ash (Fraxinus pennsylvanica Marsh.), black walnut (Juglans nigra L.), willow (Salix spp.), cottonwood hybrids (Populus spp.), red oak (Quercus rubra L.), bur oak (Quercus bicolor Willd). Shrub species included chokecherry (Prunus virginiana L.), Nanking cherry (Prunus tomentosa Thunb), wild plum (Prunus americana Marsh), red osier dogwood (Cornus stolonifera Michx), and ninebark (Physocarpus opulifolius Max.). Warm-season grasses included native grasses such as Indian grass (Sorghastrum nutans), Big Bluestem
(Andropogon gerardi), and Little Bluestem (Andropogon scoparius). Numerous forb species were present, including purple prairie clover (Petalostemum purpureum), black-eyed susan (Rudbeckia hirta), yellow coneflower (Ratibida pinnata), stiff goldenrod (Solidago rigida), prairie blazing star (Liatris pycnostachya), and others. The cool-season grass buffer was dominated by non-native forage grasses (Bromus inermis Leyss., Phleum pratense L. and Poa pratensis L). Details of the riparian buffer design, placement, and plant species are given in Schultz et al. (1995). The crop field was planted to a corn (Zea mays L.) and soybean (Glycine max L. Merr.) rotation, with corn the crop in 2006 and soybean in 2005 and 2007. Pelletized urea (133.4 kg N ha⁻¹) was applied to the crop fields (corn) in April 2006, and fall chisel plowing (15-20 cm depth) was conducted in Nov. 2006. Harvested crop yield was 3,934.1 kg dry matter (d.m.) ha⁻¹ (soybeans) in 2005 and 10,419.8 kg d.m. ha⁻¹ (corn) in 2006. The major soil association in the watershed is the Clarion- Webster- Nicolett association with minor areas of Clarion- Storden-Coland, and Canisteo-Okoboji-Nicolett (Dewitt, 1984). The areas used in this study are all located on the same soil mapping unit (Coland) and have similar topography.

2.2 Nitrous Oxide Flux and Environmental Factors Measurement
Nitrous oxide flux from soils under riparian forest buffers, warm-season and cool-season grass filters and crop fields were measured from October 2005 through December 2007. Five points were randomly selected in the areas for N₂O gas collection and soil sampling. Nitrous oxide flux measurements were conducted weekly to biweekly at mid-morning using static vented chambers (PVC, 30-cm diameter × 15 cm tall with vent). Chambers were equipped with a thermometer to measure air temperature within the chambers at the time of sampling. Ten mL of air was sampled from the chamber with a polypropylene syringe at 15 min intervals for 45 min and the gas stored in evacuated glass vials (6 mL, fit with butyl rubber stoppers) until analysis. Glass vials were prepared by alternately evacuating the vial headspace and flushing with helium to remove air (five cycles of evacuation and flushing). Nitrous oxide concentrations were determined with a gas chromatograph (Model GC17A; Shimadzu, Kyoto, Japan) equipped with a ⁶³Ni electron capture detector and a stainless steel column (0.3175-cm diam. × 74.54 cm long) packed with Porapak Q (80–100 mesh). Samples were introduced into the chromatograph using an autosampler described by Arnold et al. (2001). Nitrous oxide flux was computed from linear regression of the change in N₂O concentration with time (Holland et al., 1999). Our estimated minimum detectable flux was -0.175 g N₂O-N ha⁻¹ h⁻¹ (Parkin and Kaspar, 2006). Details of the chamber design and GC analysis are given in Parkin and Kaspar (2006).
Soil temperature and soil moisture near the chambers were measured simultaneously with N₂O gas collection at a 5-cm depth using a digital thermocouple and a digital soil moisture meter (HydroSense®, Campbell Scientific, Inc., Logan, Utah, USA). Air temperature was measured simultaneously with N₂O gas collection inside and outside the gas chamber. Continuous measurements of soil temperature, air temperature, and soil moisture at 5-cm soil depths were collected using a data logger (HOBO® Micro station data logger with sensors, Onset Computer Corporation, Bourne, MA USA) at one site per vegetation type. Daily rainfall and snow data were provided by a nearest meteorology station (Colo, IA, 42° 1’ N, 93° 19’ W) (Herzmann, 2004).

2.3 Diel Variation of N₂O Flux and Q₁₀ Relationship

In addition to regular measurements described above, the diel variation in N₂O flux was measured during 21-22 Nov. 2005, 18-19 May 2006, and 16-17 July 2007. For this assessment, three locations were randomly selected for flux measurements within each of the forest buffer, warm-season and cool-season grass filter, and the crop field. Nitrous oxide flux soil temperature was measured every three h for 24 h at all sites. To examine soil temperature sensitivity of N₂O flux during the three time diel variation measurements, we conducted nonlinear regression analyses using N₂O flux = a × Q₁₀

(soil temperature/10) (Q₁₀ represents activity increase of N₂O flux for every 10°C increase in soil temperature).

2.4 Cumulative N₂O Flux Calculations

Because fluxes were measured during the day time when soil temperatures were generally higher than the daily average soil temperatures, cumulative N₂O fluxes were calculated using soil-temperature-corrected daily flux measurements (Parkin and Kaspar, 2003, 2006). Temperature corrections were done with a Q₁₀ relationship, using the 5-cm soil temperature at the time each flux was measured, along with the daily average soil temperature for that day. The Q₁₀ factor used in these corrections was computed from diel N₂O fluxes measured using the equation:

\[
\text{Daily Average N}_2\text{O Flux} = \text{N}_2\text{O}_{\text{measured}} \times Q^{(\text{DAT}-\text{T})/10}
\]

(1)

where N₂O measured is measured N₂O flux at a specific hour, T is the soil temperature at the time the flux was measured, DAT is the daily average soil temperature, Q is the Q₁₀ factor, and Daily Average N₂O Flux is the resulting estimated daily average flux based on the single hourly measured N₂O flux.
Cumulative N₂O fluxes were calculated by linear interpolation and numerical integration of daily N₂O fluxes between sampling times.

2.5 Soil Sampling and Analysis
Six intact soil cores (5.3 cm diameter) were collected to a depth of 15 cm in each of the forest buffer, a warm-season grass filter, a cool-season grass filter, and an adjacent crop field in Oct. 2006 and Sept. 2007. A plastic sleeve liner was placed inside the metal core tube and the liner with the intact soil core removed from the tube and capped for transport to the laboratory. Soils samples were stored at 4°C until analysis. Soil pH was determined using a pH meter (Accument 910, Fisher Scientific Ltd., Pittsburgh, PA, USA) on a 1:1 diluted soil solution. Gravimetric moisture content was determined by oven drying a subsample at 105°C for 24 h and bulk density was determined by the core method (Grossman and Reinsch, 2002). For C and N analysis, soils were air dried at room temperature, sieved (2mm) and then gravimetric moisture content of the soils was determined. Total C (TC) and total N (TN) were measured using a Flash EA 2000 (ThermoFinnigan, Milan, Italy) direct combustion instrument. Soil inorganic N was extracted with 2M potassium chloride (KCl) and stored at 4°C until filtration (within 4 h of field collection of the soil cores) (Van Miegroet, 1995). Filtrates were frozen and stored until further analysis. Nitrate (NO₃⁻) and ammonium (NH₄⁺) contents were analyzed by colorimetric method (Mulvaney, 1996) with an auto analyzer (Quikchem 8000 FIA+, Lachat Instruments, Milwaukee, WI, USA).

2.6 Nitrogen inputs to sites
Nitrogen inputs as direct sources of N₂O were estimated in a warm-season and a cool-season grass filter, and a forest buffer and the adjacent crop field. Pelletized urea (133.4 kg N ha⁻¹) was applied in the crop fields (corn) in April 2006. Annual dry and wet deposition (ha⁻¹ year⁻¹) was 7.7 kg of N on the Iowa State University campus (19 km south of the study site) in Jan. 2003-Jan. 2004 (Anderson and Downing 2006) and the value was used for N input from deposition in 2006 and 2007. N inputs from soybeans residue was estimated from samples collected in five randomly located plots (50 cm × 50 cm) in the crop field after the harvest of soybeans in 2005. To estimate corn residues (Yᵣ) in 2006, we used harvest index (HI, 0.53 from Johnson et al. 2006) and harvested corn yields (Y₇ gr, 10,419.8 kg ha⁻¹ yr⁻¹) as following:

\[ Yᵣ = Y₇ gr \times (\frac{1}{HI} - 1) \] (2)
where \( Y_r \) is corn residues (kg ha\(^{-1}\)), and \( Y_{gr} \) is harvested corn grain and HI is harvest index (Johnson et al. 2006).

N inputs from dead roots in the crop field were calculated from the previous studies conducted in the same sites (Tufekcioglu et al., 1999 and 2003). Biological N fixation was not included as a direct source of N\(_2\)O because of the lack of evidence of significant emissions arising from the fixation process itself (Rochette and Janzen, 2005; IPCC, 2006).

N inputs from litter-fall within a forest buffer was estimated from monthly samples collected within five litter-fall collecting baskets (50 cm × 50 cm) placed at random locations within each forest buffer starting in Sept. 2005. In addition above-ground biomass was harvested within five randomly located plots (50 cm × 50 cm) in a warm-season and a cool-season grass filter, and a forest buffer in early Nov. of 2005 and 2006. Collected samples were dried (70°C, 48 h), weighed, and stored for TN analysis. Total N was measured by direct combustion using a Flash EA 2000 (ThermoFinnigan, Milan, Italy). N inputs from dead roots in a warm-season and a cool-season grass filter, and a forest buffer were calculated from the previous studies conducted in the same sites (Tufekcioglu et al., 1999 and 2003). In these same sites, Lee et al., (2003) estimated that 0.5 kg N transported from crop fields in run-off was retained in the riparian buffers per an event (> 20mm rainfall) and there were 13 events exceeding this threshold during 2006-2007. Based on these data, N input from runoff in riparian buffers was estimated in 2006 and 2007, respectively. Nitrogen input from groundwater discharged from crop fields to the riparian buffers was estimated by averaging lost N load in groundwater measured in wells under two of the riparian buffers (Kim, D.G., 2008. Transport and fate of nitrate and dissolved nitrous oxide in groundwater under riparian buffers adjacent to crop fields, in this dissertation).

2.7 Intergovernmental Panel on Climate Change (IPCC) N\(_2\)O Flux Calculations

The Intergovernmental Panel on Climate Change (IPCC) Tier 1 methodology (2006) separately estimates direct N\(_2\)O emission (i.e. directly from the soils to which N is added/released) and indirect N\(_2\)O emission resulting from offsite N movement (i.e. volatilization of NH\(_3\) and NO\(_X\), and leaching and runoff of N) from managed soils. The method then estimates direct N\(_2\)O emission from crop fields by multiplying N inputs by an emission factor. For this study, N inputs from synthetic fertilizer (FSN) and crop residues (FCR) estimated as described above were summed and multiplied by an emission factor (EF\(_1\)). The equation for estimating direct N\(_2\)O emission is:
\[ N_{2O}^{Direct} -N = N_{2O}^{N inputs} - (F_{SN} + F_{CR}) \times EF_1 \]  

where \( N_{2O}^{Direct} -N \) is annual direct \( N_2O \)–N emissions produced from managed soils (kg \( N_2O \)–N y\(^{-1}\)); \( N_{2O}^{N inputs} \) is annual direct \( N_2O \)–N emissions from N inputs to managed soils (kg \( N_2O \)–N y\(^{-1}\)); \( F_{SN} \) is annual amount of synthetic fertilizer N applied to soils (kg N y\(^{-1}\)); \( F_{CR} \) = amount of N in crop residues (above- and below-ground), including N-fixing crops returned to soils (kg N y\(^{-1}\)); and \( EF_1 \) is emission factor for \( N_2O \) emissions from N inputs (kg \( N_2O \)–N (kg N input)\(^{-1}\). The IPCC default value for \( EF_1 \) is 0.01. Details of calculating \( F_{CR} \) is given in IPCC (1996, 2006).

The IPCC (2006) Tier 1 estimates \( N_2O \) emission from atmospheric deposition of N volatilized from crop fields (indirect \( N_2O \) emission) using multiplying N inputs (\( F_{SN} \)) by a fraction factor (\( EF_4 \)) for volatilized N. Because synthetic fertilizer was an N input which can be volatilized in the crop fields, the equation for estimating \( N_2O \) emission is as following:

\[ N_{2O}^{(ATD)} -N = (F_{SN} \times Frac_{GASF}) \times EF_4 \]  

where \( N_{2O}^{(ATD)} -N \) is annual amount of \( N_2O \)–N produced from atmospheric deposition of N volatilized from managed soils (kg \( N_2O \)–N y\(^{-1}\)); \( F_{SN} \) is annual amount of synthetic fertilizer N applied to soils (kg N y\(^{-1}\)); \( Frac_{GASF} \) is fraction of synthetic fertilizer N that volatilizes as NH\(_3\) and NO\(_x\), (kg N volatilized (kg of N applied)\(^{-1}\), IPCC default value 0.10 for \( Frac_{GASF} \)); and \( EF_4 \) is emission factor for \( N_2O \) emissions from atmospheric deposition of N on soils and water surfaces, (kg N–N\(_2O\) (kg NH\(_3\)–N + NO\(_x\)–N volatilized)\(^{-1}\). The IPCC default value for \( EF_4 \) is 0.010.

**2.8 Statistical Analyses**

For analyzing normality of the distribution of the data, the Shapiro-Wilk normality test was performed. One way analysis of variance (ANOVA) was used to evaluate the differences in soil properties, and diel and seasonal \( N_2O \) flux by site. When the standard assumptions of normality were violated, non-parametric Kruskal-Wallis one way ANOVA on ranks was used. Differences were considered significant at the p < 0.05 level. To determine the relationship between soil properties and \( N_2O \) emission, correlation analysis using the GLM procedure was applied and NONLIN procedure was utilized for deriving the best fit of \( N_2O \) gas flux models developed by the relationships. These statistical analyses were conducted by SAS ver 8.1 (SAS institute, 1999).
3 Results

3.1 Soil Properties and Periods Dried and Frozen Soil
Soil texture was loam at all sites (Marquez et al., 2004). Soils in forest buffer and warm and cool-season grass filters had significantly (one way ANOVA) lower bulk density, higher pH, TC, TN, and NH₄⁺ than crop fields, while soil NO₃⁻ was not significantly different among the sites (Table 1).

Soils had longer dry (soil moisture < 15%) and frozen (soil temperature < 0°C) periods in 2007 than in 2006 (Fig. 4 (D) and (E)). From 15 June to 15 Aug. 2006 (93 d), soils were extremely dry (< 15%) within crop fields for 12 days, within forest buffers 0 days, and within grass filters 51 days. In comparison, from 15 June to 15 Aug. 2007 (93 d), soils were extremely dry (< 15%) within crop fields for 78 days, within forest buffers for 32 days, and within grass filters for 24 days. From January to March 2006 (90 days), soils were frozen (< 0°C) within crop fields for 47 days, within forest buffers for 17 days, and within grass filters for 49 days. In comparison, from January to March 2007 (90 days), soils were frozen (< 0°C) within crop fields for 82 days, within forest buffers for 46 days, and within grass filters for 62 days.

3.2 Diel Variation of N₂O Flux and Cumulative Diel N₂O Emission
Diel variation of N₂O flux and soil temperature in the crop field and riparian buffers are shown in Fig. 1. There was no significant difference in N₂O flux between the crop field and riparian buffers during the 21-22 Nov. 2005 sampling. There was also no significant correlation between soil temperature (5 cm depth, 2-5°C) and N₂O flux in crop fields and riparian buffers during this late fall period. In contrast, in both 18-19 May 2006, and 16-17 July 2007, N₂O flux in the crop field was significantly higher (7 to 13 times in May 2006, 12 to 18 times in July 2007) than riparian buffers during the 24 hour period (Figure 1). Significant correlations between soil temperature (5-cm depth) and N₂O flux were only found within crop fields during 18-19 May 2006 (Pearson coefficient \( r = 0.77 \) \( p = 0.02 \)) and 16-17 July 2007 (Pearson coefficient \( r = 0.48 \) \( p = 0.02 \)). The resulting Q₁₀ models (N₂O flux = a \( \times Q₁₀ (\text{soil temperature/10}) \)) and Q₁₀ factors were:

May 2006 (soil temperature 11-17°C):
N₂O flux (mg N₂O-N ha⁻¹ h⁻¹) = 28.9 \( \times Q₁₀ (\text{soil temperature/10}) \) (R² = 0.67)
Q₁₀ factor 12.78

July 2007 (soil temperature 23-27°C):
$N_2O$ flux (mg $N_2O$-N ha$^{-1}$ h$^{-1}$) = 411.0 × 2.27$^{(soil\ temperature/10)}$ ($R^2$ = 0.87)

Q$10$ factor 2.27

The cumulative diel $N_2O$ emission estimated indicate that $N_2O$ emissions from crop fields was 2 to 5-fold higher that riparian buffers during 21-22 Nov. 2005, 7 to11-fold greater during 18-19 May 2006, and 12 to14-fold higher during 16-7 July 2007. (Fig. 2)

3.3 Seasonal Variation of $N_2O$ Flux and Cumulative $N_2O$ Emission

When assessed over a season, $N_2O$ flux within cropped fields was significantly correlated with air temperature (Pearson coefficient $r = 0.38 \ p = 0.0001$), soil temperature (5 cm depth) ($r = 0.42 \ p < 0.0001$) and soil moisture (5 cm depth) ($r = 0.35 \ p = 0.005$). In all riparian buffers, $N_2O$ flux was significantly correlated with air temperature (Pearson coefficient $r = 0.1-0.5 \ p < 0.01$) and soil temperature (5 cm depth) ($r = 0.3-0.6 \ p < 0.0001$) during this same period. The average of observed $N_2O$ fluxes in crop fields (39.4 ± 7.1 kg $N_2O$-N ha$^{-1}$ d$^{-1}$, $n = 76$) was significantly higher than in riparian buffers (2.8-11.0 kg $N_2O$-N ha$^{-1}$ d$^{-1}$, $n = 72-93$) ($p < 0.0001$), but there were no differences among vegetation types in riparian buffers (Tukey’s Studentized Range Test) (Fig. 3).

Q$10$ factors used for correcting daily average $N_2O$ flux in crop fields were distinguished for three different field soil temperature ranges (< 10°C, 10-20°C, > 20°C) as follows:

(1) soil temperature < 10°C condition; no valid Q$10$ factor, Daily Average $N_2O$ Flux = $N_2O$ measured
(2) soil temperature 10-20°C condition; Q$10$ factor 12.78 was applied
(3) soil temperature > 20°C condition; Q$10$ factor 2.27 was applied

Because there was no significant effect of soil temperature on diel $N_2O$ flux (no valid Q$10$ factor) in forest buffer, and warm-season and cool-season grass filters, measured $N_2O$ flux was used as a diel average $N_2O$ flux.

In both 2006 and 2007, annual cumulative $N_2O$ emission was significantly greater in the crop field (7.2 kg $N_2O$-N ha$^{-1}$ in 2006 and 16.8 kg $N_2O$-N ha$^{-1}$ in 2007) than in forest buffers (1.8 kg $N_2O$-N ha$^{-1}$ in 2006 and 4.5 kg $N_2O$-N ha$^{-1}$ in 2007) and grass filters (1.8 kg $N_2O$-N ha$^{-1}$ in 2006 and 3.4 kg $N_2O$-N ha$^{-1}$ in 2007) (Table 2). The cumulative $N_2O$ emission was not significantly different from zero in forest buffers (95% confidence interval (CI): -1.1 to 8.3 kg $N_2O$-N ha$^{-1}$) and grass filters (95% CI: -
0.04 to 5.5 kg N$_2$O-N ha$^{-1}$) in 2007. The annual cumulative N$_2$O emission in the crop field, forest buffers, and grass filters in 2007 were 2 to 2.5-fold larger than 2006 (Table 2).

3.4 N$_2$O Peak Emission, N$_2$O Uptake, and their Contribution to Annual Emission

Several peak N$_2$O emissions contributed significantly to annual N$_2$O emissions in both the crop fields and riparian buffers (Fig. 4 (A) and (B)). In crop field 2006, a peak emission (8-fold increase but because of scale not clearly shown in Fig. 4 (A)) followed fertilizer application, and this emission contributed 12.9% of annual N$_2$O emission. Also, two large peak emissions following the thawing of frozen soil (13-fold increase, February) and rewetting of dry soil (37-fold increase, November) contributed 33.8% of the annual N$_2$O emission. In crop fields during 2007, a peak emission followed the thawing of frozen soil (28-fold increase, March) and three peak emissions followed rewetting of dry soil (5 to 70-fold increase, July to October). These four peak emissions contributed 70.3% of annual N$_2$O emission. All of the peak emissions returned to lower levels within a week. In warm-season and cool-season grass filters during 2006, two peak emissions (July and December) followed the rewetting of dry soil, and contributed 17.0% of annual N$_2$O emission. In grass filters during 2007, a peak emission after the thawing of frozen soil (March) and two peak emissions after rewetting of dry soil (June and December) contributed 31.1% of the annual N$_2$O emission. In forest buffers during 2006, a peak emission after the rewetting of dry soil (July) contributed 10.8% of annual N$_2$O emission, and in 2007, a peak emission after the thawing of frozen soil (March) and two peak emissions after rewetting of dry soil (June and December) contributed 70.5% of annual N$_2$O emission. Across all vegetation types, N$_2$O peak emissions were 3 to 10-fold greater than base-line levels after the thawing of frozen soil or rewetting of dry soil and the peaks returned to lower levels within a week. Soils within crop fields showed higher peak rates of N$_2$O emission than riparian buffers in both 2006 and 2007. As a result, the contribution of peak emissions to annual N$_2$O emission was larger in crop fields than in riparian buffers during both years, with the contribution higher in 2007 than 2006.

Negative N$_2$O fluxes (< -0.175 g N$_2$O-N ha$^{-1}$ h$^{-1}$ or -17.5 µg N$_2$O-N m$^{-2}$ h$^{-1}$, minimum detectable flux) were observed during all seasons within all vegetation types (Fig. 4 and 5). There was no significant difference among sites ($p = 0.99$) and the negative fluxes showed no significant relation to soil or air temperature or soil moisture ($p > 0.05$). The negative N$_2$O fluxes were most frequently observed (52%) in the 0 to 5°C soil temperature range, and observed maximum negative N$_2$O flux was -0.95 g N$_2$O-N ha$^{-1}$ h$^{-1}$ (-94.5 µg N$_2$O-N m$^{-2}$ hr$^{-1}$) (Fig. 5). Viewed on a cumulative basis, in 2006, less than
0.01% of produced N$_2$O was taken up in soils in crop fields, and riparian buffers, and 0.33 - 0.47% of produced N$_2$O was taken up in soils in crop fields and riparian buffers in 2007 (Table 2).

