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EMISSION OF THE GREENHOUSE GAS NITROUS OXIDE FROM RIPARIAN FOREST BUFFERS, WARM-SEASON AND COOL-SEASON GRASS FILTERS AND CROP FIELDS

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Abstract: Denitrification is recognized as the major mechanism for reducing nitrate in riparian buffers and thus diminishing non-point source pollution (NPS) of surface water bodies subject to high nitrogen 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_2O), a greenhouse gas also involved in stratospheric ozone depletion. It is therefore important to quantify the emissions of N_2O from different kinds of vegetated riparian buffer systems, and identify ways to minimize emissions while simultaneously maximizing denitrification. We measured N_2O emissions from soils; nitrate (NO_3^--N) and dissolved N_2O in groundwater; and soil properties in riparian forest buffers, warm-season and cool-season grass filters, and a crop field located in the Bear Creek watershed in central Iowa. Results suggest that N_2O emissions from soils in all riparian buffers were significantly less than in the crop field, but no differences among types of riparian buffers were observed. Nitrate in outflow groundwater of riparian buffers was significantly lower than in inflow groundwater of riparian buffers. However, dissolved N_2O in inflow and outflow groundwater of riparian buffers were not significantly different from one another. These results are useful in developing management protocols for riparian forest and other perennial vegetation practices for NPS pollution attenuation and additional multiple benefits.

Key Words: riparian forest buffer, filter strip, water quality, nitrate, greenhouse gas, nitrous oxide, groundwater.

INTRODUCTION

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., 2004). Many studies have shown that riparian buffers can reduce sediment erosion to surface waters by 70 to 95% (Lee et al. 2003), N fluxes by 5 to more than 90% (Dukes et al. 2002) and P losses by 27 to 97% (Kuusemets et al. 2001). Denitrification is recognized as the major mechanism for reducing nitrate (NO_3^--N) within riparian systems, with removal generally ranging from 2–7 g N m^{-2} y^{-1} (Watts and Seitzinger 2000).

It recently has been hypothesized that increased denitrification within riparian areas may trade a water quality concern for an atmospheric resulting from the greenhouse effect of N_2O produced during nitrification and denitrification and its contribution to ozone depletion concern (Groffman et al. 1998). The global warming potential of N_2O is 298 times that of carbon dioxide (CO_2) and

25 times that of methane (CH_4) in a 100-year time horizon (Forster et al. 2007). Some studies (Groffman et al. 1998, 2000, Hefting et al. 2003, 2006) have concluded that N transformation within riparian buffers with high NO_3^--N loads results in a significant increase of greenhouse gas emission. In contrast, because riparian buffers efficiently decrease NO_3^--N, a source of N_2O emissions, riparian buffers could provide an opportunity to decrease dissolved N_2O emissions if we can develop reliable strategies for decreasing N_2O production during denitrification (Groffman 2000). Studies supporting this proposition include Blicher-Mathiesen and Hoffman (1999), who reported that denitrification in a riparian soil can act as a sink for dissolved N_2O in the inflowing groundwater as well as for N_2O produced internally. However, very few studies have addressed these issues and the data that can be utilized to evaluate these possibilities are extremely limited. Clearly, there is a need to evaluate processes influencing production, consumption, and transport of N_2O in different riparian buffers and to assess the potential to decrease emissions.

An objective of this study was to compare N_2O emission from riparian buffer systems established for water quality improvement comprised of forest, warm-season grasses, and cool-season grasses and an adjacent crop field. A second objective was to quantify transport and fate of NO_3^--N and dissolved N_2O in groundwater under crop fields and riparian buffers, and assess whether groundwater exported from crop fields and riparian buffers is a significant source of dissolved N_2O.

MATERIALS AND METHODS

The study area consisted of three forest buffers, three warm-season grass filters, one cool-season grass filter, and a crop field, all located within the riparian zone within the Bear Creek watershed, Story County and Hamilton County, Iowa, United States of America. Bear Creek is a third order stream with typical discharges of 0.3 to 1.4 m^3 sec^{-1}. The watershed drains 6,810 ha of farmland, with nearly 90% of the area in a corn-soybean rotation. 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 the cool-season grass filter was previously under livestock grazing. Details of the riparian buffer design, placement, and plant species are given in Schultz et al. (2004). The crop field was planted to a corn (*Zea mays* L.) and soybean (*Glycine max* L. Merr.) rotation, with corn in 2006 and soybeans in 2005 and 2007. The areas used in this study are all located on the same soil mapping unit (Coland) and have similar topography.