### 3.5 Nitrogen inputs and Ratio of N$_2$O Emission to N Inputs

In 2006, N fertilizer (133.4 kg N ha$^{-1}$) was applied in the crop field (corn) resulting in a larger N input to the crop field than riparian buffers. However, in 2007, N input to the crop field was less than riparian buffers, mainly due to no fertilizer application. Nitrogen input from crop residues and dead roots in the crop field was 82.1 and 92.2 kg N ha$^{-1}$ in 2006 and 2007, respectively (Tables 3 and 4). Annual dry and wet deposition was 7.7 kg N ha$^{-1}$ in the crop field and riparian buffers. Total N inputs in crop field was 323.1 kg N ha$^{-1}$ through 2006 and 2007.

Nitrogen input from litters and dead roots in riparian buffers was estimated at 83.6 and 69.0 kg N ha$^{-1}$ in 2006 and 2007, respectively (Table 3). N input from runoff in riparian buffers was estimated at 0.5 and 6.0 kg N ha$^{-1}$ in 2006 and 2007, respectively. Nitrogen input from groundwater discharged from crop fields to the riparian buffers was 36.1 kg N ha$^{-1}$ in 2006 and 2007. Total N inputs in riparian buffer was 246.7 kg N ha$^{-1}$ through 2006 and 2007 and this indicates N inputs in riparian buffers is 23.6% less than one of crop field.

The ratio of measured N$_2$O emission to N inputs to soils in crop field in 2006 (0.03) was 3-fold higher than the ratio of riparian buffers in 2006 (0.01). In 2007, the ratio of measured N$_2$O emission to N inputs to soils in crop field (0.17) was over 5-fold higher than to riparian buffers (0.03). Overall, the ratio of measured N$_2$O emission to N inputs to soils in crop field (0.07) was over 3-fold higher than the ratio of riparian buffers (0.02) (Table 4).

### 3.6 Comparison of measured N inputs and N$_2$O Emission with estimated values by IPCC Method

Estimated N input from crop residues and dead roots in the crop field by IPCC method (2006) was at 56.4 and 118.3 kg N ha$^{-1}$ in 2006 and 2007, respectively (Table 3). Compared to the measured N input values (Table 3), the IPCC method underestimated 31% in 2006 and overestimated 28% in 2007 in the crop field. In crop field, estimated N$_2$O emission (by IPCC 2006) was 2.0 kg N ha$^{-1}$ and 1.2 kg N ha$^{-1}$ in 2006 and 2007, respectively (Table 4). The ratio of measured N$_2$O emission to estimated N$_2$O emission in crop fields was 3.5 and 14.2 in 2006 and 2007, respectively; the overall ratio was 7.5
through 2006 and 2007 (Table 4) and this indicate IPCC method underestimate N$_2$O emission about 87% in crop field.

4 Discussion

4.1 N$_2$O Emissions and Emission Factors in Crop Field and Riparian Buffers

In our studies, measured N$_2$O emissions from soils within all perennial riparian vegetation types (1.8 kg N$_2$O-N ha$^{-1}$ in 2006 and 3.4-4.5 kg N$_2$O-N ha$^{-1}$ in 2007) were significantly lower than within the crop fields (7.2 kg N$_2$O-N ha$^{-1}$ in 2006 and 16.8 kg N$_2$O-N ha$^{-1}$ in 2007) and there were no observed differences in N$_2$O emissions among the different riparian buffer vegetation types (Fig. 2). Recent studies (Weller et al., 1994; Groffman et al., 1998; Dhondt et al., 2004) have measured 0.1-5.3 kg N ha$^{-1}$ yr$^{-1}$ of N$_2$O emissions from soils within riparian buffers, similar to observations within this study. In similar studies within the temperate regions, the mean N$_2$O emission (kg N$_2$O-N ha$^{-1}$ yr$^{-1}$) were measured within crop fields as 3.6 ± 0.5 kg N$_2$O-N ha$^{-1}$ yr$^{-1}$, within fertilizer-applied grassland as 8.0 ± 1.4 kg N$_2$O-N ha$^{-1}$ yr$^{-1}$, within grassland without fertilizer as 1.4 ± 0.4 kg N$_2$O-N ha$^{-1}$ yr$^{-1}$, and within forests as 0.7 ± 0.3 kg N$_2$O-N ha$^{-1}$ yr$^{-1}$ (Stehfest and Bouwman, 2006). Nitrous oxide emission from soils in unfertilized grass lands and forest within this study were similar to N$_2$O emission from soils within riparian buffers in 2006 in our studies. Interestingly, our observed N$_2$O emission from riparian buffers and crop fields in 2007 was 2-fold larger than 2006, and the values were larger than the average N$_2$O emission in temperate regions (Table 2). In addition, the emission factor (ratio of measured N$_2$O emission to N inputs, EF) of riparian buffers within our studies was 0.02, well below the EF observed within crop fields (0.07) (Table 4). Since N input to the riparian buffers was lower than in crop fields and the total area of riparian buffers within the watershed is very small (about 76 ha, 1 % of total area), the contribution to annual N$_2$O emission of the watershed is small (220 kg N yr$^{-1}$). Ryszkowski and Mander (2004) also observed that N$_2$O emission was higher in cultivated fields than buffer zones and concluded that the higher N$_2$O emission rates from cultivated fields can be explained by higher pH values which promote denitrification, as well as higher concentration of NO$_3^-$ providing substrate for denitrification. Teiter and Mander (2005) reported N$_2$O emissions from the riparian gray alder stand which varied from -0.4 to 58 μg N$_2$O-N m$^{-2}$ h$^{-1}$ and concluded that the global warming potential of the riparian alder forest from N$_2$O was relatively low. Our results, along with those of past studies, suggest that riparian buffers should not be considered a major source of N$_2$O greenhouse gas emission.
However, some studies (Walker et al., 2002; Clément et al., 2002; Hefting et al., 2003) have shown much higher N$_2$O emissions (16-24.5 kg N ha$^{-1}$ yr$^{-1}$) from soils within riparian buffers. Hefting et al. (2003) observed that N$_2$O emissions were significantly higher in the forested buffer system (20 kg N ha$^{-1}$ yr$^{-1}$) than within the grassland buffer zone (2-4 kg N ha$^{-1}$ yr$^{-1}$). They suggested that the higher rates of N$_2$O emissions within the forested buffer zone were associated with higher nitrate concentration in the groundwater, and concluded that N transformation by buffer zones with high nitrate loading resulted in a significant increase of greenhouse gas emission. This is consistent with the work of Ullah and Zinati (2006) who reported that prolonged N loading resulted in higher N$_2$O emissions in riparian forest soils compared to emission rates from non-exposed forest soils. Hefting et al. (2006) observed that N$_2$O emissions were significantly higher (12.4 mg N m$^{-2}$ d$^{-1}$) along the flow-path with high NO$_3^-$ removal when compared with the flow-path with low nitrate removal (2.58 mg N m$^{-2}$ d$^{-1}$), and concluded that locations with high NO$_3^-$ removal efficiency also contribute significantly to increased N$_2$O emission from riparian zones.

Considering all of these results, it is likely that N$_2$O emission from riparian buffers is highly site specific and may vary with site characteristics such as soil type, magnitude and speciation of N input, and hydrologic characteristics (Walker et al., 2002). In this study, low N inputs in riparian buffers is one of factors which caused less N$_2$O emission from riparian buffers than adjacent crop field and other studies (Walker et al., 2002; Clément et al., 2002; Hefting et al., 2003).

4.2 Peak N$_2$O Emission in Crop Field and Riparian Buffers

Peak emissions following rewetting dry soils and thawing frozen soils, and the contribution of peak emissions to annual N$_2$O emission will be discussed.

In crop fields 2007, even though N inputs were less than crop fields 2006, both annual N$_2$O emission and the EF were larger than crop fields 2006 (Table 4). This N$_2$O emission from cropped soils observed 2007 is also larger than average N$_2$O emission observed within in similar studies in temperate regions (Stehfest and Bouwman, 2006), and the emission factor (0.17) is also larger than other reports (Bouwman et al., 2002; Stehfest and Bouwman, 2006; Novoa and Tejeda, 2006) and the IPCC (2006)'s default value (0.01, uncertainty range 0.003-0.03). A similar pattern was also observed within soils within riparian buffers in 2007. These observations indicate that N$_2$O emission from soils within crop fields and riparian buffers were caused by additional factors beyond N input. One such factor may be the peak N$_2$O emissions observed within crop fields and riparian buffers...
during each year. There were several peak emissions following rewetting dry soils and thawing frozen soils in both sites (Fig. 4), and the peak emissions significantly contributed (30-70%) to the amount of annual N₂O emission.

Numerous studies have observed increased soil N₂O emission following wetting of dry soil in tropical areas (Nobre et al., 2001), semiarid areas (e.g. Wulf et al., 1999; Saetre and Stark, 2005), Mediterranean areas (Fierer and Schimel, 2002), dry tropical forests (García-Méndez et al. 1991; Davidson et al. 1993), savanna (Scholes et al., 1997), agricultural lands (e.g. Kusa et al., 2002; Mikha et al., 2005) and in laboratory studies (e.g. Appel, 1998; Hütsch et al., 1999). The increase rates ranged from 5-fold up to 1000-fold (e.g. Prieme and Christensen, 2001; Saetre and Stark, 2005) and magnitudes of the episodic N₂O emission increase varied depending on soil texture (Appel, 1998; Austin et al., 2004), soil water content (Appel, 1998), root responses (Cui and Caldwell, 1997), amount of added water (Ruser et al., 2006) and the characteristics and availability of substrates (e.g. Van Gestel et al., 1993; Schaeffer et al., 2003). Based on these studies and our results, it is apparent that even a single wetting event could account for a large proportion of annual emission rates of N₂O (e.g. Prieme and Christensen, 2001; Nobre et al., 2001).

Thawing frozen soils can also lead to increased N₂O emissions (e.g. Herrmann and Witter, 2002; Müller et al., 2003). Although though the duration of such elevated emission is limited mostly to a few days, they have been found to be an important source of the total annual emissions from agricultural land (e.g. Wagner-Riddle and Thurtell, 1998; Teepe et al., 2004), forests (e.g. Papen and Butterbach-Bahl, 1999; Teepe et al., 2000), and grasslands (Kammann et al., 1998). Matzner and Borken (2008) observed that the emissions of N₂O after thawing frozen soils were in some cases significantly larger from arable soils than from forest soils. In temperate region, observed N₂O emissions during freezing-thawing periods in spring may account for up to 70% of the total yearly N₂O losses (e.g. Teepe et al., 2000; Regina et al., 2004). Such events usually occurred when soil temperature is near 0°C (e.g. Chen et al., 1995; Müller et al., 2003). Matzner and Borken (2008) stated that the increase in N₂O emission after thawing increases with colder temperatures of frozen soil.

In our sites, we observed that crop field had N₂O peak events of greater magnitude than riparian buffers (Fig. 3). This result is similar to studies reviewed by Matzner and Borken (2008) in that the emissions of N₂O after thawing frozen soils were sometimes significantly larger from arable soils
than from forest soils. In our observations, soils within crop field had lower soil temperature in winter and higher soil temperature and longer dry periods in summer compared with soils within riparian buffers. This may explain peak emissions during periods of rewetting and thawing was higher in crop field than riparian buffers. Several explanations are plausible for the observed difference in soil temperature and soil moisture within crop field and riparian buffers. Vegetation within riparian buffers provides more shade, preventing high temperature increases during the summer months and provides insulation, preventing severe temperature decrease during winter months. In contrast, soils within crop field exposed to direct sunlight during the summer months and cold wind during the winter months. Riparian vegetation will also result in lower soil bulk density and higher organic matter (Marquez et al., 1999; Tufekcioglu et al., 2001; Bharati et al., 2002), resulting in higher soil moisture. In contrast, soils within crop fields exposed to direct sunlight, with higher bulk density, and lower soil organic matter will tend to hold less soil moisture compared with riparian buffer soils. We observed that the contribution of peak emissions to annual N$_2$O emission was larger in 2007 than 2006 in both crop fields and riparian buffers. The period soils were frozen during winter months and the period soil were dried during summer months were longer in 2007 compared with 2006, and this may explain the higher peak emissions during periods of rewetting and thawing observed in 2007. Since N$_2$O flux was not measured in crop field April to May 2006, and fertilizer was applied and rained at the period (Fig. 4 (A)), we might have missed peak N$_2$O flux in response to rainfall after fertilizer application (Parkin and Kaspar, 2006; Baggs et al., 2003; Sehy et al., 2003). Also since N$_2$O flux was not measured in crop field in August and September to October in crop field 2006 (Fig. 4 (A)), and there were several rewetting events during the periods, we might have missed peak emissions in the periods. These missed peak emissions also may cause less contribution of peak emissions to annual N$_2$O emission in crop field 2006.

4.3 Implications of Peak N$_2$O Emission in a Future Warmer Climate

It has been reported that there will be the increase of droughts associated with summer drying and intense precipitation in a future warmer climate (Easterling et al., 2000; Wang, 2005; Burke et al., 2006; Meehl et al., 2006; Rowell and Jones, 2006 Alexander et al., 2006; Sillmann and Roeckner, 2008). Also the increase in freeze and thaw frequency (Gu et al. 2008) and the increased impacts on the area and depth of permafrost regions (Lawrence and Slater, 2005; Yamaguchi et al., 2005) are predicted in a future warmer climate. The observed peak N$_2$O emissions during the thawing of frozen soils and rewetting of dry soils in crop fields 2007 have important implication for greenhouse gases emission in a changing climate. This should not be viewed as an unusual event. Rather, it represents
a consequence of predicted climate change on greenhouse gas emissions. Also the observed large
difference between measured N$_2$O emission and estimated N$_2$O emission by IPCC method (2006)
(87% underestimation by IPCC method) suggests that the current IPCC (2006) N$_2$O emission
estimation based on N input may underestimate emissions in the regions where soil rewetting and
thawing are common or potentially can be increased by future climate change. Additional studies are
warranted to clarify the relationships between antecedent soil moisture/soil temperature and the
frequency of dry-wet/frozen-thawed cycles and the subsequent effect on soil N$_2$O flux. The resulting
improvements in N$_2$O emission models would improve the accuracy of the N balance of terrestrial
ecosystems and predict the impact of anthropogenic climate change on such factors as 1) the increase
of summer drying in a future warmer climate with associated increased risk of drought (e.g.
Alexander et al., 2006; Sillmann and Roeckner, 2008) and 2) the increase in freeze and thaw
frequency (Gu et al. 2008) and impacts on the area and depth of permafrost regions (Lawrence and
Slater, 2005; Yamaguchi et al., 2005).

5 Conclusions
Annual N$_2$O emissions from soils within all riparian buffers (1.8 kg N$_2$O-N ha$^{-1}$ in 2006 and 3.4-4.5
kg N$_2$O-N ha$^{-1}$ in 2007) were significantly lower than within crop field (7.2 kg N$_2$O-N ha$^{-1}$ in 2006
and 16.8 kg N$_2$O-N ha$^{-1}$ in 2007) and no differences were observed among the different kinds of
riparian buffers. Over a 2-year period, the emission factor of soils in riparian buffers (0.02) was
about one third of the crop field (0.07) with N input lower within soils in riparian buffers than the
crop field. While N$_2$O peak emissions following the rewetting of dry soils and thawing of frozen
soils contributed significantly to annual N$_2$O emission in the crop field, soils in riparian buffers were
less sensitive to the events. These results suggest that N$_2$O emission from soils within riparian buffers
was less than one within adjacent crop field. In addition, this study also suggests 1) larger N$_2$O gas
emissions in rewetting dry soils and thawing frozen soils represent the consequence of future warm
climate on greenhouse gas emissions, 2) N input cannot always explain N$_2$O flux and 3) N input
based IPCC methodology for estimating N$_2$O emission may provide underestimation in the regions
where with frequent rewetting of dry soils and thawing of frozen soils. Additional studies
characterizing N$_2$O peak emissions and negative N$_2$O flux are needed to better understand N$_2$O flux
and N cycle within these systems, and to predict the impacts of future climate change.
References


Table 1. Soil properties (mean ± standard error) \((n = 6-9\) except bulk density \((n = 27)\)) of the sites. Soil samples (depth 0-15 cm) were collected in a forest buffer, a warm-season grass filter, a cool-season grass filter, and an adjacent crop field in Oct. 2006 and Sept. 2007.

<table>
<thead>
<tr>
<th>Site</th>
<th>Soil texture†</th>
<th>Bulk density (\text{mg m}^{-3})</th>
<th>pH</th>
<th>TC (\text{g kg}^{-1}) soil</th>
<th>TN (\text{mg N kg}^{-1}) soil</th>
<th>(\text{NH}_4)-N</th>
<th>(\text{NO}_3)-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crop field</td>
<td>Loam</td>
<td>1.67 ± 0.02a‡</td>
<td>5.9 ± 0.1c</td>
<td>22.8 ± 1.0c</td>
<td>1.9 ± 0.1c</td>
<td>1.7 ± 0.2b</td>
<td>1.0 ± 0.5a</td>
</tr>
<tr>
<td></td>
<td>Loam, Sandy</td>
<td>1.10 ± 0.03c</td>
<td>7.3 ± 0.1a</td>
<td>42.9 ± 3.2a</td>
<td>3.8 ± 0.3a</td>
<td>4.1 ± 0.6a</td>
<td>0.7 ± 0.2a</td>
</tr>
<tr>
<td>Warm-season grass filter</td>
<td>Loam</td>
<td>1.29 ± 0.05b</td>
<td>6.7 ± 0.2b</td>
<td>29.1 ± 2.7bc</td>
<td>2.6 ± 0.2bc</td>
<td>3.9 ± 0.5a</td>
<td>0.2 ± 0.1a</td>
</tr>
<tr>
<td>Cool-season grass filter</td>
<td>Loam</td>
<td>1.19 ± 0.04bc</td>
<td>6.9 ± 0.1ab</td>
<td>32.4 ± 1.6bc</td>
<td>2.9 ± 0.1b</td>
<td>4.3 ± 0.4a</td>
<td>0.9 ± 0.3a</td>
</tr>
</tbody>
</table>

† Marquez et al., 2004
‡ Values in the same column followed by a different letter are significantly different \((p < 0.05)\)
Table 2. Nitrous oxide production, uptake, uptake rate and total emission within soils in the crop field, forest buffers, and grass filters in 2006 and 2007.

<table>
<thead>
<tr>
<th>Site</th>
<th>2006 (kg N₂O-N ha⁻¹)</th>
<th>2007 (kg N₂O-N ha⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Production</td>
<td>Uptake</td>
</tr>
<tr>
<td>Crop fields</td>
<td>7.2</td>
<td>9.5×10⁻⁴</td>
</tr>
<tr>
<td>Forest buffers</td>
<td>1.8</td>
<td>7.8×10⁻⁴</td>
</tr>
<tr>
<td>Grass filters</td>
<td>1.8</td>
<td>-</td>
</tr>
</tbody>
</table>

† Uptake rate (%) = (Uptake/Production) ×100
Table 3. Nitrogen inputs from crop residues ($n = 5$), dead roots ($n = 5$), and plant litter ($n = 5$) of the previous year in crop field and riparian buffers in 2006 and 2007 and estimated N inputs (IPCC 2006) from crop residues and dead roots of the previous year in crop fields in 2006 and 2007.

<table>
<thead>
<tr>
<th>Site</th>
<th>Measured N (kg N ha$^{-1}$)</th>
<th>IPCC-Estimated N (kg N ha$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Crop residues</td>
<td>Dead roots§</td>
</tr>
<tr>
<td>Crop field (2006) †</td>
<td>53.1</td>
<td>29.0</td>
</tr>
<tr>
<td>Crop field (2007) ‡</td>
<td>61.2</td>
<td>31.0</td>
</tr>
<tr>
<td>Forest buffer (2006)</td>
<td>-</td>
<td>22.8</td>
</tr>
<tr>
<td>Warm season grass filter (2006)</td>
<td>-</td>
<td>15.1</td>
</tr>
<tr>
<td>Cool season grass filter (2006)</td>
<td>-</td>
<td>30.5</td>
</tr>
<tr>
<td>Average of riparian buffers (2006)</td>
<td>-</td>
<td>22.8</td>
</tr>
<tr>
<td>Forest buffer (2007)</td>
<td>-</td>
<td>22.8</td>
</tr>
<tr>
<td>Warm season grass filter (2007)</td>
<td>-</td>
<td>15.1</td>
</tr>
<tr>
<td>Cool season grass filter (2007)</td>
<td>-</td>
<td>30.5</td>
</tr>
<tr>
<td>Average of riparian buffers (2007)</td>
<td>-</td>
<td>22.8</td>
</tr>
</tbody>
</table>

† From soybeans
‡ From corn
§ N in dead roots (0 to 125-cm, fine and small root) was calculated from Tufekcioglu et al., 1999, 2000, and 2003.
§§ Used harvested annual dry matter (d.m.) yield: 3,934.1 kg d.m. ha$^{-1}$ (soybeans) in 2005 and 10,419.8 kg d.m. ha$^{-1}$ (corn) in 2006.
Table 4. Measured (Mea.) N inputs and N2O emission, ratio of measured (Mea.) N2O emission to N inputs, estimated (Est.) N2O emission by IPCC 2006 method, and the ratio of measured (Mea.) N2O emission to estimated (Est.) N2O emission in crop fields and riparian buffers. A unit of all N input and measured (Mea.) and estimated (Est.) N2O-N is kg N ha⁻¹.