Nitrous oxide flux from soils under riparian forest buffers, warm-season and cool-season grass filters, and the crop field were measured weekly from October 2005 through December 2007 (no measurement in mid April to mid May, August, and September to October 2006 in the crop field). Nitrous oxide flux samples were collected at mid-morning using static vented chambers and nitrous oxide concentrations were determined with a gas chromatograph. Nitrous oxide flux was calculated from the linear slope of N_2O concentration change over time (Holland et al. 1999). Soil temperature and soil moisture at 5-cm soil depths were measured simultaneously

with N_2O gas collection at one site per vegetation type. Daily rainfall and snow data were provided by the nearest meteorology station (Colo, IA). Cumulative N_2O fluxes were calculated by linear interpolation and numerical integration of soil-temperature-corrected daily flux measurements between sampling times. Six intact soil cores (5.3 cm diameter) were collected to a depth of 15 cm in each of the vegetation types in Oct. 2006 and Sept. 2007. Soils were analyzed for soil pH, gravimetric moisture content, total C (TC) and total N (TN), and soil inorganic N [NO_3^--N and ammonium (NH_4^+-N)].

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). Groundwater sampling and monitoring was conducted monthly in monitoring wells and stilling wells from Nov. 2005 to Apr. 2008 and samples were analyzed for NO_3^--N, Cl-, pH, dissolved organic carbon, and dissolved N_2O. Hydraulic head was measured with an electronic water level tape. 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). Cumulative annual flux of NO_3^--N and dissolved N_2O-N in groundwater at the crop field edge of the buffers was estimated using measured concentrations, average linear velocity, effective porosity, and cross sectional area of the aquifer adjacent to Bear Creek.

Normality of the distribution of the data was analyzed using the Shapiro-Wilk normality test. 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 flux, correlation analysis using the GLM procedure was applied and NONLIN procedure was utilized for deriving the best fit of N_2O flux models developed by the relationship between soil temperature and N_2O flux. These statistical analyses were conducted in SAS version 8.1 (SAS institute, 1999).

<div align="center">RESULTS</div>

Soil properties

Soils within the forest buffer and warm and cool-season grass filters had significantly lower bulk density, higher pH, TC, TN, and NH_4^+ than crop fields, while soil NO_3^--N was not significantly different. Soils had longer dry (soil moisture $< 15\%$) and frozen (soil temperature $< 0^oC$) periods in 2007 than in 2006. From 15 June to 15 Aug. 2006 (93 d), soils were extremely dry 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 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 within the crop field 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 within the crop field for 82 days, within forest buffers for 46 days, and within grass filters for 62 days.