<table>
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</thead>
<tbody>
<tr>
<td>2006</td>
<td>133.4</td>
<td>82.1</td>
<td>7.7</td>
<td>223.2</td>
<td>7.2</td>
<td>0.03</td>
<td>1.9</td>
<td>0.13</td>
<td>2.0</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>2007</td>
<td>-</td>
<td>92.2</td>
<td>7.7</td>
<td>99.9</td>
<td>16.8</td>
<td>0.17</td>
<td>1.2</td>
<td>-</td>
<td>1.2</td>
<td>14.2</td>
<td></td>
</tr>
<tr>
<td>2006-2007</td>
<td>133.4</td>
<td>174.3</td>
<td>15.4</td>
<td>323.1</td>
<td>24.0</td>
<td>0.07</td>
<td>3.1</td>
<td>0.13</td>
<td>3.2</td>
<td>7.5</td>
<td></td>
</tr>
</tbody>
</table>

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</tr>
</thead>
<tbody>
<tr>
<td>2006</td>
<td>83.6</td>
<td>0.5</td>
<td>36.1</td>
<td>7.7</td>
<td>127.9</td>
<td>1.8</td>
<td>0.01</td>
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<tr>
<td>2007</td>
<td>69.0</td>
<td>6.0</td>
<td>36.1</td>
<td>7.7</td>
<td>118.8</td>
<td>4.0</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>2006-2007</td>
<td>152.6</td>
<td>6.5</td>
<td>72.2</td>
<td>15.4</td>
<td>246.7</td>
<td>5.8</td>
<td>0.02</td>
<td></td>
</tr>
</tbody>
</table>

† Biological N fixation was not included as a direct source of N2O because of the lack of evidence of significant emissions arising from the fixation process itself (Rochette and Janzen, 2005; IPCC 2006).
‡ Pelletized urea (133.4 kg N ha⁻¹) was applied in the crop fields (corn) in April 2006.
§ From previous year
 §§ In an event (> 0.02 mm runoff), 0.5 kg N in run-off flowed from crop fields was retained in the riparian buffers (calculated from Lee et al. 2003). During 2006-2007, there were 13 events (> 20 mm rainfall) in the sites.
¶ Average of reduced N load in groundwater under two different riparian buffers (data from Kim et al. (2008))
# Annual dry and wet deposition (ha⁻¹ year⁻¹) was 7.7 kg of N on the Iowa State University campus (19 km south of the study site) in Jan. 2003-Jan. 2004 (Anderson and Downing, 2006).
↑↑ Annual amount of direct N₂O–N emissions produced from managed soils. Used harvested annual dry matter (d.m.) yield: 3,934.1 kg d.m. ha⁻¹ (soybeans) in 2005 and 10,419.8 kg d.m. ha⁻¹ (corn) in 2006.
↑↓ Annual amount of N₂O-N produced from atmospheric deposition of N volatilized from managed soils.
Figure 1. Diel variation of N₂O flux and soil temperature (5cm dept) in crop field, forest buffer, warm-season and cool-season grass filter in 21-22 November 2005 (A and B), 18-19 May 2006 (C and D) and 16-17 July 2007 (E and F). Observations are mean values with standard errors of the mean.
Figure 2. Cumulative diel N₂O emission in crop field, forest buffer, warm-season and cool-season grass filter in 21-22 November 2005, 18-19 May 2006 and 16-17 July 2007.
Figure 3. Daily \( \text{N}_2\text{O} \) flux from soils within crop fields and riparian buffers in 2006 and 2007 (\( n = 72-93 \)). I, II, and III indicate replicates. The lower boundary of the box indicates the 25th percentile, the line within the box marks the median, and the upper boundary of the box indicates the 75th percentile. Error bars indicate the 90th and 10th percentiles. Solid circles indicate outliers.
Figure 4. Nitrous oxide emissions (A, B), daily precipitation (C), daily soil moisture (D), and soil temperature (E) in forest buffers, grass filters, and adjacent crop field during 2006 and 2007.
Figure 5. Observed negative N$_2$O flux (< 0.175 g N$_2$O-N ha$^{-1}$ h$^{-1}$) and on-site soil temperature (5cm depth) in forest buffers, grass filters, and adjacent crop field during 2006 and 2007.
Transport and fate of nitrate and dissolved nitrous oxide in groundwater under riparian buffers adjacent to crop fields

A paper to be submitted to Journal of Environmental Quality

Richard C. Schultz, Thomas M. Isenhart, Timothy B Parkin, James R. Raich, Thomas E. Loynachan

Abstract

Denitrification is recognized as the major mechanism for decreasing nitrate (NO$_3^-$) in groundwater under riparian buffers and thus diminishing non-point source (NPS) pollution of surface water bodies subject to high nitrogen (N) loads. However, increasing denitrification in riparian buffers may trade the problem of NPS pollution of surface waters for increased nitrous oxide (N$_2$O) greenhouse gas emissions because N$_2$O produced in the denitrification process can be dissolved in groundwater and is eventually emitted into the air when groundwater flows into a stream or a river. It is therefore important to quantify dissolved N$_2$O inputs to streams from riparian buffers. We measured concentrations of NO$_3^-$; chloride (Cl$^-$); pH; and dissolved N$_2$O, oxygen (DO), and organic carbon (DOC) in groundwater under a multi-species riparian buffer, a cool-season grass filter, and the adjacent crop field located in the Bear Creek watershed in central Iowa, U.S.A. We also measured depth to the groundwater and the Creek water stage. In both the multi-species riparian buffer and the cool-season grass filter, NO$_3^-$ concentrations in groundwater were significantly decreased compared to those in the crop field, by 48-59%. Total N loading to Bear Creek from the crop fields was estimated to be 14 to 58 kg ha$^{-1}$ yr$^{-1}$ lower as a result of the riparian buffers, consistent with their design objective of enhancing surface-water quality. However, dissolved N$_2$O concentrations in groundwater did not differ among locations (6-14 µg L$^{-1}$), nor did DO (2.6-5.0 mg L$^{-1}$) or DOC (0.7-1.9 mg L$^{-1}$) concentrations. These results suggest that the riparian buffers decreased NO$_3^-$ concentrations in near-surface groundwater, without increasing N$_2$O losses, and new emission factor (dissolved N$_2$O-N/NO$_3^-$-N ratio, 0.0041) for groundwater leached from riparian buffers was proposed. Based on these results, we suggest a modified IPCC method for estimating indirect N$_2$O emissions in the riparian buffers of existing agroecosystems. The modified method demonstrates how riparian buffers can be accounted for in the IPCC's inventory method.
1 Introduction

Important functions of riparian buffers related to non-point source (NPS) pollution control include filtering and retaining sediment and immobilizing, storing, and transforming chemical inputs from uplands (Schultz et al., 2000). Many studies have shown that riparian buffers, depending on their widths, vegetation composition, inflow concentrations and hydrogeologic conditions, can reduce sediment in runoff by 70 to 95% (e.g. Lee et al., 2000 and 2003), N by 5 to > 90 % (e.g. Dukes et al., 2002; Mayer 2007), and P by 27 to 97% (e.g. Uusi-Kamppa et al., 2000; Kuusemets et al., 2001). Denitrification is recognized as a major mechanism for decreasing nitrate (NO₃⁻) in riparian buffers (e.g. Groffman and Hanson, 1997; Watts et al., 2000). Denitrification is controlled by the availability of oxygen (O₂), NO₃⁻, and carbon (C) (e.g. Hill et al., 2000; Hill and Cardaci, 2004), and the presence of healthy populations of denitrifying organisms. Riparian buffers, which provide a carbon-rich environment, can increase denitrification directly, by enhancing the availability of C to denitrifiers, and indirectly, through increasing the consumption of O₂ by heterotrophic microbes (e.g. Groffman, 1994; Hill, 1996).

Nitrous oxide is a potent greenhouse gas (Wang et al., 1976) with a global warming potential that is 298 times that of carbon dioxide (CO₂) and 25 times that of methane (CH₄) over a 100-year time horizon (Forster et al., 2007). In the groundwater under agricultural fields receiving N applications, or in riparian zones receiving groundwater or runoff water, excessive NO₃⁻ may be transformed to N₂O through the process of denitrification (IPCC, 2006). The Intergovernmental Panel on Climate Change (IPCC, 2006) defined this process as indirect N₂O emissions, in contrast to direct N₂O emissions which describe N₂O emission from N sources such as fertilizers and crop residues in managed soils. Since numerous studies have recognized NO₃⁻ decrease by increased denitrification in the riparian buffers (e.g. Groffman and Hanson, 1997; Watts et al., 2000), it has recently been hypothesized that the increased denitrification in riparian buffers may be trading a decrease in NO₃⁻ transport to surface waters for increased N₂O emissions (Groffman et al. 1998 and 2000), that is, trading water pollution for atmospheric pollution. In contrast, because riparian buffers efficiently decrease NO₃⁻, a source of indirect N₂O emissions, riparian buffers could provide an opportunity to decrease indirect N₂O emissions if we can develop reliable strategies for decreasing N₂O production during denitrification (Groffman, 2000). Studies supporting this proposition include Weller et al. (1994), who reported that N₂O production in a riparian forest was not an important fate of NO₃⁻ removed from cropland discharges. Blicher-Mathiesen and Hoffman (1999) reported that denitrification in a riparian soil can act as a sink for dissolved N₂O in the inflowing groundwater as
Numerous studies have emphasized the effect of vegetation on denitrification in riparian buffers. However, there are some conflicting results regarding the relationship between vegetation type and denitrification rate in riparian buffers. While some studies (e.g. Hubbard and Lowrance, 1997; Verchot et al., 1997) found higher groundwater nitrate removal or denitrification rates in forested riparian zones, other studies (e.g. Groffman et al., 1991; Schnabel et al. 1996) found higher removal in grass-dominated riparian sites. Some studies (e.g. Sabater et al. 2003; Hefting et al. 2003; Dhondt et al. 2004) also found no significant difference in groundwater nitrate removal or denitrification rate between forested and grass dominated riparian sites. Such results suggest that there is a need to evaluate how different types of vegetation affect dissolved N\textsubscript{2}O in groundwater under riparian buffers.

The overarching objective of this study was to quantify dissolved N\textsubscript{2}O in groundwater moving from intensively row-cropped fields through riparian buffers of two vegetation types and to relate these patterns to observed patterns of groundwater NO\textsubscript{3}\textsuperscript{-} concentration. The study was intended to address whether groundwater exported to the stream from riparian buffers is a significant source of N\textsubscript{2}O emissions and to determine whether these emissions are affected by differing riparian vegetation.

2 Material and methods

2.1 Study site

The study was conducted on two sites within the Bear Creek watershed, Story County and Hamilton County, Iowa, United States of America (42° 11’ N, 93° 30’ W). Bear Creek is a third order stream with typical discharges of 0.3 to 1.4 m\textsuperscript{3} sec\textsuperscript{-1}. The watershed drains 6,810 ha of farmland, with nearly 90 percent of these acres in maize-soybean rotation. The study area was once a tallgrass prairie ecosystem containing wet prairie marshes and pothole wetlands in topographically low areas and forests along higher order streams. An ongoing objective of the Bear Creek watershed project has been to establish riparian buffers along the upper portions of the watershed as willing landowners and cost-share opportunities are identified. This has provided a variety of sites of different streamside vegetation and buffer age to utilize in assessing the spatial and temporal variability of riparian buffers in reducing NPS pollution. This study was conducted in two riparian buffers established in 1990 on opposite sides of Bear Creek. One site is an established cool-season grass filter (length 35 m × width
20 m) along the north side of the creek. The dominant grass species in this cool-season grass filter are smooth brome (*Bromus inermis* Leysser), timothy (*Phleum pretense* L.), and Kentucky bluegrass (*Poa pratensis* L.). The other site is a multi-species riparian buffer (length 35 m × width 20 m) which consists of a forested buffer and a warm season grass filter along the south side of the creek. Hybrid poplars (*Populus X euroamericana* ‘Eugenei’), ninebark (*Physocarpus opulifolius* (L.) Maxim) and redosier dogwood (*Cornus sericea* L.) were planted in the forest buffer. Switchgrass (*Panicum virgatum* L.), a native warm season grass, was planted as a grass filter adjacent to the crop field. Details of the riparian buffer design, placement, and plant species are given in Schultz et al. (1995). The upslope crop fields are farmed in an annual maize-soybean rotation. Maize (*Zea mays* L.) usually was planted in early May and harvested at the end of October. The soybean crop (*Glycine max* (L.) Merr.) was planted in mid-May and harvested in mid-September. The study sites are on Coland soil (fine-loamy, mixed, mesic Cumulic Haplaquoll) which is well drained to poorly drained and formed from till or local alluvium and colluvium derived from till (DeWitt, 1984). The sites are underlined by alluvium of the DeForest Formation, which consists of an about 2 m thick sand aquifer overlain by 1.5 m of loam (Spear 2003). At each site, 12 monitoring wells were installed in three transects from the crop field edge to the creek along proposed groundwater flow paths, and a stilling well was installed to record the surface water elevation of the creek (Simpkins et al. 2002). In this study, at each site, 3 monitoring wells at the crop field edge of the buffers, and 3 monitoring wells and a stilling well at the creek edge of the buffers were used (Fig. 1).

### 2.2 Groundwater sampling and monitoring

Groundwater sampling and monitoring was conducted monthly in monitoring wells and stilling wells from November 2005 to April 2008 (Fig. 1). To determine water table elevation prior to sampling, hydraulic head was measured with an electronic water level tape. For measurement of NO$_3^-$ and Cl$^-$ groundwater was collected in polyethylene bottles using a peristaltic pump. For measurement of DOC, groundwater was collected in glass bottles. Samples for NO$_3^-$ and DOC were acidified with 20 µL of concentrated H$_2$SO$_4$. Dissolved oxygen was determined using a portable photometer (Oxygen 2 SAM and Vacu-vials®, CHEMetrics, Virginia, USA) with a detection limit of 0.1 mg L$^{-1}$, and pH was measured in the field using a portable pH meter (pH tester 2, Eutech Instruments, Singapore) with a detection limit of 0.1 pH. Groundwater samples for measuring dissolved N$_2$O were obtained inline by filling a 10 ml syringe connected to a peristaltic pump and injecting the sample into 20 ml evacuated glass vials containing 0.3 mL 80% ZnCl for preserving dissolved N$_2$O (Blicher-Mathiesen and Hoffman 1999). Samples were packed in ice in the field and refrigerated (4℃) in the laboratory.
Additional data for this study included monthly groundwater samples collected from 1997 to 1999 in the same monitoring and stilling wells at each site (Spear 2003).

2.3 Chemical analysis
Samples for NO$_3^-$ were analyzed utilizing UV-second derivative spectroscopy (Crumpton et al. 1992) with a detection limit of 0.1 mg L$^{-1}$. Chloride samples were analyzed with an ion specific electrode (Orion 9617BNWP, Thermo Scientific, Massachusetts, USA) with a detection limit of 0.1 mg L$^{-1}$. Dissolved organic carbon samples were filtered through a 0.45 µm filter and analyzed by persulfate oxidation on a carbon analyzer (Phoenix 8000, Tekmar-Dohrmann™, Ohio, USA) with a detection limit of 0.1 mg L$^{-1}$. Vials storing groundwater samples of dissolved N$_2$O were warmed to room temperature (21-22°C), shaken, and brought to atmospheric pressure with He. A gas chromatograph (Model GC17A, Shimadzu, Kyoto, Japan) equipped with a $^{63}$Ni electron capture detector and a stainless steel column (0.3175 cm diameter × 74.54 cm long) with Porapak Q (80–100 mesh) was used to analyze headspace gas concentrations (Parkin and Kaspar, 2006). Dissolved gas concentrations were determined using the Bunsen coefficient relationship (Tiedje, 1994) and estimated detection limit was 0.6 µg L$^{-1}$ (Spear 2003).

2.4 Mass flux calculations
Mass flux of NO$_3^-$ in groundwater at the crop field edge of the buffers and groundwater at the creek edge of the buffers was estimated using the equation:

$$F_x = v_x n_e \text{Conc}$$  \hspace{1cm} (1)

where,

- $F_x$ is mass flux (g day$^{-1}$ m$^{-2}$),
- $v_x$ is average linear velocity (m day$^{-1}$),
- $n_e$ is effective porosity (unitless, 0.15 from Spear 2003),
- Conc is concentration in g m$^{-3}$ or mg L$^{-1}$ (Fetter 1999).

Mass flux was then multiplied by cross sectional area of the aquifer adjacent to Bear Creek to estimate total load of NO$_3^-$ (g d$^{-1}$) to riparian buffers and Bear Creek. The cross sectional area was determined by creating a hypothetical rectangle (35 m wide × 2 m height) representing the aquifer adjacent to Bear Creek.
2.5 Ratio of N inputs to runoff and N leaching in crop fields (Frac_{LEACH-(H)}) and the ratio of dissolved N$_2$O to nitrate in groundwater (Emission factor, EF$_{5g}$)

The IPCC (2006) estimates indirect N$_2$O emission from N leaching in agro-ecosystems multiplying N inputs by fraction of all N lost to leaching and runoff (Frac_{LEACH-(H)}) and emission factor for N$_2$O emissions from N leaching and runoff (EF$_5$). The EF$_5$ consists of emission factors for groundwater (EF$_{5g}$), rivers (EF$_{5r}$), and estuaries (EF$_{5e}$).

\[ N_2O_{(L)-N} = N_{inputs} \times Frac_{LEACH-(H)} \times EF_5 \]  \hspace{1cm} (2)

where,

- \(N_2O_{(L)-N}\) = annual amount of N$_2$O–N produced from leaching and runoff of N additions to managed soils in regions where leaching/runoff occurs, kg N$_2$O–N yr$^{-1}$
- \(N_{inputs}\) = annual amount of synthetic fertilizer N, animal manure, compost, sewage sludge and other organic N additions, and crop residues applied/returned to soils in regions where leaching/runoff occurs, kg N yr$^{-1}$
- \(Frac_{LEACH-(H)}\) = fraction of all N added to mineralized in managed soils in regions where leaching/runoff occurs that is lost through leaching and runoff, 0.30, kg N (kg of N additions)$^{-1}$
- \(EF_5\) = emission factor for N$_2$O emissions from N leaching and runoff, 0.0075, kg N$_2$O–N (kg N leached and runoff)$^{-1}$

\[ EF_5 = EF_{5g} (0.0025) + EF_{5r} (0.0025) + EF_{5e} (0.0025) \] \hspace{1cm} (3)

\(EF_{5g}, EF_{5r},\) and \(EF_{5e}\) are emission factors for groundwater, in rivers, and in estuaries, respectively.

In this study, the Frac_{LEACH-(H)} was estimated by the ratio of N inputs to runoff and leaching N in crop fields. Nitrogen inputs included the annual amount of synthetic fertilizer N applied to crop fields (FSN) and N inputs from crop residue (FCR). Leaching N was estimated by N in groundwater discharged from crop fields, and runoff N was estimated in Kim et al., (2008, Emission of the greenhouse gas nitrous oxide from riparian forest buffers, warm-season and cool-season grass filters, and crop fields, in this dissertation). In this study, the EF$_{5g}$ was estimated by the mean of the ratio of dissolved N$_2$O concentration to NO$_3$– concentration (dissolved N$_2$O-N/NO$_3$-N ratio) in groundwater discharged from crop fields, a multi-species riparian buffer and a cool-season grass filter.
2.6 Statistical analysis

The Shapiro-Wilk normality test was performed to determine the normal distribution of the data. A two sample t-test was used to evaluate differences in concentrations of NO₃⁻; Cl⁻; pH; and dissolved N₂O, DO, and DOC in groundwater at the crop field edge of the buffers and groundwater at the creek edge of the buffers. When the standard assumption of normality and equal variance were violated, the Mann-Whitney rank sum test was used. One way ANOVA was used to evaluate the difference in groundwater tables and creek water stage (need to be consistent with the first mention of this variable). GLM was utilized to determine correlations between groundwater water quality parameters and dissolved N₂O. Statistical analyses were conducted by SAS ver 8.1 (SAS institute, 1999).

3 Results

3.1 Groundwater and creek elevations

In the cool-season grass filter, the groundwater elevation at the crop field edge of the buffer and the groundwater elevation at the creek edge of the buffer were significantly different \((p < 0.0001) \) from each other in both 1997-1999 and 2005-2008. The groundwater elevation at the crop field edge of the buffer \((318.16 \pm 0.03 \text{ masl}, n = 69)\) was significantly higher than at the stream edge of buffer \((317.43 \pm 0.02 \text{ masl}, n = 74)\) for the entire period (Tukey's Studentized Range Test), indicating general groundwater flow from the crop fields to Bear Creek. However, the groundwater elevation at the creek edge of the buffer \((317.43 \pm 0.02 \text{ masl}, n = 74)\) and creek elevation \((317.35 \pm 0.04 \text{ masl}, n = 66)\) were not significantly different (Tukey's Studentized Range Test) during the entire period. In summer 1998, early spring 2006, and summer 2007, the groundwater elevation adjacent to the creek and the creek elevation were very similar. In December 2007, the groundwater elevation adjacent to creek was lower than the creek elevation, indicating the possibility for creek water movement into the riparian aquifer.

Within the multi-species riparian buffer, the groundwater elevation within all wells and Bear Creek elevation were significantly different in both the 1997-1998 and 2005-2008 periods \((p < 0.0001)\), again indicating general groundwater flow from the crop fields to Bear Creek under the buffer. In contrast the cool-season grass filter, the groundwater elevation at the creek edge of the buffer \((317.60 \pm 0.03 \text{ masl}, n = 73)\) was significantly higher than the creek elevation \((317.34 \pm 0.04 \text{ masl}, n = 58)\) (Tukey's Studentized Range Test) during the entire period, indicating that there was no movement of the creek water into the riparian aquifer.
3.2 Nitrate concentration, flux, and reduction rate

In the cool-season grass filter, NO$_3^-$ concentration in groundwater adjacent to crop field showed a repeated seasonal trend with the concentration highest in winters and lowest in summers (Fig. 2). However, NO$_3^-$ concentration in groundwater adjacent to the creek did not show any seasonal trend (Fig. 2). Average NO$_3^-$ concentrations were 9.5 mg L$^{-1}$ and 4.9 mg L$^{-1}$ in groundwater wells adjacent to crop fields and groundwater wells adjacent to creek, respectively, during 1997-1999 (Fig. 3), and 9 mg L$^{-1}$ and 3.3 mg L$^{-1}$, respectively, during 2005-2008 (Fig. 4). In this cool-season grass filter site, NO$_3^-$ concentrations in groundwater adjacent to crop fields were significantly higher than those adjacent to the creek during both 1997-1999 (Mann-Whitney rank sum test $p < 0.0001$) and 2005-2008 (Mann-Whitney rank sum test $p < 0.0001$). The average NO$_3^-$ concentration in groundwater within the cool-season grass filter decreased by 48.4 % in 1997-1999 and 58.8 % in 2005-2008 when comparing wells nearest the steam with those nearest the crop field.

In the multi-species riparian buffer, NO$_3^-$ concentration in groundwater adjacent to crop field showed a repeated seasonal trend with the concentration highest in winters and lowest in summers (Fig. 2). However, NO$_3^-$ concentration in groundwater adjacent to the creek did not show any seasonal trend (Fig. 2). Average NO$_3^-$ concentrations were 4.9 mg L$^{-1}$ and 5.0 mg L$^{-1}$ in groundwater wells adjacent to crop fields and in groundwater wells adjacent to the creek, respectively, during 1997-1999 (Fig. 3), and 4.0 mg L$^{-1}$ and 2.0 mg L$^{-1}$ respectively, during 2005-2008 (Fig. 4). The differences in concentrations during 1997-1999 were not significant (Mann-Whitney rank sum test $p = 0.91$) (Fig. 3) but, within this same buffer, average NO$_3^-$ concentration in groundwater decreased by 49.5 % in 2005-2008 across the riparian buffer (Mann-Whitney rank sum test $p < 0.0001$) (Fig. 4).

In 2005-2008, the average N load (kg yr$^{-1}$) was 58.2% and 50.0% lower in groundwater nearest the creek compared to near the crop field edge in the cool-season grass filter and the multi-species riparian buffer, respectively. Actual reduction in load was 57.9 kg N ha$^{-1}$ yr$^{-1}$ and 14.2 kg N ha$^{-1}$ yr$^{-1}$ in the cool-season grass filter and the multi-species riparian buffer, respectively (Table 1).

3.3 Chloride concentration and the ratio of nitrate to chloride

Average Cl$^-$ concentrations in groundwater ranged between 13.2 and 13.4 mg L$^{-1}$ within a cool-season grass filters during 1997-1999 and between 20.6 and 20.9 mg L$^{-1}$ within the multi-species riparian buffer during the same period (Fig. 3). During 2005-2008, average Cl$^-$ concentrations in groundwater
ranged between 18.2 and 20.6 mg L\(^{-1}\) within grass filters and between 18.2 and 20.8 mg L\(^{-1}\) within the multi-species riparian buffer (Fig. 4). None of these differences in Cl\(^-\) concentrations were significant.