Soil N$_2$O flux

When assessed seasonally, N$_2$O flux in the crop field was significantly correlated with air temperature, soil temperature, and soil moisture. In all riparian buffers, N$_2$O flux was significantly correlated with air temperature and soil temperature during this same period. The average of observed N$_2$O fluxes in the crop field (39.4 ± 7.1 g N$_2$O-N ha^{-1} d^{-1}, n = 76) was significantly higher than in riparian buffers (2.8-11.0 g N$_2$O-N ha^{-1} d^{-1}, n = 72-93), but there were no differences among riparian buffer vegetation types (Fig. 1). In both 2006 and 2007, annual cumulative N$_2$O emission was significantly greater 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) than in forest buffers (1.8 kg N$_2$O-N ha^{-1} in 2006 and 4.5 kg N$_2$O-N ha^{-1} in 2007) and grass filters (1.8 kg N$_2$O-N ha^{-1} in 2006 and 3.4 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.
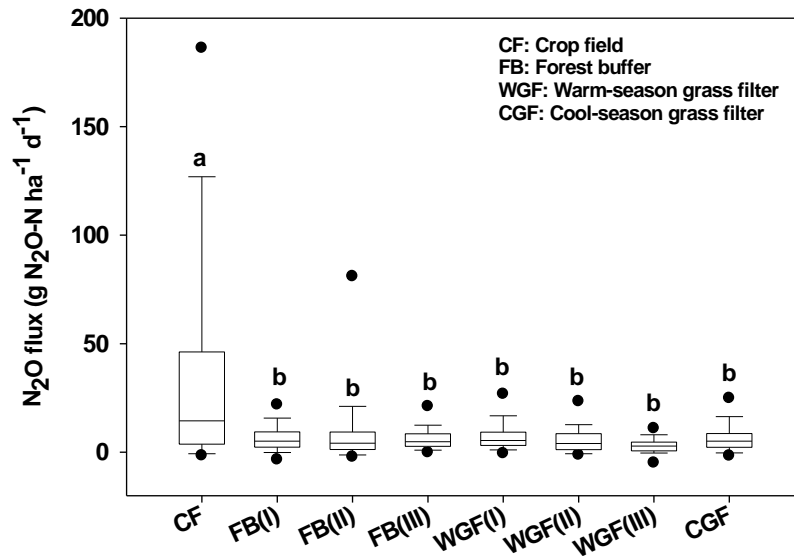

Figure 1. Daily N$_2$O flux from soils within the crop field and riparian buffers in 2006 and 2007 (n = 72-93). I, II, and III indicate replicates. The lower boundary of the box indicates the 25th percentile, the line within the box marks the median, and the upper boundary of the box indicates the 75th percentile. Error bars indicate the 90th and 10th percentiles. Solid circles indicate outliers.

Several periods of peak N$_2$O emission contributed significantly to annual N$_2$O emission in both the crop field and riparian buffers (Fig. 2 (A) and (B)). 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 the crop field 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 the crop field than in riparian buffers during both years, with the contribution higher in 2007 than 2006.
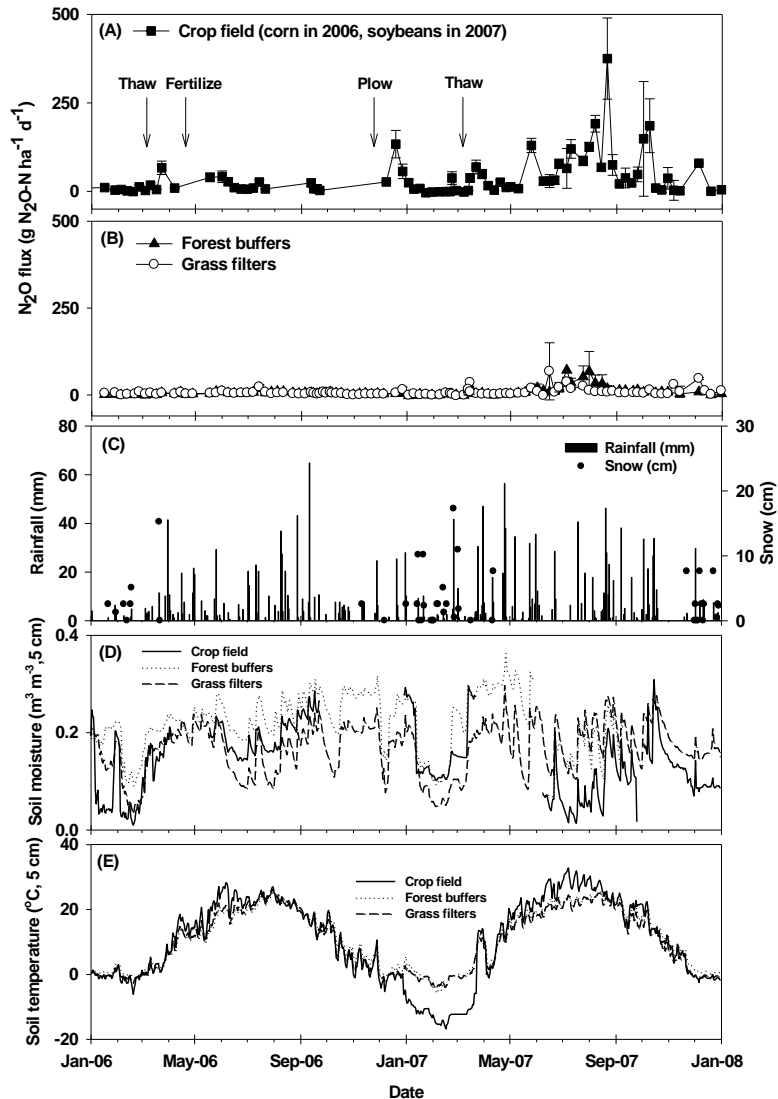
Figure 2. Nitrous oxide emissions (A, B), precipitation (C), and daily average of soil moisture (D) and soil temperature (E) in forest buffers (n = 3), grass filters (n = 4), and adjacent crop field (n = 1) during 2006 and 2007. Observations are mean values with standard errors of the mean in (A) and (B).