In the cool-season grass filter, the average NO\(_3^-\)/Cl\(^-\) ratio within groundwater adjacent to crop fields was significantly higher than adjacent to the creek in both 1997-1999 (Mann-Whitney rank sum test \(p < 0.0001\)) and 2005-2008 (Mann-Whitney rank sum test \(p < 0.0001\)) (Fig. 3, 4 and 5). Within groundwater under the multi-species riparian buffer, there was no significant difference in the average NO\(_3^-\)/Cl\(^-\) ratio of groundwater adjacent to crop fields and adjacent to the creek in 1997-1999 (Mann-Whitney rank sum test \(p = 0.41\)) (Fig. 3 and 5). However, within this same system, the average NO\(_3^-\)/Cl\(^-\) ratio within groundwater adjacent to crop fields was significantly higher than that adjacent to the creek in 2005-2008 (Mann-Whitney rank sum test \(p < 0.0001\)) (Fig. 4 and 5).

### 3.4 Dissolved N\(_2\)O

Dissolved N\(_2\)O concentration in groundwater under both riparian buffers showed a repeated seasonal trend, with the concentration highest in winters and lowest in summers (Fig. 6). Average dissolved N\(_2\)O concentrations in groundwater ranged between 6.8 and 7.8 µg L\(^{-1}\) within the cool-season grass filter during 1997-1999 and between 6.0 and 6.1 µg L\(^{-1}\) within the multi-species riparian buffer during the same period (Fig. 3). During 2005-2008, average dissolved N\(_2\)O concentrations in groundwater ranged between 11.6 and 14.4 µg L\(^{-1}\) within the cool-season grass filters and between 9.0 and 9.1 µg L\(^{-1}\) within the multi-species riparian buffer (Fig. 4). Within groundwater under the cool-season grass filter, there was no significant difference in dissolved N\(_2\)O concentrations in wells adjacent to the crop fields and adjacent to the creek during both 1997-1999 (Mann-Whitney rank sum test \(p = 0.49\)) and 2005-2008 (Mann-Whitney rank sum test \(p = 0.29\)). This pattern was repeated in groundwater under the multi-species riparian buffer, with no significant difference in dissolved N\(_2\)O concentrations in groundwater adjacent to crop fields and the creek during both 1997-1999 (Mann-Whitney rank sum test \(p = 0.96\)) and 2005-2008 (Mann-Whitney rank sum test \(p = 0.93\)).

### 3.5 Dissolved oxygen, dissolved organic carbon, pH, and water temperature

Dissolved oxygen concentration in groundwater under the grass filter adjacent to crop fields (5.0 ± 0.3 mg L\(^{-1}\)) was significantly higher than adjacent to the creek (2.6 ± 0.3 mg L\(^{-1}\)) in 1997-1999 (two sample t-test \(p < 0.0001\)) (Fig. 3 and 4). However there was no significant difference within this same system in DO concentration in groundwater adjacent to crop fields and adjacent to the creek (2.7-3.3 mg L\(^{-1}\)) in 2005-2008 (two sample t-test \(p = 0.34\)). Within the multi-species riparian buffer,
there was no significant difference in DO concentration in groundwater adjacent to crop fields and adjacent to the creek during both 1997-1999 (2.8-3.4 mg L⁻¹) (two sample t-test \( p = 0.29 \)) and 2005-2008 (2.7-3.3 mg L⁻¹) (two sample t-test \( p = 0.24 \)).

In both buffer sites, the average dissolved organic carbon (DOC) concentration (0.6-1.1 mg L⁻¹) within the groundwater was not significantly different adjacent to crop fields and adjacent to the creek during either 1997-1999 (two sample t-test \( p > 0.1 \)) or 2005-2008 (two sample t-test \( p > 0.1 \)) (Fig. 3 and 4). Similarly, there was no significant difference in groundwater temperature under either buffer type within wells adjacent to crop fields and adjacent to the creek during either 1997-1999 (two sample t-test \( p > 0.1 \)) or 2005-2008 (two sample t-test \( p > 0.1 \)).

Within the grass filter, pH in groundwater adjacent to crop fields (7.5) was significantly higher than adjacent to the creek in 1997-1999 (7.3) (two sample t-test \( p = 0.03 \)); however, there was no significant differences in 2005-2008 (7.4-7.5) (two sample t-test \( p = 0.30 \)). Within the multi-species riparian buffer, there was no significant difference in pH in groundwater adjacent to crop fields and adjacent to the creek during either 1997-1999 (7.5) (two sample t-test \( p = 0.70 \)) or 2005-2008 (7.4) (two sample t-test \( p = 0.62 \)).

### 3.6 Relation between dissolved N₂O concentrations and water characteristics

There was a significant negative relationship between water temperature and dissolved N₂O concentration in groundwater adjacent to both crop fields and the creek within the grass filter (Pearson coefficient \( r = -0.31, p = 0.003 \)) and the multi-species riparian buffer (Pearson coefficient \( r = -0.39, p = 0.006 \), in respect). There was also a significant relationship between DO and dissolved N₂O concentration in groundwater adjacent to the creek within the multi-species riparian buffer (Pearson coefficient \( r = 0.30, p = 0.048 \)). Nitrate concentration and pH did not show a significant correlation with dissolved N₂O concentrations in either the groundwater adjacent to crop fields or the creek (all \( p > 0.05 \)).

### 3.7 Ratio of N inputs to runoff and leaching N in crop fields (Frac̅ LEACH-[H]) and ratio of dissolve N₂O to nitrate in groundwater (EF₅g)

The annual amount of synthetic fertilizer N applied to crop fields (FSN) and N inputs from crop residue (FCR) in the Bear Creek watershed were 454,220.3 kg N yr⁻¹ and 354,455.3 kg N yr⁻¹, respectively in 2005-2008 (Table 2). Leaching (TL) and run-off (TR) N from crop fields in Bear
Creek watershed were 14,451.5 NO3-N kg yr⁻¹ (Table 2) and 35,615.8 kg N yr⁻¹ (Table 3), respectively.

The calculated ratio of N inputs (F_soil + F_animal, 1,047,877.4 kg N yr⁻¹) to runoff and leaching N (TR+TL, 50,067.3 kg N yr⁻¹), Frac_LEACH_IN, is 0.05 (Table 3).

The mean of the ratio of dissolved N₂O concentration to NO₃⁻ concentration (dissolved N₂O-N/NO₃-N ratio) in groundwater discharged from crop fields in this study (n = 99) is 0.0022 (95% C.I. 0.0013-0.0031) (Fig. 7 (A)). The mean of dissolved N₂O/NO₃-N ratio in groundwater in groundwater discharged from riparian buffers in this study (n = 101) is 0.0041 (95% C.I. 0.0028-0.0054) (Fig. 7 (B)).

4 Discussion
4.1 Transport and fate of nitrate
Nitrate concentration in groundwater was significantly decreased under the grass filter in both 1997-1999 and 2005-2008 and under the multi-species riparian buffer in 2005-2008. Processes that may decrease NO₃⁻ concentration in groundwater include dilution of groundwater, uptake by vegetation, and denitrification. Andress (1999), using an isotopic method, found denitrification occurring in the grass filter site. Our data showed the concomitant decrease in the NO₃⁻/Cl⁻ ratio in both sites with a significant decrease in NO₃⁻ concentration and an insignificant change in the Cl⁻ concentration. These results suggest that dilution from a converging or diverging flow path were not a major factor contributing to the decrease in groundwater NO₃⁻ concentration (e.g. Vidon and Hill, 2004; Davis et al. 2007). However, mixing with upgradient groundwater which has lower NO₃⁻ concentration and similar Cl⁻ concentration could also be a possible dilution mechanism. Uptake of NO₃⁻ by vegetation was not investigated in this study but is well known to occur in riparian buffers. A meta-analysis of N removal in riparian buffers by Mayer et al. (2007), documented mean removal efficiency of N in groundwater of 76.7 ± 4.3 % (n = 65) of the incoming N flux. In our studies, there was no significant NO₃⁻ decrease observed during 1997-1999 under the multi-species riparian buffer. Andress (1999) and Simpkins et al. (2002) demonstrated that this site, then a 7-year-old buffer, has a sand aquifer which might cause groundwater to bypass processing by the plant-soil complex and allow transport of nitrate directly creek. Several studies have documented the importance of hydrogeologic setting, specifically the direction of groundwater flow and the position of the water table in thin sand aquifers underlying the buffers, in determining buffer N removal efficiency (Puckett, 2004). To the point of this study however, the multi-species riparian buffer has been shown to be a site of significant NO₃⁻
removal as the groundwater moves from cropped fields to the creek. The age of the buffer could also be a potential contributing factor for the difference found in N removal efficiency.

4.2 Fate and transport of dissolved N$_2$O

The dissolved N$_2$O concentration in groundwater was not significantly changed during travel under either the cool-season grass filter or the multi-species riparian buffer in 1997-1999 and 2005-2008. The dissolved N$_2$O concentrations in both sites (6-14 µg L$^{-1}$) were similar to those (0-6.3 µg N L$^{-1}$) reported by Davidson and Firestone (1988), Davidson and Swank (1990), Papen and Butterbach-Bahl (1999), Blicher-Mathiesen and Hoffmann (1999), Höll et al. (2005) and Davis et al. (2007) and less than those reported by Weller et al. (1994) (17.2 ug N L$^{-1}$), and Well et al. (2001) (10.2–53.2 µg N L$^{-1}$). Davis et al. (2007) reported that both dissolved N$_2$O and NO$_3^-$ were significantly lower in the riparian area than in the adjacent cropping system. Weller et al. (1994) also found that N$_2$O production in a riparian forest was not an important fate of N removed from cropland discharges.

Blicher-Mathiesen and Hoffman (1999) reported that denitrification in a riparian soil can act as a sink for dissolved N$_2$O in the inflowing groundwater as well as for N$_2$O produced in the riparian sediment. Clough et al. (2007) reported significant consumption of $^{15}$N$_2$O injected into groundwater in an upland-marsh transition zone of a salt marsh and a forested alluvial riparian zone. These studies commonly concluded that dissolved N$_2$O is decreased in riparian areas.

Our results regarding NO$_3^-$ decrease without increasing dissolved N$_2$O can be explained two different ways. First, it may be that denitrification completed the reduction of NO$_3^-$ to N$_2$ without producing N$_2$O (Blicher-Mathiesen and Hoffman, 1999). In the groundwater, very low concentrations of DO (<2 ppm) were often observed and the anaerobic environment might support completion of denitrification (e.g. Desimone and Howes, 1996; Spalding and Parrott, 1994; Starr and Gillham, 1993). This possibility is supported by the significant relationship we found between DO and dissolved N$_2$O. Second, produced N$_2$O in groundwater can be released into unsaturated soil above groundwater table. In the riparian buffer sites, the estimated NO$_3^-$ decrease in groundwater was 36.1 kg N ha$^{-1}$ yr$^{-1}$ (average of reduced load in the grass filter and the multi-species riparian buffer, Table 1) and N$_2$O emission measured on the soil surface was 1.8-4.5 kg N$_2$O-N ha$^{-1}$ yr$^{-1}$ through 2006 to 2007 (Kim et al. 2008, Emission of the greenhouse gas nitrous oxide from riparian forest buffers, warm-season and cool-season grass filters, and crop fields, in this dissertation). The data indicate that the ratio of N$_2$O emission measured on the soil surface to reduced N in the groundwater ranged from
0.05 to 0.12. The amount of N\textsubscript{2}O emission included N\textsubscript{2}O produced in unsaturated soil and almost all N\textsubscript{2}O was produced from the surface 0-15 cm of 0-125cm soil cores collected in the unsaturated soil (Kim et al., 2008, Distinguishing sources of nitrous oxide in riparian forest buffers, warm-season and cool-season grass filters, and crop fields, in this dissertation). These results suggest that N\textsubscript{2}O upward fluxes from the groundwater into the unsaturated zone may not be significant. Deurer et al. (2008) found that a zone for N\textsubscript{2}O exchange occurred at the interface between the saturated and unsaturated zone of the soil and that zone acted as a source and sink for N\textsubscript{2}O in an aquifer in northern Germany. They estimated that upward fluxes from the exchange zone into the unsaturated zone ranged between 0.0009 to 0.3 kg N\textsubscript{2}O ha\textsuperscript{-1} yr\textsuperscript{-1} and the yearly downward fluxes into the exchange zone had about the same order of magnitude. These suggest that NO\textsubscript{3}\textsuperscript{-} decrease without increasing dissolved N\textsubscript{2}O in the groundwater may be caused by complete denitrification. Based on these results, it is suggested that riparian buffers should be considered insignificant sources of indirect N\textsubscript{2}O emissions.

4.3 IPCC methodology for indirect N\textsubscript{2}O emissions within riparian buffer established adjacent to cropped fields

Our results estimate the N\textsubscript{2}O emission factor of groundwater leached from crop fields at 0.0022 (95% C.I. 0.0013-0.0031), and the emission factor of groundwater leached from riparian buffers at 0.0041 (95% C.I.0.0028-0.0054).

The Intergovernmental Panel for Climate Change (2006) reported that the previously used N\textsubscript{2}O emission factor for groundwater leached from crop fields (0.015) (IPCC, 1996) was too high and they modified the emission factor of 0.0025 based on several studies (Hiscock et al., 2003; Reay et al., 2004; Sawamoto et al., 2005). Our work supports the new emission factor.

As discussed above, riparian buffers adjacent to crop fields can decrease significant amounts of NO\textsubscript{3}\textsuperscript{-} in groundwater leached from the crop fields before the NO\textsubscript{3}\textsuperscript{-} enters receiving waters. Study results also estimate that the groundwater leached from riparian buffers has different N\textsubscript{2}O emission factor than the groundwater leached from crop fields. Therefore, where riparian buffers are adjacent to crop fields we suggest that the current IPCC (2006) estimation equation can be improved by adding a NO\textsubscript{3}\textsuperscript{-} reduction factor for riparian buffers (RF\textsubscript{N}) and replacing the N\textsubscript{2}O emission factors for groundwater (EF\textsubscript{5g}) with emission factors for groundwater in riparian buffers (EF\textsubscript{5RBg}). The nitrate reduction factor in riparian buffers (RF\textsubscript{N}) can be estimated as 0.77 since most riparian buffers reduce nitrogen in groundwater by 76.7 % (Mayer et al. 2007) and EF\textsubscript{5RBg} can be estimated at 0.0041 as calculated in this study.
According to the IPCC (2006), the global estimation of indirect N\textsubscript{2}O emission from N leaching in agro-ecosystems (Tier 1) is calculated as follows,

\[ \text{N}_2\text{O}_{(L)} - \text{N} = \text{N inputs} \times \text{Frac}_{\text{LEACH-(H)}} \times \text{EF}_5 \]  \hspace{1cm} (4)

This equation can be modified with the RF\textsubscript{N} and EF\textsubscript{5RBg} as follows,

\[ \text{N}_2\text{O}_{(L)} - \text{N} = \text{N inputs} \times \text{Frac}_{\text{LEACH-(H)}} \times (1 - RF\textsubscript{N}) \times \text{EF}_{RB} \]  \hspace{1cm} (5)

where,

- RF\textsubscript{N} = nitrate reduction factor in riparian buffers, 0.77
- EF\textsubscript{RB} = emission factor for N\textsubscript{2}O emissions from N leaching through riparian buffers if they exist, 0.0091, kg N\textsubscript{2}O-N (kg N leached) \textsuperscript{-1}
  \[ = \text{EF}\textsubscript{5RBg} (0.0041) + \text{EF}\textsubscript{5r} (0.0025) + \text{EF}\textsubscript{5e} (0.0025) \]
- EF\textsubscript{5RBg}, EF\textsubscript{5r}, and EF\textsubscript{5e} are emission factors for groundwater in riparian buffers, in rivers, and in estuaries, respectively.

Applying the newly developed RF\textsubscript{N} and EF\textsubscript{5RBg} can lower the magnitude of the emission factors for estimating indirect N\textsubscript{2}O emission by nearly 72% (Table 4). Such modifications would allow the function of riparian buffers as sinks of dissolved N\textsubscript{2}O to be accounted for in the IPCC methodology for inventorying indirect N\textsubscript{2}O emissions produced from crop fields.

The default value of the fraction of the fertilizer and manure N lost to leaching and surface runoff (Frac\textsubscript{LEACH-(H)}) currently used by IPCC (2006) is 0.3, and an uncertainty range 0.1-0.8 was reported by Seitzinger and Kroeze (1998). Mosier et al. (1998) concluded that the value is one of the greatest uncertainties in the total N\textsubscript{2}O estimate. Lower values of 0.15-0.2 have been substituted for the default by several countries (Nevison, 2000). Thoms et al. (2005) suggested that a value of 0.07 (0.03-0.1) as appropriate for New Zealand conditions. Our studies estimate the calculated Frac\textsubscript{LEACH-(H)} at 0.05, a similar value to that suggested for New Zealand (Thoms et al., 2005). Substituting the Frac\textsubscript{LEACH-(H)} (0.05) for the IPCC default Frac\textsubscript{LEACH-(H)} (0.3), and applying newly developed RF\textsubscript{N} and EF\textsubscript{5RBg} would reduce the magnitude of default of emission factors for estimating indirect N\textsubscript{2}O emission by 95.8 % (Table 4).
5 Conclusions

Monitoring of groundwater under a cool-season grass filter and a multi-species riparian buffer during 1997-1999 and 2005-2008 indicated that the concentrations of dissolved N$_2$O was not significantly changed, even when the concentrations of groundwater NO$_3^-$ were decreased by 49.5% under the multi-species riparian buffers and 58.8% under the cool-season grass filter, over the same time periods. The concomitant decrease in the NO$_3^-$/Cl$^-$ ratio in those sites with significant NO$_3^-$ concentration decrease provides evidence that dilution from a converging or diverging flow path was not a major factor contributing to the decreased NO$_3^-$ concentration in groundwater, and infers that denitrification is the major loss mechanism. Based on these results, we suggest that riparian buffers established adjacent to crop fields to increase denitrification didn't increase dissolved N$_2$O in groundwater. Our results indicated that the N$_2$O emission factor of groundwater leached from crop fields was 0.0022, a value similar to the new IPCC (2006) emission factor (EF$_{5g}$, 0.0025). It is suggested that new emission factors for groundwater leached from riparian buffers (EF$_{SRB}_g$, 0.0041) and the fraction of all N added to/mineralized in managed soils in regions where leaching/runoff occurs (Frac$_{LEACH-(H)}$, 0.06) be included in the IPCC inventory estimates. These factors would modify the IPCC’s inventory methodology for estimating indirect N$_2$O emission in agroecosystems where riparian buffers are being established to act as sinks for non-point source NO$_3^-$. 
References


Mosier, A., C. Kroeze, C. Nevison, O. Oenema, S. Seitzinger, and O. van Cleemput. 1998. Closing the global N2O budget: nitrous oxide emissions through the agricultural nitrogen cycle -


Table 1. Summarizing parameters used to estimate total N flux discharged from crop fields (In) and adjacent riparian buffers (Out) and estimated reduced N load and the reduction rate in the cool-season grass filter and multi-species riparian buffer in 2005-2008.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Unit</th>
<th>Cool-season grass filter</th>
<th>Multi-species riparian buffer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average linear velocity (Vx)†</td>
<td>m d⁻¹</td>
<td>0.23</td>
<td>0.13</td>
</tr>
<tr>
<td>Effective porosity (ne)</td>
<td>no unit</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Concentration (Conc)‡</td>
<td>mg N L⁻¹ or g m⁻³</td>
<td>7.9</td>
<td>4</td>
</tr>
<tr>
<td>Mass flux (Fx)</td>
<td>g N d⁻¹ m⁻²</td>
<td>0.27255</td>
<td>0.078</td>
</tr>
<tr>
<td>Section length§</td>
<td>m</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Section height¶</td>
<td>m</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Total flux</td>
<td>kg N yr⁻¹</td>
<td>7.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Reduction rate</td>
<td>%</td>
<td>58.2</td>
<td>50.0</td>
</tr>
<tr>
<td>Reduced load#</td>
<td>kg N ha⁻¹ yr⁻¹</td>
<td>57.9</td>
<td>14.2</td>
</tr>
</tbody>
</table>

†Spear 2003
‡Mean concentration of NO₃⁻ (Fig. 3)
§The length of riparian buffers
¶The sites are underlined by 2m thick sand aquifer
#Reduced N load per area of riparian buffers, area of a riparian buffer = length 35 m × width 20 m
Table 2. Summarizing parameters used to calculate total N flux in groundwater from crop fields in the Bear Creek watershed.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Unit</th>
<th>North of Creek</th>
<th>South of Creek</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average linear velocity (Vx)†</td>
<td>m d(^{-1})</td>
<td>0.23</td>
<td>0.13</td>
<td>-</td>
</tr>
<tr>
<td>Effective porosity (ne)</td>
<td>no unit</td>
<td>0.15</td>
<td>0.15</td>
<td>-</td>
</tr>
<tr>
<td>Concentration (Conc.) ‡</td>
<td>mg N L(^{-1})</td>
<td>7.9</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>Mass flux (Fx)</td>
<td>g N d(^{-1})m(^{-2})</td>
<td>0.273</td>
<td>0.078</td>
<td>-</td>
</tr>
<tr>
<td>Section length§</td>
<td>m</td>
<td>56,473</td>
<td>56,473</td>
<td>-</td>
</tr>
<tr>
<td>Section height¶</td>
<td>m</td>
<td>2</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>Total N flux</td>
<td>kg N yr(^{-1})</td>
<td>11,236.0</td>
<td>3,215.6</td>
<td>14,451.5</td>
</tr>
</tbody>
</table>

†Spear 2003
‡Mean concentration of NO\(_3\) (Fig. 3)
§The length of Bear Creek
¶The sites are underlined by 2m thick sand aquifer
Table 3. Summarizing parameters used to calculate the ratio of N inputs to runoff and leaching N in crop fields (Frac \textsubscript{LEACH-(H)}) in 2005-2008.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Unit</th>
<th>Bear Creek watershed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Corn fields</td>
</tr>
<tr>
<td>Area†</td>
<td>ha yr(^{-1})</td>
<td>3,404.95</td>
</tr>
<tr>
<td>N Fertilizer application rate‡</td>
<td>kg N ha(^{-1}) yr(^{-1})</td>
<td>133.4</td>
</tr>
<tr>
<td>F(_{SN})</td>
<td>kg N yr(^{-1})</td>
<td>454,220.3</td>
</tr>
<tr>
<td>N residue rate §</td>
<td>kg N ha(^{-1}) yr(^{-1})</td>
<td>92.2</td>
</tr>
<tr>
<td>F(_{CR})</td>
<td>kg N yr(^{-1})</td>
<td>313,936.4</td>
</tr>
<tr>
<td>F(<em>{SN} + F</em>{CR})</td>
<td>kg N yr(^{-1})</td>
<td>768,156.7</td>
</tr>
<tr>
<td>Runoff rate ¶</td>
<td>kg N ha(^{-1}) yr(^{-1})</td>
<td>5.23</td>
</tr>
<tr>
<td>Total runoff (TR)</td>
<td>kg N yr(^{-1})</td>
<td>17,807.9</td>
</tr>
<tr>
<td>Total leaching (TL)#</td>
<td>kg N yr(^{-1})</td>
<td>ND</td>
</tr>
<tr>
<td>TR+TL</td>
<td>kg N yr(^{-1})</td>
<td>ND</td>
</tr>
<tr>
<td>Frac \textsubscript{LEACH-(H)} ††</td>
<td>no unit</td>
<td>ND</td>
</tr>
</tbody>
</table>

† assumed 50% corn fields and 50% soy bean fields
‡ Kim D. G., 2008. Emission of the greenhouse gas nitrous oxide from riparian forest buffers, warm-season and cool-season grass filters, and crop fields, in this dissertation.
¶ Calculated form Lee et al. (2003)
# Total N flux in groundwater from crop fields in the Bear Creek watershed (Table 2).
†† TR+TL/ F\(_{SN} + F_{CR}\)
Table 4. Default factors of IPCC (2006), the new factors for riparian buffers (RB) applied case, the new factors for both RB and new Frac\(_{LEACH-(H)}\) applied case, and reduced rate of total factor values (%) applying new factors.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Value</th>
<th>Factor</th>
<th>Value</th>
<th>Factor</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frac(_{LEACH-(H)})</td>
<td>0.3</td>
<td>Frac(_{LEACH-(H)})</td>
<td>0.3</td>
<td>Frac(_{LEACH-(H)})</td>
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<tr>
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<td>RF(_N) †</td>
<td>0.23</td>
<td>RF(_N) †</td>
<td>0.23</td>
</tr>
<tr>
<td>EF(_{5r\dagger})</td>
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<td>EF(_{SRBg})§</td>
<td>0.0041</td>
<td>EF(_{SRBg})§</td>
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<tr>
<td>EF(_{5e\dagger})</td>
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<td>EF(_{5e\dagger})</td>
<td>0.0025</td>
<td>EF(_{5e\dagger})</td>
<td>0.0025</td>
</tr>
<tr>
<td>Frac(_{LEACH-(H)}) • EF(_5)</td>
<td>0.0023</td>
<td>-</td>
<td>-</td>
<td>Frac(_{LEACH-(H)}) • RF(<em>N) • EF(</em>{RB})</td>
<td>0.0006</td>
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<tr>
<td>Reduction of factor values (%)‡</td>
<td>-</td>
<td>72.1</td>
<td>95.8</td>
<td></td>
<td></td>
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</table>

† RF\(_N\) is nitrate reduction factor in riparian buffers.
‡ EF\(_{5p}\), EF\(_{5r}\), and EF\(_{5e}\) are emission factors for groundwater, in rivers, and in estuaries, respectively.
§ EF\(_{SRBg}\) is emission factor for groundwater in riparian buffers.
Figure 1. Map showing location of monitoring wells (●) and creek stilling wells (■) in a cool-season grass filter (A) and a multi-species riparian buffer (B) in the Bear Creek watershed. In a cool season grass filter (A), monitoring wells R8, R12, and R40 are adjacent to creek and monitoring wells R39, R1, and R9 are adjacent to creek. In a multi-species riparian buffer (B), monitoring wells R13, R17, and R21 are adjacent to creek and monitoring wells R16, R20, and R24 are adjacent to creek. Figures (A and B) are from Johnston (1998).
Figure 2. Seasonal variation of groundwater NO$_3^-$ concentration in groundwater under a cool-season grass filter and a multi-species riparian buffer in 1997-1999 (data from Spear 1999) and 2005-2008.
<table>
<thead>
<tr>
<th>Groundwater flow direction</th>
<th>Crop field</th>
<th>Multi-species riparian buffer</th>
<th>Bear Creek</th>
<th>Cool-season grass filter</th>
<th>Crop field</th>
<th>Groundwater flow direction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>→ →</td>
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<td>20.9 (1.0)</td>
<td>13.4 (1.0)</td>
<td>13.2 (0.9)</td>
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<td></td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>4.9 (0.5)</td>
<td>5 (0.4)</td>
<td>4.9 (2.4)</td>
<td>9.5(0.7)*</td>
<td>NO₃⁻</td>
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</tr>
<tr>
<td>NO₃⁻/Cl⁻</td>
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<td>0.2 (0.0)</td>
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<td>0.8(0.1)*</td>
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<tr>
<td>Dissolved N₂O</td>
<td>6.1(1.0)</td>
<td>6 (0.7)</td>
<td>6.8(0.8)</td>
<td>7.8(1.2)</td>
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<td></td>
</tr>
<tr>
<td>DOC</td>
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<td>pH</td>
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<td>7.3(0.0)</td>
<td>7.5(0.0)</td>
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<td></td>
</tr>
</tbody>
</table>

Figure 3. Groundwater characteristics adjacent to crop fields and Bear Creek in a multi-species riparian buffer and a cool-season grass filter in 1997-1999. Unit for Cl⁻, NO₃⁻, DOC, and DO is mg L⁻¹ and unit of dissolved N₂O is µg L⁻¹. The value inside a parenthesis is a standard error and a asterisk (*) indicates $p < 0.05$. The number of measurements: Cl⁻ ($n = 21-23$), NO₃⁻ ($n = 26-29$), NO₃⁻/Cl⁻ ($n = 17-22$), dissolved N₂O ($n = 26-27$), DOC ($n = 3$), DO ($n = 19-21$), and pH ($n = 3$).
## Figure 4

Groundwater characteristics adjacent to crop fields and Bear Creek in a multi-species riparian buffer and a cool-season grass filter in 2005-2008. Unit for Cl⁻, NO₃⁻, DOC, and DO is mg L⁻¹ and unit of dissolved N₂O is µg L⁻¹. The value inside a parenthesis is a standard error and an asterisk (*) indicates $p < 0.05$. The number of measurements: Cl⁻ ($n = 29$), NO₃⁻ ($n = 29$), NO₃⁻/Cl⁻ ($n = 29$), dissolved N₂O ($n = 25-26$), DOC ($n = 8$), DO ($n = 26-27$), and pH ($n = 21$).

<table>
<thead>
<tr>
<th></th>
<th>Crop field</th>
<th>Multi-species riparian buffer</th>
<th>Bear Creek</th>
<th>Cool-season grass filter</th>
<th>Crop field</th>
<th>Groundwater flow direction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Groundwater flow direction</strong></td>
<td>→ →</td>
<td>→ →</td>
<td>← ←</td>
<td>← ←</td>
<td>← ←</td>
<td>Groundwater flow direction</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>20.8 (1.2)</td>
<td>18.2 (0.6)</td>
<td>18.2 (0.6)</td>
<td>20.6 (1.2)</td>
<td>Cl⁻</td>
<td></td>
</tr>
<tr>
<td>NO₃⁻</td>
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<td>2.0 (0.2)*</td>
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<td>7.9 (0.5)*</td>
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</tr>
<tr>
<td>NO₃⁻/Cl⁻</td>
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<td>0.1 (0.0)*</td>
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<td>0.4 (0.0)*</td>
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<tr>
<td>Dissolved N₂O</td>
<td>9.0 (1.1)</td>
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<td>DOC</td>
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<td>2.7 (0.3)</td>
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<td>pH</td>
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<td>7.4 (0.1)</td>
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<td>pH</td>
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</tr>
</tbody>
</table>
Figure 5. Seasonal variation of the NO$_3^-$/Cl$^-$ ratio in groundwater under a cool-season grass filter and a multi-species riparian buffer in 1997-1998 (data from Spear 1999) and 2005-2008.
Figure 6. Seasonal variation of dissolved N$_2$O concentration in groundwater under a cool-season grass filter and a multi-species riparian buffer in 1997-1999 (data from Spear 1999) and 2005-2008.
Figure 7. Relationship between NO$_3$-N and dissolved N$_2$O-N concentration in groundwater discharged from crop fields (A) and riparian buffers (B) in 1997-1999 and 2005-2008 in this study (●, $n = 99-101$) and data from David et al. (2007) (○, $n = 7$). Default of EF 5g (---), and EF$_{5g}$ of this study and David et al. (2007) (EF$_{5RBg}$) (—) and 95% confidence interval of the EF$_{5g}$ of this study and David et al. (2007) (EF$_{5RBg}$) (―).
Distinguishing sources of nitrous oxide in a riparian forest buffers, warm-season and cool-season grass filters, and an adjacent crop field

A paper to be submitted to Soil Biology & Biochemistry

Richard C. Schultz, Thomas M. Isenhart, Timothy B Parkin, James R. Raich, Thomas E. Loynachan

Abstract
Denitrification within riparian buffers is recognized as a major mechanism for reducing nitrate (NO$_3^-$) and thus diminishing non-point source (NPS) pollution of surface water bodies subject to high nitrogen (N) loads. However, increasing denitrification rates in riparian buffers may be trading the problem of NPS pollution of surface waters for atmospheric deterioration and increased global warming potential because denitrification produces nitrous oxide (N$_2$O), a greenhouse gas involved in stratospheric ozone depletion. It is therefore important to quantify the emissions of N$_2$O and N$_2$ from different kinds of vegetated riparian buffer systems and adjacent crop fields and evaluate whether N$_2$O emission from riparian buffer systems is larger than one from adjacent crop fields. We sampled soils in a forested riparian buffer, a warm-season and a cool-season grass filter, and a crop field located in the Bear Creek watershed in central Iowa. We measured soil properties, nitrification potential rate, and denitrification enzyme activity (DEA), and conducted incubation experiments with inhibitors (CH$_3$F, C$_2$H$_2$, and O$_2$) to determine N$_2$O fluxes, sources of N$_2$O, and the ratio of N$_2$O to N$_2$. Our results indicated that soils in riparian buffers had similar or greater nitrification potential rates and DEA than those in the crop field; however, there was less N$_2$O flux from incubated soil samples in all riparian buffers (0-15 cm depth, -0.07 to 0.47 µg N$_2$O-N kg$^{-1}$ h$^{-1}$) than in the crop field (0-15 cm depth, 3.9 ±1.8 µg N$_2$O-N kg$^{-1}$ h$^{-1}$), and no difference in N$_2$O flux among the different kinds of riparian buffers. Soil incubation with inhibitors suggested that the main sources of N$_2$O might be nitrifier denitrification (68.8 %) and denitrification (23.1 %) in the crop field soil and nitrifier denitrification (50-59 %) in the riparian buffer soils. The ratio of N$_2$O to N$_2$ in riparian buffer soil (0.88-6.8) was less than that found in crop field soil (16.5). These results suggest that N$_2$O emissions from soils in all riparian buffers were significantly less than those in the crop field.

1 Introduction
Non-point source (NPS) pollutants such as sediment, nutrients, and pesticides are major causes of water quality problems worldwide (Duda, 1993; Tonderski A., 1996; Carpenter et al., 1998).
Riparian buffers have been recommended as effective tools for reducing NPS pollutant transport to receiving waters in areas of row-crop agriculture (e.g. Sabater et al., 2003; Hubbard et al., 2004). Numerous studies have identified denitrification as the major NO$_3^-$ loss mechanism within riparian systems (e.g. Groffman and Hanson, 1997; Watts et al., 2000). Recently, it has been hypothesized that increased denitrification within riparian systems may be trading a water quality problem for an atmospheric problem as a result of nitrous oxide (N$_2$O) emissions produced during denitrification processes adding to the greenhouse effect (Wang et al., 1976) and ozone depletion (Crutzen, 1970). The global warming potential of N$_2$O is 296 times that of carbon dioxide (CO$_2$) and almost 13 times that of methane (CH$_4$) in a 100-year time horizon (IPCC 2007). Some studies (Groffman et al., 1998, 2000; Hefting et al., 2003, 2006; Dhondt et al., 2004) conclude that N transformation within riparian systems subjected to high nitrate loads results in a significant increase of greenhouse gas emissions. Groffman et al. (2002) suggested that the Intergovernmental Panel on Climate Change (IPCC) inventory might be improved by including more measurements of riparian N$_2$O fluxes, with a particular focus on the relative importance of N$_2$O vs N$_2$ production.

Besides denitrification, N$_2$O can be produced from nitrification (e.g. Firestone and Davidson, 1989) and nitrifier denitrification (Webster and Hopkins, 1996; Wrage et al., 2001, 2004c, 2005; Ma et al., 2007). Nitrifier denitrification is the pathway whereby ammonia (NH$_3$) is oxidized to nitrite (NO$_2^-$), followed by the reduction of NO$_2^-$ to nitric oxide (NO), N$_2$O and molecular nitrogen (N$_2$) (Wrage et al., 2001). The transformation is carried out by autotrophic NH$_3$-oxidizers (AOB) (Wrage et al., 2001). Codenitrification (Laughlin and Stevens, 2002) and non-biological processes such as chemodenitrification (Cleemput and Baert, 1984; Martikainen and De Boer, 1993; Daum and Schenk, 1998; Mørkved et al., 2007) can be sources of N$_2$O. High nitrification rates are well-documented in crop fields where manure and N fertilizers are applied (Granli and Bøckman, 1994). In these systems, nitrification-associated N$_2$O emission is often estimated as the major source of total N$_2$O emission from soil (e.g. Kester et al., 1997; Bollmann and Conrad, 1998; Wolf and Brumme, 2002). Ambus (1998) reported that nitrification contributed to more than 60% of total N$_2$O production in a riparian grassland in Denmark. Ma et al. (2008) found nitrification to be the primary source of N$_2$O emission from ephemeral wetland soils. Wrage et al. (2004a) reported that N$_2$O production was generally dominated by reduction processes, either denitrification or nitrifier denitrification, in four European grasslands. The distinction between sources of N$_2$O is a complex issue (e.g. Wolf and Russow, 2000; Wrage et al., 2001, and 2004b). Several authors have recently suggested that additional studies should be conducted to quantify N$_2$O emissions and identify source mechanisms within various regions, in different landscape settings, and under different vegetation communities.
Over the last fifteen years, conservation systems comprised of re-established perennial plant systems have been promoted to reduce non-point source N transport to receiving waters. In the United States, nearly $7.7 \times 10^5$ ha of riparian practices have been established through the Conservation Reserve Program (USDA, 2008). To reduce the potential of these systems as sources of N$_2$O, it is important to quantify the emissions of N$_2$O and N$_2$ from different kinds of vegetated riparian buffer systems and identify ways to reduce the emission of N$_2$O and increase the emission of N$_2$.

Acetylene (C$_2$H$_2$) and oxygen (O$_2$) inhibition techniques have been used to distinguish between sources of N$_2$O and determine the N$_2$O to N$_2$ ratio (e.g. Davidson et al., 1986; Webster and Hopkins, 1996; Wrage et al., 2004a). However, uncertainty concerning the reliability of C$_2$H$_2$ and O$_2$ as inhibitors has recently been reported. Wrage et al. (2004b) observed that C$_2$H$_2$ did not affect N$_2$O production in *Nitrosospira briensis*, one of the common ammonia-oxidizing bacteria in soils, and it was suggested that this incomplete inhibition may lead to an underestimation of both nitrification and nitrifier denitrification and an overestimation of denitrification and other sources of N$_2$O (e.g. chemodenitrification and heterotrophic nitrification) (Wrage et al., 2004c). Shaw et al. (2006) suggested that the attempt to identify sources of N$_2$O through use of O$_2$ suppression of denitrification (Webster and Hopkins, 1996; Wrage et al., 2004c) should consider that nitrifier denitrification might not be suppressed by O$_2$. It was proposed that incompletely blocked nitrifier denitrification may lead to an overestimation of N$_2$O production from nitrification and an underestimation of N$_2$O production from nitrifier denitrification (Wrage et al., 2004c). While an $^{18}$O-$^{15}$N enrichment method was suggested as a more reliable tool than the use of inhibitors (Wrage et al., 2005), it was reported that stable isotope analysis of O$_2$ to determine the source of N$_2$O is limited by exchange of the oxygen between water and nitrogen oxides (Kool et al., 2007). While all methods to distinguish sources of N$_2$O have significant limitations, the inhibition methods are relatively simple to apply and results have been accumulated from various studies. Therefore, results from inhibition methods can be compared with previous results and results can be reassessed when a new method is available to accurately distinguish sources of N$_2$O.

The objectives of this study were to distinguish the sources of N$_2$O in riparian buffers and crop fields and assess the differences in N$_2$O and N$_2$ production among cropped fields and three vegetation types in riparian buffers.
2 Materials and methods

2.1 Study site and soil sampling

The study area consists of reestablished riparian buffers of three vegetation types (trees, warm-season grasses, and cool-season grasses) and crop fields located within the Bear Creek watershed, Story County and Hamilton County, Iowa, United States (42° 11’ N, 93° 30’ W). Land use within the Bear Creek watershed is predominantly agriculture, with over 93% of the area dedicated to annual row crops of corn and soybeans. Most of the area was originally covered with prairie vegetation except for riparian forests along the lower third of the creek. The major soil association in the watershed is the Clarion-Webster-Nicolett association with minor areas of Clarion- Storden-Coland, and Canisteo-Okoboji-Nicolett (Dewitt, 1984). The study sites were on Coland soil (fine-loamy,mixed, mesic Cumulic Haplaquoll), which is well drained to poorly drained and formed from till or local alluvium and colluvium derived from till (DeWitt, 1984). Riparian buffers of three vegetation types were established on the study site in 1990 in previously cultivated soils. Five rows, at 1.2 x 1.8 m spacing, of Hybrid poplars (Populus × euroamericana Eugenei) were planted in the forest buffer. Switchgrass (Panicum virgatum L.), a native warm season grass, was planted in the warm season grass filter. Dominant grass species within the cool-season grass site were smooth brome (Bromus inermis Leysser), timothy (Phleum pratense L.), and Kentucky bluegrass (Poa pratensis L.). These same species were also found in the poplar understory. Details of the riparian buffer design, placement and plant species are given in Schultz et al. (1995). Cropped fields were under an annual maize-soybean rotation. Maize (Zea mays L.) was usually planted in the early May and harvested at the end of October. Soybean (Glycine max (L.) Merr.) was normally planted in mid-May and harvested in mid-September.

In each site, three plots (50 cm × 50 cm) were randomly selected for soil sampling. Three intact soil cores (diameter 5.3 cm) were collected to a depth of 100 cm in all three plots of each site in October 2006. The cores were taken directly adjacent to each other in each of the plots. A plastic liner was placed inside the soil core tube and this liner with the intact soil core was pulled from the tube and capped for transport to the laboratory. Incubation experiments with the intact soil cores were conducted within four hours after sampling. Soil samples were then stored at 4°C until analysis of chemical properties. The soil cores were used to determine denitrification enzyme activity (DEA) and N₂O flux at four sample depths (0-15, 15-30, 30-60, 60-100 cm). Six intact soil cores (diameter 5.3 cm) were collected in a similar way to a depth of 15 cm in all three plots of the sites in September 2007. The cores were taken directly adjacent to each other in each of the plots. These soil cores were
used to determine nitrification potential, DEA, N₂O flux, and the N₂O to N₂ ratio and to distinguish sources of N₂O.

2.2 Nitrification potential
The nitrification potential of the soils was determined on 15 g subsamples via the shaken slurry method (Hart et al., 1994). The soil was placed in a 250 ml Erlenmeyer flask containing 100 ml of a solution of 0.2 M KH₂PO₄, 0.2 M K₂HPO₄ and 50 mM (NH₄)₂SO₄. Samples were incubated on an orbital shaker at 180 rpm for 24 h at 22°C. Nitrate from the centrifuged supernatant was measured by colorimetric method (Mulvaney, 1996) using an auto-analyzer (Quikchem 8000 FIA+, Lachat Instruments, Milwaukee, WI).

2.3 Denitrification enzyme activity (DEA)
The assay of DEA developed by Smith and Tiedje (1979) was used for quantification of denitrification potential. The method is based on the ability of acetylene (C₂H₂) to inhibit the reduction of N₂O to N₂ (Balderston et al. 1976; Yoshinari and Knowles, 1976), making N₂O the terminal product of denitrification. Soil samples were sieved (5 mm) and 50 g of wet soil placed in a stoppered 350 ml glass Erlenmeyer flasks with 50 ml of nutrient broth containing 1 mM KNO₃, 1 mM glucose, and 1 g L⁻¹ chloramphenicol. Chloramphenical was used to inhibit potentially interfering protein synthesis. The flasks were evacuated three times and flushed with helium four times in a continuous cycle. The overpressure of helium was released to bring the glass cylinder pressure to ambient air pressure. Twenty-five ml of C₂H₂ was added and the samples shaken on a reciprocal shaker for two hours. Nine ml of the headspace gas was sampled after 30 and 90 min and stored until analysis in 6 mL evacuated glass vials fitted with butyl rubber stoppers. The glass vials were prepared by alternately evacuating the vial headspace and flushing with helium to remove air (five cycles of evacuation and flushing). Concentration of N₂O was converted to an N loss rate using equations from Tiedje (1994).

2.4 Incubation experiments for N₂O flux, sources of N₂O and N₂O to N₂ ratio
Nitrous oxide fluxes were measured at four sample depths (0-15, 15-30, 30-60, 60-100 cm) using the three replicate 100 cm intact soil cores collected in October 2006. Intact soil cores (diameter 5.3 cm, length 8 cm) were taken from the soil core of each depth and they were inserted into 350 ml glass jars with gas-tight lids containing a gas-sampling port. The soil cores were incubated at 12°C (on site soil temperature, 5cm depth) and emitted gas was sampled 3 hrs and 16 hrs later.
Using the 0-15 cm intact soil cores collected in September 2007, nitrous oxide fluxes, sources of N\textsubscript{2}O, and N\textsubscript{2}O to N\textsubscript{2} ratio were determined by methods developed by Davidson et al. (1986) and Webster and Hopkins (1996) (Table 1). Intact soil cores (diameter 5.3 cm, length 8 cm) were taken from the 15 cm soil cores and they were inserted into three 350 ml glass jars with gas-tight lids containing a gas-sampling port. Soil cores of each site were assigned to one control and five further treatments (with 3 replicates each) (Table 1). Both 10 Pa C\textsubscript{2}H\textsubscript{2} and 10 kPa CH\textsubscript{3}F were used to inhibit NH\textsubscript{3} oxidation (Balderston et al., 1976; Yoshinari and Knowles, 1976; Miller et al., 1993), and consequently to inhibit N\textsubscript{2}O production from both autotrophic nitrification and nitrifier denitrification. Ten kPa C\textsubscript{2}H\textsubscript{2} was used to inhibit the reduction of N\textsubscript{2}O to N\textsubscript{2} in the last step of denitrification (Davidson et al., 1986). To suppress denitrification and nitrifier denitrification, 100 kPa O\textsubscript{2} (Robertson and Tiedje, 1987) incubations were established by flushing with pure O\textsubscript{2}. In incubations with both 10 Pa C\textsubscript{2}H\textsubscript{2} and 100 kPa O\textsubscript{2}, neither nitrification pathways nor denitrification should take place. Thus, N\textsubscript{2}O in these incubations had to be produced by other sources, such as chemodenitrification (Robertson and Tiedje, 1987). All soil cores were incubated at 22\textdegree C (on-site soil temperature, 5cm depth) and emitted gas was sampled after 3 hrs and 16 hrs and stored in evacuated glass vials until analysis.