Groundwater N$_2$O flux

Within the cool-season grass filter sites, average NO$_3^-$-N concentration was 9.5 mg L^{-1} in groundwater wells adjacent to crop fields and 4.9 mg L^{-1} in wells adjacent to creek, during 1997-1999 (Fig. 3), and 9 and 3.3 mg L^{-1}, respectively, during 2005-2008 (Fig. 4), representing a decrease of 48% in 1997-1999 and 59% in 2005-2008. In Jan. 2006-Dec. 2007, NO$_3^-$-N flux in groundwater from the crop field to the cool-season grass filter was 14.2 kg N and NO$_3^-$-N flux from the cool-season grass filter to the creek was 5.1 kg N (Fig. 3). This indicates that 9.1 kg N

was removed from the groundwater as it flowed from the crop field through the cool-season grass filter.

	Crop field	Multi-species riparian buffer	Bear Creek	Cool-season grass filter	Crop field	
Groundwater flow direction	→ →	→ →		← ←	← ←	Groundwater flow direction
Cl^-	20.6 (1.2)	20.9 (1.0)		13.4 (1.0)	13.2 (0.9)	Cl^-
NO_3-N	4.9 (0.5)	5 (0.4)		4.9 (2.4)*	9.5(0.7)*	NO_3-N
NO_3^-/Cl^-	0.3 (0.1)	0.2 (0.0)		0.4(0.0)*	0.8(0.1)*	NO_3^-/Cl^-
Dissolved N_2O-N	6.1(1.0)	6 (0.7)		6.8(0.8)	7.8(1.2)	Dissolved N_2O-N
DOC	1.1(0.1)	0.6 (0.4)		0.7(0.4)	0.9(0.4)	DOC
DO	3.4(0.5)	2.8(0.2)		2.6(0.3)	5(0.3)	DO
pH	7.5(0.0)	7.5(0.0)		7.3(0.0)	7.5(0.0)	pH

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 (data from Spear 2003). Unit for Cl^-, NO_3^--N, DOC, and DO is mg L^{-1} and unit of dissolved N_2O-N is μg L^{-1}. The value inside parenthesis is standard error of the mean and an asterisk (*) indicates $P < 0.05$. The number of measurements: Cl^- (n = 21-23), NO_3^--N (n = 26-29), NO_3^-/Cl^- (n = 17-22), dissolved N_2O-N (n = 26-27), DOC (n = 3), DO (n = 19-21), and pH (n = 3).

Within the riparian forest buffer, average NO_3^--N concentrations were 4.9 mg L^{-1} in groundwater wells adjacent to the crop field and 5.0 mg L^{-1} in wells adjacent to the creek, respectively, during 1997-1999 (Fig. 3), and 4.0 and 2.0 mg L^{-1}, respectively, during 2005-2008 (Fig. 4). The differences in concentrations during 1997-1999 were not significant (Fig. 3) but, within this same buffer, average NO_3^--N concentration in groundwater decreased by 49.5% in 2005-2008 (Fig. 4). In Jan. 2006-Dec. 2007, NO_3^--N flux in groundwater from the crop field to the multi-species riparian buffer was 4.4 kg N and groundwater NO_3^--N flux from the multi-species riparian buffer to the creek was 2.1 kg N (Fig. 4). This indicates the NO_3^--N flux was 2.3 kg N (52.2%) lower in groundwater nearest the creek compared to near the crop field edge.