The amounts of N\textsubscript{2}O produced by different sources and N\textsubscript{2}O to N\textsubscript{2} ratio were calculated as follows. The means of 3 replicates were used for these calculations.

\[
\text{N}_2\text{O nitrification} = \text{N}_2\text{O}_0 - \text{N}_2\text{O}_{AO} \quad (1)
\]
\[
\text{N}_2\text{O denitrification (using 10 Pa C}_2\text{H}_2) = \text{N}_2\text{O}_A - \text{N}_2\text{O}_{AO} \quad (2)
\]
\[
\text{N}_2\text{O denitrification (using 10 K Pa CH}_3\text{F) = N}_2\text{O}_M - \text{N}_2\text{O}_{AO} \quad (3)
\]
\[
\text{N}_2\text{O nitrifier denitrification} = \text{N}_2\text{O}_C - \text{N}_2\text{O nitrification (1)} - \text{N}_2\text{O denitrification (2)} - \text{N}_2\text{O}_{AO} \quad (4)
\]
\[
\text{N}_2\text{O other} = \text{N}_2\text{O}_{AO} \quad (5)
\]
\[
\text{N}_2\text{ denitrification} = \text{N}_2\text{O production under 10 kPa C}_2\text{H}_2 - \text{N}_2\text{O denitrification (2)} \quad (6)
\]
\[
\text{N}_2\text{O to N}_2 \text{ ratio} = \frac{\text{N}_2\text{O}_C}{\text{N}_2\text{ denitrification (6)}} \quad (7)
\]
The subscripts C, A, M, AA, O and AO refer to the incubation type that was used to differentiate between the processes as shown in Table 1.

2.5 Soil properties and gas analysis
Soil pH was determined using a pH meter (Accument 910, Fisher Scientific Ltd., Pittsburgh, PA, USA) on a 1:1 diluted soil solution. Gravimetric moisture content was determined by oven drying a subsample at 105°C for 24 h and bulk density was determined by the core method (Grossman and Reinsch, 2002). For C and N analysis, soils were air dried at room temperature and sieved (2mm), and then soil water content was determined. Total C (TC) and total N (TN) were measured using a Flash EA 2000 (ThermoFinnigan, Milan, Italy) direct combustion instrument. Soil inorganic N was extracted with 2 M potassium chloride (KCl) and filtrated within 4 h of field collection of the soil cores (Mulvaney, 1996). Filtrates were frozen (-10 °C) and stored until further analysis. Nitrate (NO$_3^-$) and ammonium (NH$_4^+$) contents were analyzed by colorimetric method (Mulvaney, 1996) with an auto analyzer (Quiqchem 8000 FIA+, Lachat Instruments, Milwaukee, WI, USA). N$_2$O was measured with a gas chromatograph (GC) (Model GC17A; Shimadzu, Kyoto, Japan) equipped with a $^{63}$Ni electron capture detector and a stainless steel column (0.3175 cm diameter × 74.54 cm long) with Porapak Q (80–100 mesh). Samples were introduced into the GC using an auto-sampler described by Arnold et al. (2001). Based on measurements of standard N$_2$O gases, our estimated minimum detectable flux was estimated to be 0.02 µg N$_2$O-N kg$^{-1}$ h$^{-1}$ for the incubation experiments.

2.6. Statistical analyses
For analyzing the normal distribution of the data, the Shapiro-Wilk normality test was performed. One way analysis of variance (ANOVA) with Tukey's studentized range test was used to evaluate the differences in soil properties, nitrification potential, DEA, and N$_2$O fluxes by site. Differences were considered significant at the $p < 0.05$ level. To determine the relationship between soil properties and nitrification potential, DEA, N$_2$O fluxes, and the ratio of N$_2$O to N$_2$, correlation analysis using the GLM procedure was applied. These statistical analyses were conducted using SAS version 8.1 (SAS institute, 1999).

3. Results
3.1 Soil properties
Soil properties (depth 0-15cm) of the crop fields and three riparian buffer vegetation types are shown in Table 2. The soil texture was loam in all sites (Marquez et al., 2004). Bulk density (One way
ANOVA \( p < 0.0001 \), pH (One way ANOVA \( p = 0.0003 \)), TC (One way ANOVA \( p < 0.01 \)), TN (One way ANOVA \( p < 0.01 \)), and NH\(_4^+\) (One way ANOVA \( p < 0.0001 \)) in soils of the sites were significantly different. Soils in riparian buffers had significantly lower bulk density, and higher pH and NH\(_4^+\) than crop field soils (Tukey's studentized range test). Soils in forest buffer had significantly higher TC than crop field soils and soils in forest buffer and cool-season-grass filter had significantly higher TN than crop field soils (Tukey's studentized range test). Soil NO\(_3^-\) was not significantly different between the sites (One way ANOVA \( p = 0.3 \)).

### 3.2 Nitrification potential rate

Nitrification potential rates were significantly different between soils in crop fields and riparian buffer vegetation types (One way ANOVA \( p < 0.001 \), Fig. 1). Soils of the cool-season grass filter (1.9 ± 0.24 mg N kg\(^{-1}\) h\(^{-1}\)) had significantly larger nitrification potentials than those of the crop fields and other riparian buffers (0.25-1.14 mg N kg\(^{-1}\) h\(^{-1}\)) (Tukey's studentized range test). There was no significant relationship between nitrification potential rates and soil properties (Table 3).

### 3.3 Denitrification enzyme activity

The first experiment conducted in October 2006 indicated that DEA was significantly different between soils in crop fields and riparian buffer vegetation types (One way ANOVA \( p < 0.05 \), Fig. 2A). The denitrification enzyme activity of soils in the forest buffer (1.43 ± 0.80 mg N\(_2\)O-N kg\(^{-1}\) h\(^{-1}\)) and the cool-season grass filter (1.74 ± 0.16 mg N\(_2\)O-N kg\(^{-1}\) h\(^{-1}\)) was significantly greater than that of the crop field and the warm-season grass filter (0.44-0.54 mg N\(_2\)O-N kg\(^{-1}\) h\(^{-1}\)) (Tukey's studentized range test). There was no significant relation between DEA and soil properties (Table 3). The second experiment conducted in September 2007 confirmed these results (Fig. 2B). Denitrification enzyme activity of soils in the forest buffer (0.81 ± 0.27 mg N\(_2\)O-N kg\(^{-1}\) h\(^{-1}\)) was significantly (One way ANOVA \( p < 0.05 \)) greater than that in the crop field and warm-season grass filter (0.18-0.26 µg N\(_2\)O-N kg\(^{-1}\) h\(^{-1}\)) and the DEA of soils in cool-season grass filter was not significantly different from either that of the forest buffers or the crop field and the warm-season grass filter (Tukey's studentized range test). There was no significant relation with soil properties (Table 3).

### 3.4 Nitrous oxide flux, sources of N\(_2\)O, and N\(_2\)O:N\(_2\)

Nitrous oxide production from the 0-100 cm soil cores in the control incubations are presented in Fig. 3. In the 0-15 cm depths, N\(_2\)O production from crop field soils (3.9 ±1.8 µg N\(_2\)O-N kg\(^{-1}\) h\(^{-1}\)) were significantly larger than those from forest buffer soils (-0.07±0.01 µg N\(_2\)O-N kg\(^{-1}\) h\(^{-1}\)), warm season
grass filter soils (0.27 ± 0.21 µg N₂O-N kg⁻¹ h⁻¹) and cool season grass filter soils (0.47 ± 0.41 µg N₂O-N kg⁻¹ h⁻¹) (One way ANOVA p < 0.002). There was no significant difference between N₂O productions from the different riparian buffers soils (Tukey’s studentized range test). All the production rates were not significantly different from zero (95% confidence interval). N₂O production did not show any relationship with soil NH₄⁺ and NO₃⁻ contents (Pearson coefficient r = -0.06 - 0.15 p > 0.1); however, there was a negative trend between N₂O flux and soil pH (Pearson coefficient r = -0.94 p = 0.06). In soil from 15-100 cm depth, N₂O flux from crop field soils and riparian buffer soils were not significantly different (Tukey’s studentized range test). Forest buffer soils (0-15 cm depth) and warm season grass filter soils (30-60 cm and 60-100 cm depths) had negative N₂O fluxes (-0.07 ± 0.01 µg N₂O-N kg⁻¹ h⁻¹, -0.04 ± 0.03 µg N₂O-N kg⁻¹ h⁻¹, and -0.14 ± 0.1 µg N₂O-N kg⁻¹ h⁻¹, respectively) of a magnitude larger than the estimated minimum detectable flux (0.02 µg N₂O-N kg⁻¹ h⁻¹).

There was no significant difference between N₂O emission from soils treated with 10 Pa C₂H₂ or 10 kPa CH₃F (two sample t-test p > 0.05) due to the large variability of the fluxes, especially for the cool-season grass filter soil (Fig. 4). Denitrification N₂O was estimated from N₂O emission from soils treated with 10 Pa C₂H₂ (Equation 2). Nitrous oxide fluxes and their sources in incubated soils with inhibitors are presented in Table 3. The N₂O flux from crop field soils was 0.56 ± 0.18 µg N₂O-N kg⁻¹ h⁻¹ which was significantly higher than fluxes from the forest buffer (0.06 ± 0.01 µg N₂O-N kg⁻¹ h⁻¹), the warm-season grass filter (0.13 ± 0.03 µg N₂O-N kg⁻¹ h⁻¹) and the cool-season grass filter (0.14 ± 0.01 µg N₂O-N kg⁻¹ h⁻¹) (One way ANOVA p < 0.001) soils. There was no difference in N₂O flux among the different riparian buffers (Tukey’s studentized range test). The main source of produced N₂O was nitrifier denitrification in crop field soils and all riparian buffers soils (Table 3). In crop fields, N₂O from nitrifier denitrification and denitrification produced 68.8% and 23.1%, respectively. In the forest buffer, the warm-season grass filter, and the cool-season grass filter, N₂O from nitrifier denitrification led to 59.9%, 58.6% and 56.0% of the N₂O production, respectively. N₂O from other sources (e.g. chemodenitrification and heterotrophic nitrification) was significant in the crop field (7.0%), forest buffer (44.7%), warm-season grass filter (16.5 %), and cool-season grass filter (30.7%) soils. In the forest buffer soils, -0.017 µg N₂O-N kg⁻¹ h⁻¹ was calculated to have been produced during the denitrification process which corresponds to 19.0% of the total N₂O emission.

N₂O from denitrification, nitrifier denitrification and total N₂O flux were positively correlated with the bulk density and negatively correlated with pH and NH₄⁺ (Table 4). Nitrification potential rates
and DEA did not show significant relations with N₂O from nitrification, denitrification, nitrifier denitrification and other sources (Table 3). The ratio of N₂O to N₂ in crop field soils (16.5) was higher than in riparian buffers (the forest buffer soils (6.8), the warm-season grass filter soils (0.88), and the cool-season grass filter soils (0.32)) (Fig. 5), and the ratio of N₂O to N₂ showed a negative correlation with NH₄⁺ (Table 4).

4 Discussion
This study was conducted to identify the source of N₂O and quantify the emissions of N₂O and N₂ from different kinds of vegetated riparian buffer systems and adjacent crop fields. In the following, we will first discuss nitrification potentials and DEA of these soils and later discuss the results from inhibitor experiments including the ratio of N₂O to N₂, the source of N₂O, the negative N₂O fluxes, and uncertainties associated with the inhibition technique.

4.1 Nitrification potential and denitrification enzyme activity
Nitrification potential of soils under the cool-season grass filter (1.9 ± 0.24 mg N kg⁻¹ h⁻¹) was significantly higher than in soils under the crop field or other riparian buffers (0.25-1.14 mg N kg⁻¹ h⁻¹). In the literature, ranges of 0.1-1 mg N kg⁻¹ h⁻¹ have been reported for nitrification potentials (Norton, 2000). Generally, lower values are found in soils under perennial vegetation than in fertilized or manured agricultural soils (Norton, 2000). In contrast to this, we found a higher nitrification potential in the cool-season grass filter soils than in the crop field soils.

Denitrification enzyme activity of soils in the forest buffer and the cool-season grass filter (0.81-1.74 mg N₂O-N kg⁻¹ h⁻¹) were higher than in the crop field and the warm-season grass filter (0.18-0.54 mg N₂O-N kg⁻¹ h⁻¹). Johnson (2003) reported similar values of 0.99-3.16 mg kg⁻¹ h⁻¹ of DEA in the same cool-season grass filter and 0.36-0.38 mg kg⁻¹ h⁻¹ of DEA in the same warm season grass filter. Denitrification enzyme activity measured in this study was also within the range of those measured using a comparable method in other riparian areas (0.03-1.80 mg N₂O-N kg⁻¹ h⁻¹) (Groffman et al. 1992; Pinay et al., 2000; Flite et al. 2001; Clement et al., 2002; Cosandey et al. 2003; Dhondt et al., 2004; Rich and Myrold, 2004; Hunt et al., 2004; McCarty et al. 2007; Oehler et al. 2007; Hunt et al., 2007) and agricultural soils (0.02-0.92 mg N₂O-N kg⁻¹ h⁻¹) (Myrold and Tiedje, 1985; Simek et al. 2000). Decomposition of litter fall and roots results in higher soil C and provides patches of organic matter within riparian buffer soils that help enhance the denitrification process (Gold et al. 1998; Jacinthe et al. 1998; Dornbush et al., 2002; Tufekcioglu et al., 2003; Rotkin-Ellman et al. 2004).
4.2 N₂O flux and N₂O to N₂ ratio

N₂O flux in cropped soils was greater than in any of the riparian buffer soils. The ratio of N₂O to N₂ in the crop field soils (16.5) was also greater than in any of the riparian buffer soils (0.88-6.8). This is consistent with other studies that estimated the ratio of N₂O to N₂ of agricultural soils to be between 0.5-10 (Weier et al., 1993; Cho et al., 1997; Wolf and Brumme, 2003; Zaman et al., 2007; Mkhabela et al., 2008), while the ratio reported in other riparian and natural areas ranged between 0.002-0.38 (Groffman et al, 2000; Bol et al., 2003; Hefting et al., 2006). There was a significant negative correlation between N₂O flux and soil pH within the cropped (pH 5.9) and riparian soils (pH 6.7-7.3). It is well known that N₂O reductase is inhibited at low pH (e.g. Knowles, 1982; Thomsen et al. 1994). The ratio of N₂O to N₂ was found to increase with decreasing soil pH (Nägele and Conrad, 1990; Struwe and Kjøller, 1994; Daum and Schenk et al., 1998). Several laboratory experiments using pH modifying treatments and field experiments where acidifying fertilizers were applied found that at lower soil pH, denitrification liberates more N₂O and the ratio N₂O to N₂ is increased (Koskinen and Keeney, 1982; Weier and Gilliam, 1986; Struwe and Kjøller, 1994; Šimek and Cooper, 2002; Wolf and Brumme, 2003; Venterea, 2007). It is likely that higher N₂O flux and the ratio of N₂O to N₂ in the crop field than in any of the riparian buffer soils may be explained by lower soil pH in crop fields.

4.3 N₂O source

More than a half of the N₂O emitted from cropped soils and soils under perennial vegetation was found to have originated from nitrifier denitrification according to the method used. Nitrifier denitrification is the pathway whereby ammonia (NH₃) is oxidized to nitrite (NO₂⁻), followed by the reduction of NO₂⁻ to nitric oxide (NO), N₂O and molecular nitrogen (N₂) (Wrage et al., 2001). The greater N₂O producuction by nitrifier denitrification in low pH crop field soils supports Venterea (2007)’s argument that nitrifier denitrification may be promoted at lower pH. However, Wrage et al. (2004c) reported no significant effect of pH on N₂O produced by nitrifier denitrification, while NO₂⁻ stimulated, and low O₂ decreased, emissions. Previous research has shown the source of N₂O emissions from soil to vary under different ecosystems. For example, Ambus (1998) found that nitrification-associated N₂O emission contributed more than 60% of total N₂O production within a riparian grassland. Kester et al. (1997) reported nitrification dominated N₂O production in the soils collected in a meadow in the Netherlands in spring, and denitrification was the main source of N₂O in the soils collected in the same site in the
autumn. Tilsner et al. (2003) reported denitrification as the predominant N$_2$O source in a meadow in Germany. Similarly, denitrification has been reported as the most important source for N$_2$O production from soils in various forested systems (MacDonald et al., 1997; Ambus, 1998; Wolf and Brumme, 2002 and 2003; Ambus et al., 2006). However, these studies did not separate nitrifier denitrification from nitrification or denitrification. Recent studies have reported nitrifier denitrification as a main source of soil-emitted N$_2$O. For example, Webster and Hopkins (1996) reported that denitrifying nitrifiers were the predominant source of N$_2$O emitted from the drier soils in arable fields. Using a natural abundance incubation method, Wrage et al. (2004a) found N$_2$O production in European grasslands to be generally dominated by reduction processes, either denitrification or nitrifier denitrification. Wrage et al. (2005), using a dual-isotope labeling method, identified nitrifier denitrification and fertilizer denitrification to be the main sources of N$_2$O, each accounting for 44% of the total N$_2$O emission from soils sampled from an arable field. These results corroborated those found with soil inhibition methods conducted at the same time. Ma et al. (2007) also suggested nitrifier denitrification to be the dominant source of N$_2$O emissions from soils in arctic lowlands, and Charpentier et al. (2007) reported that nitrifier denitrification could account for 40-50% of soil-emitted N$_2$O within a South Pacific subtropical gyre.

4.4 Negative N$_2$O flux

Significant negative N$_2$O fluxes (-0.04 to -0.14 ± 0.1 N$_2$O-N µg kg$^{-1}$ h$^{-1}$) were observed from soils of the riparian forest buffer, (Fig. 3) which the inhibition tests indicated were the result of denitrification. As reviewed by Chapuis-Lardy et al. (2007), such negative N$_2$O fluxes may indicate consumption of atmospheric N$_2$O within soils. Since Blackmer and Bremner (1976) reported constant N$_2$O reduction rates of between -0.57 and -1.11 µg N g$^{-1}$ d$^{-1}$ from nine cultivated Iowa soils, net negative N$_2$O fluxes have been observed under various conditions in both incubation experiments and field studies from the tropics to temperate areas, and within natural and agricultural systems (Chapuis-Lardy et al., 2007). Chapuis-Lardy et al. (2007) suggested that complete denitrification (reduction of N$_2$O to N$_2$) is responsible for the observed negative N$_2$O fluxes. This conclusion is supported by Vieten et al. (2008), who reported that assimilatory reduction of N$_2$O was not a significant factor for negative N$_2$O fluxes within grasslands and forests soils in Switzerland and Germany. Chapuis-Lardy et al. (2007) summarized conditions promoting negative N$_2$O fluxes within soils as follows: 1) negative N$_2$O fluxes seem to be stimulated by low availability of mineral N, 2) soil temperature has an effect but this is not straightforward, and 3) soil pH and O$_2$ content seem to be negatively correlated with N$_2$O reduction. Based on current knowledge, it is not yet possible to clearly identify a set of conditions.
promoting negative N$_2$O fluxes (Chapuis-Lardy et al., 2007). Our data showed that soils in the riparian forest buffer had higher DEA than soils in the cool-season or warm-season grass buffers and in the crop field. This study supports the proposal that complete denitrification may be responsible for negative N$_2$O fluxes.

4.5 Limitations of inhibition techniques for distinguishing N$_2$O source

In this study, incubation experiments with the inhibitors CH$_3$F, C$_2$H$_2$ and O$_2$ were used to distinguish between nitrification and nitrifier denitrification as sources of N$_2$O. Miller et al. (1993) suggested that 10 kPa CH$_3$F is useful in discriminating N$_2$O production as an alternative of C$_2$H$_2$. However, our results indicated that the inhibitory effect of both CH$_3$F and C$_2$H$_2$ was highly variable within the soils studied, and that there was no significant difference in N$_2$O emission from soils treated with either C$_2$H$_2$ or CH$_3$F (Fig. 4). We observed that several of the soil incubations (especially, cool season grass filter) with CH$_3$F or C$_2$H$_2$ produced (Fig. 4) more N$_2$O than the controls produced (Fig. 5). Similar results were reported by Wrage et al. (2004c) and the results suggest that CH$_3$F and C$_2$H$_2$ incompletely inhibit NH$_3$ oxidation and both autotrophic nitrification and nitrifier denitrification (Wrage et al., 2004c). This incomplete inhibition may lead to an underestimation of both nitrification and nitrifier denitrification and an overestimation of denitrification and other sources (chemodenitrification and heterotrophic nitrification) (Wrage et al., 2004c). Thus, a possible qualification to interpretation of our data regarding the sources of N$_2$O and the ratio of N$_2$O to N$_2$ may issue from the uncertainties associated with the inhibition technique.

4.6 Implications for management of riparian buffers

Our data showed higher DEA in soils of riparian buffers than those of crop fields and this suggests that soils in riparian buffers have a higher potential for denitrification than crop field soils. Inhibitor incubation experiments showed that (nitrifier) denitrification was the main source of N$_2$O in soils of riparian buffers and riparian buffer soils had less N$_2$O flux with lower N$_2$O to N$_2$ ratio than crop field soils. These are supported by the results that soil N$_2$O emission was significantly less in the riparian buffers than in the crop field in 2006-2007 (Kim, D.G., 2008. Emission of the greenhouse gas nitrous oxide from riparian forest buffers, warm-season and cool-season grass filters, and crop fields, in this dissertation). These results suggest that N$_2$O emissions from soils in all riparian buffers were significantly less than those in the crop field and the riparian buffers reducing NPS pollutant problems (Schultz et al. 2003) should not be considered a trade-off for global warming and ozone depletion problems.
References


Williams-Jacobse, J.G.F.M. (Eds.), Non CO2 greenhouse gases: scientific understanding, control points and policy aspects. Millpress, Rotterdam, pp. 159–166.


Šimek, M., Cooper, J. E., 2002. The influence of soil pH on denitrification: progress towards the understanding of this interaction over the last 50 years. European Journal of Soil Science 53, 345-354.


Table 1. Inhibitors used on the 0-15 cm intact soil cores collected in September 2007 and the effects on soil processes generating N₂O.

<table>
<thead>
<tr>
<th>Affected process</th>
<th>Control (C)</th>
<th>10 Pa C₂H₂ (A)</th>
<th>10 kPa CH₃F (M)</th>
<th>10 kPa C₂H₂ (AA) †</th>
<th>100 kPa O₂ (O)</th>
<th>10 Pa C₂H₂ and 100 kPa O₂ (AO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrification</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Nitrifier denitrification</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Denitrification</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Other</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

† Ten kPa C₂H₂ inhibits the reduction of N₂O to N₂ in the last step of denitrification. So the final product of denitrification is N₂O.

(+) process can take place; (-) process is blocked; after Davidson et al. (1986) and Webster and Hopkins (1996). The letters given in brackets in the first row are the abbreviations used in the text for this incubation.
Table 2. Soil properties (mean ± standard error) ($n = 6-9$ except bulk density ($n = 27$)) of the sites. Soil samples (depth 0-15 cm) were collected in a forest buffer, a warm-season grass filter, a cool-season grass filter, and an adjacent crop field in Oct. 2006 and Sept. 2007.