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 and 2005-2008 (Fig. 3, 4). 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 (Fig. 3). 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 (Fig. 4).

	Crop field	Multi-species riparian buffer	Bear Creek	Cool-season grass filter	Crop field	
Groundwater flow direction	→ →	→ →		← ←	← ←	Groundwater flow direction
Cl^-	20.8 (1.2)	18.2 (0.6)		18.2 (0.6)	20.6 (1.2)	Cl^-
NO_3-N	4.0 (0.3)*	2.0 (0.2)*		3.3 (0.3)*	7.9 (0.5)*	NO_3-N
NO_3-N flux	4.4	2.1		5.1	14.2	NO_3-N flux
NO_3^-/Cl^-	0.2 (0.1)*	0.1 (0.0)*		0.2 (0.0)*	0.4 (0.0)*	NO_3^-/Cl^-
Dissolved N_2O-N	9.0 (1.1)	9.1 (1.3)		14.4 (2.2)	11.6 (1.5)	Dissolved N_2O-N
Dissolved N_2O-N flux	8.3	7.7		20.0	19.7	Dissolved N_2O-N flux
DOC	1.2 (0.1)	1.0 (0.1)		1.1 (0.1)	1.9 (0.1)	DOC
DO	3.3 (0.3)	2.7 (0.3)		2.7 (0.3)	3.3 (0.5)	DO
pH	7.4 (0.1)	7.4 (0.0)		7.4 (0.1)	7.5 (0.1)	pH

Figure 4. Groundwater characteristics (in 2005 - 2008) and NO_3^--N and dissolved N_2O-N fluxes (in Jan. 2006 - Dec. 2007) 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^-, NO_3^--N, DOC, and DO is mg L^{-1}, dissolved N_2O-N is µg L^{-1}, NO_3^--N flux is kg N (2006 and 2007 years) -1, and dissolved N2O-N flux is g N (2006 and 2007 years) -1. The value inside parenthesis is standard error of the mean and an asterisk (*) indicates P < 0.05. The number of measurements: Cl^- (n = 29), NO_3^--N (n = 29), NO_3^-/Cl^- (n = 29), dissolved N_2O-N (n = 25-26), DOC (n = 8), DO (n = 26-27), and pH (n = 21).

Within groundwater under the cool-season grass filter, there was no significant difference in dissolved N_2O-N concentration in wells adjacent to the crop fields and adjacent to the creek during both 1997-1999 and 2005-2008. In Jan. 2006-Dec. 2007, dissolved N_2O-N flux was 19.7 g N in groundwater adjacent to the crop field and 20.0 g N in the cool-season grass filter near the creek (Fig. 3). This pattern was repeated in groundwater under the multi-species riparian buffer, with no significant difference in dissolved N_2O-N concentrations in groundwater adjacent to crop fields and the creek during either 1997-1999 or 2005-2008. There was a significant negative relationship between water temperature and dissolved N_2O concentration in groundwater adjacent to both crop fields and the creek within the grass filter and the multi-species riparian buffer. There was also a significant relationship between DO and dissolved N_2O concentration in groundwater adjacent to the creek within the multi-species riparian buffer.

DISCUSSION

In our studies, measured N_2O emissions from soils within all riparian buffers were significantly lower than within the crop field and there were no observed differences in N_2O emissions among the different riparian buffer vegetation types (Fig. 1). Observed emissions in our studies were similar to N_2O emission from soils in unfertilized grass lands and forest in temperate regions (Groffman et al. 1998, Stehfest and Bouwman 2006). In contrast, some studies (Walker et al. 2002, Hefting et al. 2003) have shown much higher N_2O emission from soils within riparian areas. They suggested that the higher rates of N_2O emissions within the forested buffer zone were associated with higher NO_3^--N concentration in the groundwater, and that N transformation by buffer zones with high NO_3^--N loading resulted in a significant increase of N_2O emission. This is consistent with the work of Ullah and Zinati (2006) who reported that prolonged N loading resulted in higher N_2O emissions in riparian forest soils compared to emission rates from non-exposed forest soils. Hefting et al. (2006) reported that locations with high NO_3^--N removal efficiency also contribute significantly to increased N_2O emission from riparian zones. Considering all of these results, it is likely that N_2O 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).