<table>
<thead>
<tr>
<th>Site</th>
<th>Soil texture†</th>
<th>Bulk density mg m$^{-3}$</th>
<th>pH</th>
<th>TC g kg$^{-1}$ soil</th>
<th>TN mg N kg$^{-1}$ soil</th>
<th>NH$_4$-N</th>
<th>NO$_3$-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crop field</td>
<td>Loam</td>
<td>1.67 ± 0.02a‡</td>
<td>5.9 ± 0.1c</td>
<td>22.8 ± 1.0c</td>
<td>1.9 ± 0.1c</td>
<td>1.7 ± 0.2b</td>
<td>1.2 ± 0.5a</td>
</tr>
<tr>
<td>Forest buffer</td>
<td>Loam, Sandy loam</td>
<td>1.10 ± 0.03c</td>
<td>7.3 ± 0.1a</td>
<td>42.9 ± 3.2a</td>
<td>3.8 ± 0.3a</td>
<td>4.1 ± 0.6a</td>
<td>0.7 ± 0.2a</td>
</tr>
<tr>
<td>Warm-season grass filter</td>
<td>Loam</td>
<td>1.29 ± 0.05b</td>
<td>6.7 ± 0.2b</td>
<td>29.1 ± 2.7bc</td>
<td>2.6 ± 0.2bc</td>
<td>3.9 ± 0.5a</td>
<td>0.2 ± 0.1a</td>
</tr>
<tr>
<td>Cool-season grass filter</td>
<td>Loam</td>
<td>1.19 ± 0.04bc</td>
<td>6.9 ± 0.1ab</td>
<td>32.4 ± 1.6bc</td>
<td>2.9 ± 0.1b</td>
<td>4.3 ± 0.4a</td>
<td>0.9 ± 0.3a</td>
</tr>
</tbody>
</table>

† Marquez et al., 2004
‡ Values in the same column followed by a different letter are significantly different ($p < 0.05$)
Table 3. Nitrous oxide fluxes by sources in incubated soils from the crop field, forest buffer, warm-season grass filter, and cool-season grass filter. The percentage inside a bracket is the portion of the flux in the total N$_2$O flux.

<table>
<thead>
<tr>
<th>Site</th>
<th>Unit</th>
<th>Nitrification</th>
<th>Denitrification†</th>
<th>Nitrifier denitrification</th>
<th>Others‡</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crop field</td>
<td>N$_2$O-N µg kg$^{-1}$ hr$^{-1}$</td>
<td>5.43 $\times 10^{-3}$ (10%)</td>
<td>1.29 $\times 10^{-1}$ (23.2%)</td>
<td>3.83 $\times 10^{-1}$ (68.8%)</td>
<td>3.91 $\times 10^{-2}$ (7.0%)</td>
<td>0.56 ± 0.18a§</td>
</tr>
<tr>
<td>Forest buffer</td>
<td>N$_2$O-N µg kg$^{-1}$ hr$^{-1}$</td>
<td>8.88 $\times 10^{-3}$ (14.4%)</td>
<td>-1.17 $\times 10^{-2}$ (-19.0%)</td>
<td>3.68 $\times 10^{-2}$ (59.9%)</td>
<td>2.75 $\times 10^{-2}$ (44.7%)</td>
<td>0.06 ± 0.01b</td>
</tr>
<tr>
<td>Warm-season grass filter</td>
<td>N$_2$O-N µg kg$^{-1}$ hr$^{-1}$</td>
<td>2.95 $\times 10^{-2}$ (22.7%)</td>
<td>2.80 $\times 10^{-3}$ (2.2%)</td>
<td>7.63 $\times 10^{-2}$ (58.6%)</td>
<td>2.15 $\times 10^{-2}$ (16.5%)</td>
<td>0.13 ± 0.03b</td>
</tr>
<tr>
<td>Cool-season grass filter</td>
<td>N$_2$O-N µg kg$^{-1}$ hr$^{-1}$</td>
<td>1.08 $\times 10^{-2}$ (7.8%)</td>
<td>7.73 $\times 10^{-3}$ (5.5%)</td>
<td>7.82 $\times 10^{-2}$ (56.0%)</td>
<td>4.28 $\times 10^{-2}$ (30.7%)</td>
<td>0.14 ± 0.01b</td>
</tr>
</tbody>
</table>

†Denitrification N$_2$O was estimated from laboratory incubations with 10 Pa C$_2$H$_2$.
‡E.g. chemodenitrification and heterotrophic nitrification
§Values in the same column followed by a different letter are significantly different ($p < 0.001$).
Table 4. Correlation analyses between soil properties and nitrification potential, DEA, N\textsubscript{2}O sources, N\textsubscript{2}O:N\textsubscript{2}, and total N\textsubscript{2}O emission.

<table>
<thead>
<tr>
<th></th>
<th>Bulk density</th>
<th>pH</th>
<th>TC</th>
<th>TN</th>
<th>NH\textsubscript{4}-N</th>
<th>NO\textsubscript{3}-N</th>
<th>NP</th>
<th>DEA1</th>
<th>DEA2</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP</td>
<td>-0.57</td>
<td>0.53</td>
<td>0.49</td>
<td>0.5</td>
<td>0.57</td>
<td>0.26</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DEA1</td>
<td>-0.66</td>
<td>0.66</td>
<td>0.67</td>
<td>0.67</td>
<td>0.62</td>
<td>0.2</td>
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* p < 0.05

NP: nitrification potential rate, DEA 1: denitrification enzyme activity rate (Oct. 2006), DEA 2: denitrification enzyme activity rate (Sept. 2007), N\textsubscript{2}O_N: N\textsubscript{2}O from nitrification, N\textsubscript{2}O_D: N\textsubscript{2}O from denitrification, N\textsubscript{2}O_ND: N\textsubscript{2}O from nitrifier denitrification, N\textsubscript{2}O_Others: N\textsubscript{2}O from other source expect nitrification, denitrification and nitrifier denitrification, N\textsubscript{2}O_total : total N\textsubscript{2}O emission from the incubation experiment.
Fig. 1. Nitrification potential rate ($n = 3$) in soil (0-15 cm depth) under a crop field, forest buffer, warm-season grass filter and cool-season grass filter, conducted in September 2007. Error bars indicate standard errors. A different letter indicates significant difference at $p < 0.05$. 
Fig. 2. Denitrification enzyme activity ($n = 3$) in soils (0-15cm) under crop field, forest buffer, warm-season grass filter and cool-season grass filter, conducted in Oct. 2006 (A) and Sept. 2007 (B). Error bars indicate standard errors. A different letter indicates significant difference at $p < 0.05$. 
Fig. 3. Nitrous oxide production ($n = 3$) in incubated soils (12°C) under crop field, forest buffer, warm-season grass filter, and cool-season grass filter, conducted in Oct. 2006. Error bars indicate standard errors. A different letter indicates significant difference at $p < 0.05$. 
Fig. 4. Nitrous oxide production \((n = 3)\) from soils treated with each 10 Pa C\(_2\)H\(_2\) and 10 kPa CH\(_3\)F in soils of all the sites. Error bars indicate standard errors.
Fig. 5. The ratio of N$_2$O to N$_2$ of incubated soils (22°C) from the crop field, forest buffer, warm-season grass filter and cool-season grass filter, conducted in September 2007.
Production and consumption of methane in riparian forest buffers, warm-season and cool-season grass filters and adjacent crop fields soils

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Abstract

Riparian forest buffers and grass filters restored from cultivated crop fields to reduce non-point source pollution may have benefits as sinks of CH$_4$. On the other hand, these same riparian ecosystems are subjected to seasonal flooding and high soil moisture contents, which may provide favorable conditions for CH$_4$ production. It is therefore important to quantify the production and consumption of CH$_4$ from different kinds of vegetated riparian buffer systems and adjacent crop fields and compare their rates. We measured soil properties, weather conditions, and diel and seasonal variations of CH$_4$ flux in 7 to 17 year-old restored riparian forest buffers, warm-season and cool-season grass filters, and an adjacent crop field located in the Bear Creek watershed in central Iowa. We also conducted soil incubation experiments to quantify the production and consumption of CH$_4$ in vitro. The forest buffer and grass filter soils had significantly lower bulk density; and higher pH, total carbon (TC), total nitrogen (TN), and ammonium (NH$_4^+$) than those in the crop field. Soil incubation experiments indicated that CH$_4$ consumption was higher than CH$_4$ production in the forest buffer and grass filter soils, while crop field soils showed the opposite response. Diel and seasonal CH$_4$ fluxes in the crop field soil were not observed to be significantly different from those in the forest buffer and grass filter soils. In addition, no significant difference in CH$_4$ flux was found between the forest buffer and grass filter soils. Annual CH$_4$ flux was -0.80 kg CH$_4$-C ha$^{-1}$ yr$^{-1}$ (-1.06 kg CH$_4$ ha$^{-1}$ yr$^{-1}$), -0.46 kg CH$_4$-C ha$^{-1}$ yr$^{-1}$ (-0.61 kg CH$_4$ ha$^{-1}$ yr$^{-1}$), and 0.04 kg CH$_4$-C ha$^{-1}$ yr$^{-1}$ (0.05 kg CH$_4$ ha$^{-1}$ yr$^{-1}$) in crop fields, forest buffers and grass filters, respectively. The annual CH$_4$ flux in forest buffers and grass filters were not significantly different from zero, and the annual CH$_4$ flux in crop fields, forest buffers and grass filters were not significantly different one another. These results indicate that CH$_4$ flux in the crop field, forest buffers and grass filters were not different and CH$_4$ flux was not changed in the forest buffers and grass filters soils, despite that soil properties have changed significantly since the planting of the forest buffers and the grass filters.
1 Introduction

Methane (CH$_4$) has the second-largest radiative forcing of the long lived greenhouse gases after carbon dioxide (CO$_2$) (Forster et al. 2007). The global atmospheric concentration of CH$_4$ has been increased from a pre-industrial value of about 715 ppb to 1774 ppb in 2005, and this increase is very likely due to anthropogenic activities, predominantly agricultural activities and fossil fuel use (IPCC, 2007). Soils both produce and consume CH$_4$ (Topp and Pattey, 1997; Le Mer and Roger, 2001). In a recent review, Dutaur and Verchot (2007) summarized the processes as following: “The net CH$_4$ flux is the result of the balance between the two offsetting processes of methanogenesis (microbial production) and methanotrophy (microbial consumption). Methanogenesis is the process of microbial production of CH$_4$ under anaerobic conditions. Methanotrophy is the dominant process in upland soils, where oxidation generally exceeds production and there is a net uptake by the soil of CH$_4$ from the atmosphere.”

Non-point source (NPS) pollutants such as sediment, nutrients such as nitrogen and phosphorus, and pesticides are the major causes of water quality problems around the world (Duda 1993; Tonderski., 1996; Sabater et al., 2003). Riparian buffers have been recommended as one of the most effective tools for coping with NPS pollution (Hubbard et al. 2004; Mayer et al., 2007). Some of the important functions of riparian buffers related to NPS pollution control are filtering and retaining sediment and immobilizing, storing, and transforming chemical inputs from uplands (Schultz et al., 2000).

It is well known that forest soils are the most active sink of CH$_4$, followed by grass lands and cultivated soils, and that the uptake potential of upland soils is reduced by cultivation and especially by ammonium-N fertilizer application (Topp and Pattey, 1997; Le Mer and Roger, 2001; Dutaur and Verchot, 2007). It has been reported that land-use change can also influence CH$_4$ uptake rates. For instance, higher rates of CH$_4$ oxidation have been observed in soils afforested from croplands or pastures (e.g. Ball et al., 2002; Merino et al., 2004; Tate et al., 2007). The change in CH$_4$ uptake resulting from land-use change is attributed to changes in soil porosity, moisture content, and the number of methanotrophs (Priemé et al., 1997). Therefore, riparian forest buffers and grass filters restored from cultivated crop fields for diminishing non-point source pollution may have benefits as sinks of CH$_4$.

Riparian buffers are often flooded and also sustain relatively high soil moisture conditions caused by high water tables, long residence time and slow discharge (Schutlz et al. 2000). These conditions may be favorable for CH$_4$ production. Ambus and Christensen (1995) reported that CH$_4$ was
produced in temporarily flooded riparian areas at rates of 7,877 mg C m\(^{-2}\) yr\(^{-1}\). Methane was produced from riparian areas of ponded depressions in northern Germany at rates of 33.3 -33,030.8 mg CH\(_4\)-C m\(^{-2}\) yr\(^{-1}\) (Merbach et al., 1996). These results suggest that restored riparian buffers may be a significant source of CH\(_4\), at least when they are flooded. Therefore, the benefits of reduced non-point source pollution from riparian buffers may be offset by increased greenhouse gas emissions. It therefore is important to quantify the emission and consumption of CH\(_4\) from different kinds of vegetated riparian buffer systems, and evaluate their significance as CH\(_4\) sinks or sources, and to identify ways to maximize their sink capacities. This study attempted to answer the following questions: Are riparian buffers a more significant source of CH\(_4\) than adjacent crop fields? Do different kinds of vegetated riparian buffer systems have different CH\(_4\) fluxes?

2 Materials and Methods

2.1 Study Site
The study area consists of three forest buffers, three warm-season grass filters, one cool-season grass filter, and one adjacent crop field that are located in the Bear Creek watershed, Story County and Hamilton County, Iowa, United States (42° 11' N, 93° 30' W). The Bear Creek watershed is a typical, predominantly agricultural watershed in north central Iowa, USA. Most of the area was originally covered with prairie vegetation except for riparian forests along the lower third of the creek. Now, most of the area is cultivated with soybeans (Glycine max L. Merr.) and corn (Zea mays L.), which are grown in rotation. Restored forest buffers, and warm-season and cool-season grass filters were previously under row-crop cultivation or livestock grazing. The forest buffers and grass filters ranged in age from 7 to 17 years since establishment. Tree species included silver maple (Acer saccharinum L.), green ash (Fraxinus pennsylvanica Marsh.), black walnut (Juglans nigra L.), willow (Salix spp.), cottonwood hybrids (Populus spp.), red oak (Quercus rubra L.), bur oak (Quercus bicolor Willd). Shrub species include chokecherry (Prunus virginiana L.), Nanking cherry (Prunus tomentosa Thunb), wild plum (Prunus americana Marsh), red osier dogwood (Cornus stolonifera Michx), and ninebark (Physocarpus opulifolius Max.). Warm-season grasses include native grasses such as Indian grass (Sorghastrum nutans), big bluestem (Andropogon gerardi), and little bluestem (Andropogon scoparius) and numerous forbs (purple prairie clover (Dalea pupurea); bottle gentian (Gentiana andrewsii); prairie blazing star (Liatris pycnostachya), and others). The cool-season grass buffers are dominated by non-native forage grasses (Bromus inermis Leysser., Phleum pratense L. and Poa pratensis L). Details of the riparian buffer design, placement, and plant species are given in Schultz et al. (1995). The crop fields adjacent to the riparian buffers served as a control, representing
conditions prior to buffer establishment. The crop fields are cultivated under a soybean (*Glycine max* L. Merr.) and corn (*Zea mays* L.) rotation, and soybean was the crop in 2007. Pelletized urea (134 kg N ha$^{-1}$) is applied during corn rotation years and fall chisel plowing (15-20 cm depth) is applied. The major soil association in the watershed is the Clarion- Webster- Nicolett association with minor areas of Clarion- Storden- Coland, and Canisteo-Okoboji-Nicolett (Dewitt, 1984). The areas used in this study are all located on Coland soil (fine-loamy,mixed, mesic Cumulic Haplaquoll) which is well drained to poorly drained and formed from till or local alluvium and colluvium derived from till (DeWitt, 1984).

2.2 Field gas sampling, methane gas analyzing and flux calculation

Soil methane flux from riparian forest buffers, warm-season and cool-season grass filters and crop fields were measured in 2007. Five points were randomly selected in each of three forest buffers, three warm season-grass filters, one cool-season grass filter, and one crop field for collecting CH$_4$ gas and soil sampling. Methane gas was regularly collected with static vented chambers (PVC, diameter - 30 cm × height - 15 cm with a vent and a thermometer) weekly or biweekly (mid morning) to know the temporal variation of CH$_4$ flux. To investigate changes of CH$_4$ flux through time within a day, diel variation of CH$_4$ flux was measured on July 16-17, 2007. Three points were randomly selected in a forest buffer, a warm-season grass filter, a cool-season grass filter, and an adjacent crop field for gas collection and soil sampling. We collected gas samples every 3 hr for a day (24 hr). For CH$_4$ flux determinations, ten mL of air was sampled from the chamber with a polypropylene syringe at every 15 min for 45 min. Samples were stored 6-mL glass vials fit with butyl rubber stoppers until analysis of CH$_4$. Methane concentrations in samples were determined with a gas chromatography instrument (Model GC17A; Shimadzu, Kyoto, Japan) equipped with a flame ionization detector and a stainless steel column (0.3175 cm diameter × 74.54 cm long) with Porapak Q (80–100 mesh). Samples were introduced into the gas chromatograph using an autosampler described by Arnold et al. (2001). Methane fluxes were obtained by applying linear regression to the CH$_4$ concentration versus time data (Holland et al., 1999). The minimum detectable CH$_4$ flux was calculated with average of standard deviations of ambient air CH$_4$ concentrations analyzed by the GC ($n = 500$), chamber volume, chamber footprint, and chamber development time as following:

$$\text{Minimum detectable CH}_4\text{ flux} = \frac{2 \times \text{average of standard deviation} \times \text{chamber volume}}{\text{chamber footprint} \times \text{total chamber development time}}$$ (1)
Our estimated minimum detectable flux was 33.2 µg CH$_4$-C m$^{-2}$ h$^{-1}$. Some of the fluxes measured from the individual chambers were smaller than our detection limit. The measured values of these "nondetects" were included in computing mean fluxes (Gilbert, 1987; Chan and Parkin, 2001). Cumulative CH$_4$ fluxes from each site over the 1-day study period (July 16-17, 2007) and the 1-yr study period (Jan.-Dec. 2007) were calculated. Cumulative CH$_4$ fluxes were calculated by linear interpolation and numerical integration between sampling times.

Soil temperature (ST) and soil water content (SWC) were measured simultaneously with CH$_4$ gas collection around the chamber at a 5 cm depth using a digital thermocouple (ThermoWorks, U.S.) and a digital soil moisture meter (HydroSense®, Campbell Scientific, Inc., U.S.). Air temperature was measured simultaneously with CH$_4$ gas collection inside and outside the gas chamber. A soil temperature and soil moisture data logger (HOBO® Micro station data logger with sensors, Onset Computer Corporation, U.S.) was installed at 5 cm soil depths around a chamber per a site to measure hourly ST and SWC at each site. Daily rainfall and snow data were provided by a nearest meteorology station (Colo, IA, 42° 1' N, 93° 19' W) (Herzmann, 2004).

2.3 Soil Sampling and Analysis

Six intact soil cores (5.3-cm diameter) were collected to a depth of 15 cm in each of three plots of a forest buffer, a warm-season grass filter, a cool-season grass filter, and an adjacent crop field in Oct. 2006 and Sept. 2007. A plastic sleeve liner was placed inside the metal core tube and the liner with the intact soil core was pulled from the tube and capped for transport to the laboratory. Incubation experiments with the intact soil cores were conducted within 4hr after sampling, and soil samples were stored at 4°C until analysis. Soil pH was determined by using 1:1 diluted soil solution (Thomas, 1996). Gravimetric moisture content was determined by oven drying a subsample at 105°C for 24 hrs (Topp and Ferrè, 2002) and bulk density was determined by the core method (Grossman and Reinsch, 2002). For C and N analysis, soils were air dried at room temperature, sieved (2mm) and then gravimetric moisture content on the air-dried soils was determined. Total C (TC) and total N (TN) were measured using a Flash EA 2000 (ThermoFinnigan, Italy) direct combustion instrument. Soil inorganic N was extracted with 2M potassium chloride (KCl) and stored at 4°C until filtration (within 4hr of sampling) (Van Miegroet, 1995). Filtrates were frozen and stored until further analysis. Nitrate (NO$_3^-$) and ammonium (NH$_4^+$) contents were analyzed by colorimetric method (Mulvaney, 1996) with an auto analyzer (Quikchem 8000 FIA+, Lachat Instruments, Milwaukee, WI).
2.4 Soil incubation with control and 10 Pa acetylene (C$_2$H$_2$)

Production and consumption of CH$_4$ and net CH$_4$ flux were determined using collected intact soil cores (0-15cm depth) in September 2007. Six intact soil cores (diameter 5.3 cm × length 8 cm) collected at each site were inserted into three 350 mL glass bottles with gas-tight lids containing a gas-sampling port and all bottles were sealed. Three soil cores from each site were treated with 10 Pa C$_2$H$_2$ and other three soil cores from each site were retained as controls. They were incubated at the 22°C (on-site soil temperature) condition. Ten mL of air was sampled from the bottles with a polypropylene syringe 3 hr and 16 hr later and then it was stored until analyzing. The storing, gas analyzing and flux calculation were described above. Methane production was estimated from laboratory incubations in which CH$_4$ oxidation was inhibited by 10 Pa C$_2$H$_2$ (Chan and Parkin, 2000). Methane consumption was estimated from the difference between CH$_4$ flux under no C$_2$H$_2$ (net CH$_4$ flux) and that determined for CH$_4$ production. The amounts of production and consumption of CH$_4$ and net CH$_4$ flux were calculated as follows.

Net CH$_4$ flux = CH$_4$ flux under no C$_2$H$_2$  \hspace{1cm} (2)

CH$_4$ production = CH$_4$ flux under 10 Pa C$_2$H$_2$  \hspace{1cm} (3)

CH$_4$ consumption = CH$_4$ production - net CH$_4$ flux  \hspace{1cm} (4)

2.5 Statistical analyses

For analyzing the normal distribution of the data the Shapiro-Wilk normality test was performed. A two-sample t-test was used to evaluate differences in soil C measured in 1998-1999 and 2006-2007 in the same sites. One-way analysis of variance (ANOVA) was used to evaluate the differences in soil properties, and diel and seasonal CH$_4$ flux by site. When the standard assumptions of normality were violated, non-parametric Kruskal-Wallis one-way ANOVA on ranks was used. Differences were considered significant at the p < 0.05 level. To determine the relationship between soil properties and CH$_4$ flux, correlation analysis using the GLM procedure was applied. These statistical analyses were conducted by SAS ver 8.1 (SAS institute, 1999).

3 Results

3.1 Soil Properties

The texture of all treatment site soils was loam (Marquez et al., 2004) (Table 1). Soils in riparian buffers had significantly lower bulk density (one-way ANOVA $P < 0.0001$); and higher pH ($P =$
0.0003), TC (P < 0.01), TN (P < 0.01), and NH$_4^+$ (P < 0.0001). Soil NO$_3^-$ was not significantly different among the sites (P = 0.3) (Table 1).

From 15 June to 15 Aug. 2007 (93 d), average daily soil moisture was 8.7 ± 0.2%, 16.9 ± 0.2%, and 19.0 ± 0.2% in the crop fields (n = 93), forest buffers (n = 93), and grass filters (n = 93), respectively and they were significantly different (one-way ANOVA P < 0.0001). During the same period, average daily soil temperature in the crop fields (22.8 ± 0.3°C, n = 93) was significantly higher than those in forest buffers and grass filters (21.8°C, n = 93) (P = 0.009) (Fig. 3).

3.2 Soil incubation experiments

In the crop field soils, the magnitude of production (2.50×10^{-5} µg CH$_4$-C kg$^{-1}$ hr$^{-1}$) was larger than the magnitude of consumption (1.30×10^{-5} µg CH$_4$ kg$^{-1}$ hr$^{-1}$) and net CH$_4$ flux was 1.19×10^{-5} ± 2.0×10^{-5} µg CH$_4$-C kg$^{-1}$ hr$^{-1}$ (Fig. 1). However, in the forest buffer, warm-season grass filter and cool-season grass filter soils, the magnitude of consumption was larger than the magnitude of production, and CH$_4$ flux was -4.47×10^{-5} ± 2.3×10^{-5} µg CH$_4$-C kg$^{-1}$ hr$^{-1}$, -1.21×10^{-5} ± 5.3×10^{-6} µg CH$_4$-C kg$^{-1}$ hr$^{-1}$, -1.48×10^{-5} ± 1.2×10^{-5} µg CH$_4$-C kg$^{-1}$ hr$^{-1}$, respectively (Fig. 1). All of the CH$_4$ fluxes were not significantly different (one-way ANOVA P > 0.05) (Fig. 1).

3.3 Diel variation of CH$_4$ flux and affecting factors

During 16-17 July 2007, diel variation of CH$_4$ flux showed that there was no significant difference of CH$_4$ flux measured in every 3hr in the crop field (Kruskal-Wallis one-way ANOVA P = 0.263), forest buffer (Kruskal-Wallis one-way ANOVA P = 0.867), warm-season grass filter (one-way ANOVA P = 0.22) and cool-season grass filter (Kruskal-Wallis one-way ANOVA P = 0.098). Also there was no significant difference of CH$_4$ flux by the sites (one-way ANOVA P = 0.14) (Fig.2). Average of CH$_4$ flux (n = 8) in crop fields, forest buffer, warm-season grass filter and cool-season grass filter was 6.90 ± 12.23 µg CH$_4$-C m$^{-2}$ hr$^{-1}$, -23.64 ± 8.12 µg CH$_4$-C m$^{-2}$ hr$^{-1}$, -19.13 ± 10.55 µg CH$_4$-C m$^{-2}$ hr$^{-1}$, and -19.13 ± 10.55 µg CH$_4$-C m$^{-2}$ hr$^{-1}$, respectively. Variation of CH$_4$ flux in crop fields and riparian buffers did not have any correlation with soil temperature (P > 0.05). Cumulative CH$_4$ flux for the day (24hr) in the crop field, forest buffer, warm-season grass filter and cool-season grass filter was 165.7 µg CH$_4$-C m$^{-2}$ d$^{-1}$ (220.9 µg CH$_4$ m$^{-2}$ d$^{-1}$), -567.3 µg CH$_4$-C m$^{-2}$ d$^{-1}$ (-756.4 µg CH$_4$ m$^{-2}$ d$^{-1}$), -459.1 µg CH$_4$-C m$^{-2}$ d$^{-1}$ (-612.1 µg CH$_4$ m$^{-2}$ d$^{-1}$), and -612.7 µg CH$_4$-C m$^{-2}$ d$^{-1}$ (-816.9 µg CH$_4$ m$^{-2}$ d$^{-1}$), respectively (Fig.2).
3.4 Seasonal variation of CH$_4$ flux and annual CH$_4$ emission

Since there was no significant changes of CH$_4$ flux through time within a day (Fig. 2), daily fluxes were calculated by multiplying measured hourly fluxes (mid morning) by 24hr. Observed maximum positive daily CH$_4$ flux was 2,373.3 µg CH$_4$-C m$^{-2}$ d$^{-1}$ (Aug. 7), 2,431.7 µg CH$_4$-C m$^{-2}$ d$^{-1}$ (May 1), and 1,633.6 µg CH$_4$-C m$^{-2}$ d$^{-1}$ (Sept. 11) in crop fields, forest buffers and grass filters, respectively (Fig. 3). Observed maximum negative daily CH$_4$ flux was -2,181.6 µg CH$_4$-C m$^{-2}$ d$^{-1}$ (Jan. 16), -2,634.0 µg CH$_4$-C m$^{-2}$ d$^{-1}$ (Sept. 20), and -3,741.5 µg CH$_4$-C m$^{-2}$ d$^{-1}$ (Sept. 20) in crop fields, forest buffers and grass filters, respectively (Fig. 3). The average of observed daily CH$_4$ flux was -209.1 ± 121.2 µg CH$_4$-C m$^{-2}$ d$^{-1}$ (n = 40), -511 to 927.9 µg CH$_4$-C m$^{-2}$ d$^{-1}$ (n = 45 - 50), and -235.7 to 146.0 µg CH$_4$-C m$^{-2}$ d$^{-1}$ (n = 41 - 49) in the crop field, forest buffers and grass filters, respectively, and they are not significantly different (one-way ANOVA P = 0.56) (Fig. 4). There were no significant relationships between CH$_4$ flux and soil moisture (P > 0.05) or soil temperature (P > 0.05) in each of the sites. Cumulative CH$_4$ flux from Jan. to Dec. 2007 was -0.80 kg CH$_4$-C ha$^{-1}$ yr$^{-1}$ (-1.06 kg CH$_4$ ha$^{-1}$ yr$^{-1}$) (n = 1), -0.46 ± 0.48 kg CH$_4$-C ha$^{-1}$ yr$^{-1}$ (-0.62 ± 0.64 kg CH$_4$ ha$^{-1}$ yr$^{-1}$) (n = 3), and 0.04 ± 0.2 kg CH$_4$-C ha$^{-1}$ yr$^{-1}$ (0.06 ± 0.27 kg CH$_4$ ha$^{-1}$ yr$^{-1}$) (n = 4) in the crop field, forest buffers and grass filters, in respect, and the cumulative CH$_4$ flux in forest buffers (95% confidence interval (CI): -2.54 to 1.61 kg CH$_4$-C ha$^{-1}$ yr$^{-1}$) and grass filters (95% CI: -0.51 to 0.61 kg CH$_4$-C ha$^{-1}$ yr$^{-1}$) are not significantly different from zero. The cumulative CH$_4$ flux in the crop fields, forest buffers and grass filters are not significantly different one another (one-way ANOVA P = 0.40) (Fig. 5).

4 Discussions

4.1 Change of soil properties after restoration of riparian buffers

Soils in forest buffers and grass filters had significantly lower bulk density, higher pH, TC, TN, and NH$_4^+$ than those in adjacent crop fields. This suggests soil properties have been significantly changed since riparian buffers were established on the sites previously under row-crop cultivation. In the same sites, soil C (0-15cm soil depth) was 30.4 ± 1.6 g kg$^{-1}$ (n = 6), 24.4 ± 1.0 g kg$^{-1}$ (n = 6), and 31.0 ± 1.8 g kg$^{-1}$ (n = 6), in forest buffer, warm-season grass filter, and cool-season grass filter, respectively, in 1998 and 1999 (unpublished data, provided by Dr. James Raich). Comparing these data with those of this study (Table 1), soil C in forest buffer (42.9 ± 3.2 g kg$^{-1}$, n = 6) in this study was significantly higher than those in 1998 and 1999 (two sample t-test p = 0.006, 95% CI for difference of means: 4.5 - 20.5 g kg$^{-1}$). These results indicated that 29.3% increase in soil C of forest buffer over last 9 years. Decomposition of litter falls and roots of the vegetation may contribute to the C increase. Increased soil C caused by conservation practices such as conversion from crop lands...
to grasslands or forest has been reported (Gebhart et al., 1994; Knops and Tilman, 2000; Uri, 2000; Post and Kwon, 2000; Guo and Gifford, 2002; McLauchlan et al., 2006). Johnson et al. (2005) reported that the conservation practice increased soil organic C by $4.2 \pm 4.5$ Mg C ha$^{-1}$ year$^{-1}$ in the central USA. We observed significantly higher soil moisture and lower soil temperature in the soils of riparian buffers compared to those of crop fields. Vegetation in riparian buffers provides more shade to prevent high temperatures in the summer and the low soil bulk density and high organic matter of riparian buffers hold more soil moisture. In contrast, soils in crop fields are more exposed to direct sunlight, have high bulk density and low soil organic matter from continuous cultivation of row crops and tend to hold less soil moisture compared with riparian buffers soils.

4.2 Methane flux in riparian buffers

From the results of soil incubation with control and 10 Pa C$_2$H$_2$ experiments, we found that CH$_4$ consumption was higher than CH$_4$ production in the forest buffer, warm-season and cool season grass filter soils, while CH$_4$ consumption was less than CH$_4$ production in the crop field soils. Observed cumulative diel CH$_4$ flux showed a positive net flux in the crop field soil and a negative net flux in the forest buffer, warm-season and cool-season grass filter soils. The diel flux results are consistent with the soil incubation results. The average observed CH$_4$ flux during the year in crop fields (-209.1 \pm 121.2 \mu g \text{CH}_4-C \text{m}^{-2} \text{d}^{-1}, n = 40) was not significantly different from fluxes within forest buffers and grass filters (-511 to 927.9 \mu g \text{CH}_4-C \text{m}^{-2} \text{d}^{-1}, n = 45 - 50). Annual CH$_4$ flux was -0.80 kg CH$_4$-C ha$^{-1}$ yr$^{-1}$ (-1.07 kg CH$_4$ ha$^{-1}$ yr$^{-1}$), -0.46 kg CH$_4$-C ha$^{-1}$ yr$^{-1}$ (-0.61 kg CH$_4$ ha$^{-1}$ yr$^{-1}$), and 0.04 kg CH$_4$-C ha$^{-1}$ yr$^{-1}$ (0.05 kg CH$_4$ ha$^{-1}$ yr$^{-1}$) in crop fields, forest buffers and grass filters, respectively, and the amounts are not significantly different one another. These results suggest that CH$_4$ flux has not been changed since restoration of the forest buffers and grass filters.

The CH$_4$ flux in the forest buffers and grass filters soils is similar to results of studies conducted in other riparian areas. McLain and Martens (2006) found CH$_4$ sink averaged 26.1 \pm 6.3 \mu g \text{CH}_4 \text{m}^{-2} \text{hr}^{-1} in the semiarid riparian soils of southeastern Arizona. In a riparian alder stand in southern Estonia, Teiter and Mander (2005) observed an average CH$_4$ flux of 0.1-265 \mu g \text{CH}_4-C \text{m}^{-2} \text{hr}^{-1}. However, the CH$_4$ flux in the forest buffers and grass filters soils was lower than reported one from other studies conducted in temporarily submerged areas, rice fields, and wetlands. Ambus and Christensen (1995) found CH$_4$ was produced at rates of 7,877 mg C m$^{-2}$ yr$^{-1}$ (78.8 kg CH$_4$-C ha$^{-1}$ yr$^{-1}$) in temporarily flooded of riparian area in Denmark. Methane was produced from riparian areas in Northern Germany at rates of 33.3-33,030.8 mg CH$_4$-C m$^{-2}$ yr$^{-1}$ (0.33-330.3 kg CH$_4$-C ha$^{-1}$ yr$^{-1}$) (Merbach et al.,
Altor and Mitsch (2006) reported that annual CH$_4$ flux from intermittently flooded zones was 13 g CH$_4$-C m$^{-2}$ yr$^{-1}$ (130 kg CH$_4$-C ha$^{-1}$ yr$^{-1}$) in the Midwestern USA. Le Mer and Roger’s (2001) review of the literature found that median of CH$_4$ emissions were 720 g CH$_4$ ha$^{-1}$ d$^{-1}$ (3 mg CH$_4$ m$^{-2}$ hr$^{-1}$), 433 g CH$_4$ ha$^{-1}$ d$^{-1}$ (1.8 mg CH$_4$ m$^{-2}$ hr$^{-1}$) and 1000 g CH$_4$ ha$^{-1}$ d$^{-1}$ (4.2 mg CH$_4$ m$^{-2}$ hr$^{-1}$) in swamps ($n=11$), peat lands ($n=4$), and rice fields ($n=23$), respectively. These results suggest that forest buffers and grass filters soils are not significant sources of CH$_4$ compared to wetlands and rice fields.

The global CH$_4$ consumption rate in crop fields ($n=48$), grasslands ($n=24$), and forests ($n=91$) in temperate regions was 1.29 ± 0.16 kg CH$_4$ ha$^{-1}$ yr$^{-1}$, 5.75 ± 0.59 kg CH$_4$ ha$^{-1}$ yr$^{-1}$, and 2.40 ± 0.40 kg CH$_4$ ha$^{-1}$ yr$^{-1}$, respectively (data extracted from Dutaur and Verchot (2007)). The data indicate that CH$_4$ consumption in forest buffers and grass filters soils was very much lower than global CH$_4$ consumption rate in grasslands and forests in temperate regions. These results suggest the CH$_4$ soil oxidation ability has not been improved 7-17 years after restoration of forest buffers and grass filters from conventional crop fields, while soil properties such as soil bulk density pH, TC, and soil moisture have significantly changed. It is well known that CH$_4$ oxidation of upland soils is reduced by cultivation, especially by ammonium N-fertilizer application (e.g. Topp and Pattey, 1997; Le Mer and Roger, 2001; Dutaur and Verchot, 2007). Le Mer and Roger (2001) summarized the effects of cultural practices on CH$_4$ oxidation as following: 1) increase in NH$_4^+$ content of soil by fertilizer application inhibits CH$_4$ oxidation because NH$_4^+$ produces a competition at the level of the methane-mono-oxygenase, a transfer of the CH$_4$ oxidizing activity toward nitrification (Castro et al., 1994; Nesbit and Breitenbeck, 1992), and 2) cultural practices that destroy micro-aerophilic niches suitable for CH$_4$ oxidizers reduce CH$_4$ oxidation (Hütsch et al., 1994; Sitaula et al., 2000). Slow recovery of CH$_4$ oxidation after land use change has been reported. In a successional range of sites on former arable land in Denmark and Scotland, CH$_4$ oxidation rates took more than 100 yr to reach pre-cultivation levels (Priemé et al., 1997). Suwanwaree and Robertson (2005) found that rates of CH$_4$ oxidation in the soils of 40 to 60 yr-old successional fields were between those of the no-till and deciduous forest sites in southwest USA. Singh et al. (2007) reported that afforestation and reforestation of pastures (30-50 years later) caused changes in methane oxidation by altering the community structure of methanotrophic bacteria in these soils.

5 Conclusions
Soil properties such as soil bulk density, pH, TC, and soil moisture in forest buffers and grass filters were significantly different from adjacent crop fields. This result suggests the soil properties have
changed since restoration of forest buffers and grass filters. Results of incubation experiments indicate that amounts of CH₄ consumption were higher than CH₄ production in forest buffers and grass filters soils, while crop field soils showed the opposite response. Diel and seasonal variation of CH₄ fluxes in forest buffers, grass filters, and adjacent crop fields were not significantly different.

Annual CH₄ flux was -0.80 kg CH₄-C ha⁻¹ yr⁻¹ (-1.06 kg CH₄ ha⁻¹ yr⁻¹), -0.46 kg CH₄-C ha⁻¹ yr⁻¹ (-0.61 kg CH₄ ha⁻¹ yr⁻¹), and 0.04 kg CH₄-C ha⁻¹ yr⁻¹ (0.05 kg CH₄ ha⁻¹ yr⁻¹) in crop fields, forest buffers and grass filters, respectively, and the cumulative CH₄ flux in forest buffers and grass filters are not significantly different from zero. The cumulative CH₄ flux in crop fields, forest buffers and grass filters are not significantly different one another. These results indicate CH₄ flux in crop fields, forest buffers, and grass filters soils were not different. The CH₄ flux in forest buffers and grass filters soils is less than that reported for wetlands and rice fields known as sources of CH₄ and more than that reported for forests and grasslands known as sinks of CH₄. These suggests that the forest buffers and grass filters cannot be considered as major sources of CH₄ flux; however, potential benefits as increased sinks of CH₄ have not been accomplished in the restored forest buffers and grass filters.
References


Table 1. Soil properties (mean ± standard error) \((n = 6-9\) except bulk density \((n = 27)\)) of the sites. Soil samples (depth 0-15 cm) were collected in a forest buffer, a warm-season grass filter, a cool-season grass filter, and an adjacent crop field in Oct. 2006 and Sept. 2007.

<table>
<thead>
<tr>
<th>Site</th>
<th>Soil texture†</th>
<th>Bulk density (\text{mg m}^3)</th>
<th>pH (\text{— g kg}^{-1} \text{ soil})</th>
<th>TC (\text{— g kg}^{-1} \text{ soil})</th>
<th>TN (\text{— mg N kg}^{-1} \text{ soil})</th>
<th>(\text{NH}_4)-N (\text{— mg N kg}^{-1} \text{ soil})</th>
<th>(\text{NO}_3)-N (\text{— mg N kg}^{-1} \text{ soil})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crop field</td>
<td>Loam</td>
<td>(1.67 ± 0.02)^a‡</td>
<td>(5.9 ± 0.1)^c</td>
<td>(22.8 ± 1.0)^c</td>
<td>(1.9 ± 0.1)^c</td>
<td>(1.7 ± 0.2)^b</td>
<td>(1.2 ± 0.5)^a</td>
</tr>
<tr>
<td>Forest buffer</td>
<td>Loam, Sandy loam</td>
<td>(1.10 ± 0.03)^c</td>
<td>(7.3 ± 0.1)^a</td>
<td>(42.9 ± 3.2)^a</td>
<td>(3.8 ± 0.3)^a</td>
<td>(4.1 ± 0.6)^a</td>
<td>(0.7 ± 0.2)^a</td>
</tr>
<tr>
<td>Warm-season grass filter</td>
<td>Loam</td>
<td>(1.29 ± 0.05)^b</td>
<td>(6.7 ± 0.2)^b</td>
<td>(29.1 ± 2.7)^bc</td>
<td>(2.6 ± 0.2)^bc</td>
<td>(3.9 ± 0.5)^a</td>
<td>(0.2 ± 0.1)^a</td>
</tr>
<tr>
<td>Cool-season grass filter</td>
<td>Loam</td>
<td>(1.19 ± 0.04)^bc</td>
<td>(6.9 ± 0.1)^ab</td>
<td>(32.4 ± 1.6)^bc</td>
<td>(2.9 ± 0.1)^b</td>
<td>(4.3 ± 0.4)^a</td>
<td>(0.9 ± 0.3)^a</td>
</tr>
</tbody>
</table>

† Marquez et al., 2004
‡Values in the same column followed by a different letter are significantly different \((p < 0.05)\)
Fig. 1. Production, consumption, and net flux of CH₄ in crop field, forest buffer, warm-season grass filter and cool-season grass filter soils. Each mean represents three observations and bars are the standard errors of the means.
Fig. 2. Diel variation of CH$_4$ flux in crop field, forest buffer, warm-season grass filter and cool-season grass filter soils on 16-17 July 2007 (A) and their cumulative diel CH$_4$ flux (B). Each mean represents three observations and bars are the standard errors of the means.
Fig. 3. Methane flux (A, B), daily precipitation (C), daily soil moisture (D), and soil temperature (E) in crop fields ($n = 1$), forest buffers ($n = 3$), and grass filters ($n = 4$) in 2007. Each mean represents observations and bars are the standard errors of the means.
Fig. 4. Box plots of measured CH$_4$ flux in crop fields (CF), forest buffers (FB), warn-season grass filters (WGF), and cool-season grass filter (CGF) soils in 2007 ($n = 40-49$). I, II, and III indicate replicates. The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers (error bars) above and below the box indicate the 90th and 10th percentiles. Solid circles indicate outliers.
Fig. 5. Annual CH$_4$ flux in crop fields ($n = 1$), forest buffers ($n = 3$) and grass filters ($n = 4$) soils in 2007.
GENERAL CONCLUSIONS

Nitrous oxide emissions from soils in all riparian buffers were significantly less than those in the crop fields, but no differences among different kinds of riparian buffers were observed. Our results indicate that the emission factor (ratio of N\textsubscript{2}O emission to N inputs) of soils in riparian buffers was smaller than the crop fields. While N\textsubscript{2}O peak emissions followed by rewetting dry soils and thawing frozen soils significantly contributed to annual N\textsubscript{2}O emissions from soils in the crop fields, soils in the riparian buffers were less sensitive to such events. Soil incubation with inhibitors indicated that the main sources of N\textsubscript{2}O might be nitrifier denitrification and denitrification in the crop field soil and nitrifier denitrification in the riparian buffer soils. The ratio of N\textsubscript{2}O to N\textsubscript{2} in riparian buffer soil (0.88-6.8) was less than that found in crop field soil (16.5). These results suggest that N\textsubscript{2}O emissions from soils in all riparian buffers were significantly less than those in the crop field.

In both a multi-species riparian buffer and a cool-season grass filter, NO\textsubscript{3}\textsuperscript{-} concentrations in groundwater were significantly decreased in comparison to those in the crop field, by 48-59\%.

However, dissolved N\textsubscript{2}O concentrations in groundwater did not differ among locations (6-14 µg L\textsuperscript{-1}), nor did DO (2.6-5.0 mg L\textsuperscript{-1}) or DOC (0.7-1.9 mg L\textsuperscript{-1}) concentrations. These results suggest that the riparian buffers decreased NO\textsubscript{3}\textsuperscript{-} concentrations in near-surface groundwater, without increasing N\textsubscript{2}O losses.

Diel and seasonal CH\textsubscript{4} fluxes in crop field soil were not observed to be significantly different from those in the forest buffer and grass filter soils. In addition, no significant difference in CH\textsubscript{4} flux was found between the forest buffer and grass filter soils. Annual CH\textsubscript{4} flux was -0.80 kg CH\textsubscript{4}-C ha\textsuperscript{-1} yr\textsuperscript{-1} (-1.06 kg CH\textsubscript{4} ha\textsuperscript{-1} yr\textsuperscript{-1}), -0.46 kg CH\textsubscript{4}-C ha\textsuperscript{-1} yr\textsuperscript{-1} (-0.61 kg CH\textsubscript{4} ha\textsuperscript{-1} yr\textsuperscript{-1}), and 0.04 kg CH\textsubscript{4}-C ha\textsuperscript{-1} yr\textsuperscript{-1} (0.05 kg CH\textsubscript{4} ha\textsuperscript{-1} yr\textsuperscript{-1}) in crop fields, forest buffers and grass filters, respectively. The annual CH\textsubscript{4} flux in forest buffers and grass filters were not significantly different from zero, and the annual CH\textsubscript{4} flux in crop fields, forest buffers and grass filters were not significantly different one another. These results indicate that CH\textsubscript{4} flux was not changed in the forest buffers and grass filters soils, despite that soil properties have changed significantly since the planting of the forest buffers and the grass filters.