The magnitude and frequency of the episodic N_2O emissions observed in our studies indicate the importance of frequent measurements to reduce the uncertainty of longer-term N_2O flux measurements and may partially explain the differences in results from previous studies. Many future climate change scenarios predict more severe droughts associated with summer drying and intense precipitation in a future warmer climate (Sillmann and Roeckner 2008) and an increase in freeze and thaw frequency (Gu et al. 2008). The observed peak N_2O emissions during the thawing of frozen soils and rewetting of dry soils in the crop field 2007 have important implications for greenhouse gas emission in a changing climate which predicts a greater frequency of such conditions.

Nitrate concentration in groundwater was significantly decreased under the cool-season grass filter in both 1997-1999 and 2005-2008 and under the multi-species riparian buffer in 2005-2008. Our data showed a decrease in the NO_3^-/Cl- ratio in both sites, with a significant decrease in NO_3^--N concentration and an insignificant change in the Cl- concentration. These results suggest that dilution from a converging or diverging flow path was not a major factor contributing to the decrease in groundwater NO_3^--N concentration (e.g. Vidon and Hill 2004, Davis et al. 2007). Uptake of NO_3^--N by vegetation was not investigated in this study but is known to occur in riparian buffers (Hefting et al. 2005).

In our studies, there was no significant NO_3^--N decrease observed during 1997-1999 under the multi-species riparian buffer. However, there was a significant decrease in NO_3^--N during Jan. 2006-Dec. 2007. While not directly studied, the age of the buffer could be a potential contributing factor for the difference in N removal efficiency. Our results regarding NO_3^--N decrease without increasing dissolved N_2O in the cool-season grass filter or the multi-species riparian buffer can be explained three different ways. First, it may be that denitrification completed the reduction of NO_3^--N to N2 without producing N_2O (Blicher-Mathiesen and Hoffman 1999). In the groundwater, very low concentrations of DO (< 2 ppm) were often

observed and the anaerobic microsites might support completion of denitrification. This possibility is supported by the significant relationship found between DO and dissolved N_2O. Second, N_2O produced in groundwater can be released into unsaturated soil above the groundwater table. However, since the N_2O emission measured on the soil surface includes the N_2O produced in the unsaturated soil layer, the results suggest that release of N_2O produced in groundwater into unsaturated soil above the groundwater table to be an insignificant pathway of NO_3^--N losses. Third, vegetation and microbial communities within the riparian buffers can assimilate and immobilize NO_3^--N resulting in NO_3^--N decrease without increasing dissolved N_2O in the groundwater. Since this study did not investigate NO_3^--N losses by these pathways, we cannot exclude the possibility. Overall, it is suggested that the cool-season grass filter or the multi-species riparian buffer should be considered insignificant sources of dissolved N_2O flux.

CONCLUSIONS

Annual N_2O emissions from soils within all riparian buffers were significantly lower than within the cropped fields and no differences were observed among the different kinds of riparian buffers. While N_2O peak emissions following the rewetting of dry soils and thawing of frozen soils contributed significantly to annual N_2O emission in the crop field, soils in riparian buffers were less sensitive to the events. Monitoring of groundwater under a cool-season grass filter, a multi-species riparian buffer, and adjacent crop fields during 1997-1999 and 2005-2008 indicated that the concentration of dissolved N_2O was not significantly changed, even when the concentration of groundwater NO_3^--N 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 decrease in the NO_3^-/Cl^- ratio in groundwater under riparian buffers with significant NO_3^--N concentration decrease provides evidence that dilution from a converging or diverging flow path was not a major factor contributing to the decreased NO_3^--N concentration in groundwater. Based on these results, we suggest that the riparian buffers established adjacent to crop fields to decrease NO_3^--N did not increase dissolved N_2O in groundwater and dissolved N_2O flux from the crop fields was negligible in comparison to soil N_2O emission.

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