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## Nitrate and dissolved nitrous oxide in groundwater within cropped fields and riparian buffers

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### Abstract

Transport and fate of dissolved nitrous oxide ( $N_2O$ ) in groundwater and its significance to nitrogen dynamics within agro-ecosystems are poorly known in spite of significant potential of  $N_2O$  to global warming and ozone depletion. Increasing denitrification in riparian buffers may trade a reduction in nitrate ( $NO_3^-$ ) transport to surface waters for increased  $N_2O$  emissions resulting from denitrification-produced  $N_2O$  dissolved in groundwater being emitted into the air when groundwater flows into a stream or a river. This study quantifies the transport and fate of  $NO_3^-$  and dissolved  $N_2O$  moving from crop fields through riparian buffers, assesses whether groundwater exported from crop fields and riparian buffers is a significant source of dissolved  $N_2O$  emissions, and evaluates the Intergovernmental Panel on Climate Change (IPCC) methodology to estimate dissolved  $N_2O$  emission. We measured concentrations of  $NO_3^-$ ; chloride ( $Cl^-$ ); pH; dissolved  $N_2O$ , dissolved oxygen (DO), and organic carbon (DOC) in groundwater under a multi-species riparian buffer, a cool-season grass filter, and adjacent crop fields located in the Bear Creek watershed in central Iowa, USA. In both the multi-species riparian buffer and the cool-season grass filter, concentrations of dissolved  $N_2O$  in the groundwater did not change as it passed through the sites, even when the concentrations of groundwater  $NO_3^-$  were decreased by 50% and 59%, respectively, over the same periods. The fraction of N lost to leaching and runoff (0.05) and the modified  $N_2O$  emission factor, [ratio of dissolved  $N_2O$  flux to N input (0.00002)] determined for the cropped fields indicate that the current IPCC methodology overestimates dissolved  $N_2O$  flux in the sites. A low ratio between dissolved  $N_2O$  flux and soil  $N_2O$  emission (0.0003) was estimated in the cropped fields. These results suggest that the riparian buffers established adjacent to crop fields for water quality functions (enhanced denitrification) decreased  $NO_3^-$  and were not a source of dissolved  $N_2O$ . Also, the flux of dissolved  $N_2O$  from the cropped field was negligible in comparison to soil  $N_2O$  emission in the crop fields.

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## 1 Introduction

Nitrous oxide is a potent greenhouse gas (Wang et al., 1976) with a global warming potential that is 298 times that of carbon dioxide (CO<sub>2</sub>) and 25 times that of methane (CH<sub>4</sub>) over a 100-year time horizon (Forster et al., 2007). In groundwater under agricultural fields receiving N applications, or in riparian zones receiving groundwater or runoff water, excessive NO<sub>3</sub><sup>-</sup> may be transformed to N<sub>2</sub>O through the process of denitrification (Mosier et al., 1998; Nevison, 2000; IPCC, 2006). Denitrification is recognized as a major mechanism for decreasing NO<sub>3</sub><sup>-</sup> in riparian buffers (e.g. Groffman and Hanson, 1997; Watts et al., 2000). Denitrification is controlled by the availability of oxygen (O<sub>2</sub>), NO<sub>3</sub><sup>-</sup>, carbon (C), and the population of denitrifying organisms (e.g. Hill et al., 2000; Hill and Cardaci, 2004). Riparian buffers, which provide a C-rich environment, can increase denitrification directly by enhancing the availability of C to denitrifiers, and indirectly, through increasing the consumption of O<sub>2</sub> by heterotrophic microbes (e.g. Groffman, 1994; Hill, 1996). Since numerous studies have recognized that NO<sub>3</sub><sup>-</sup> concentrations in groundwater decrease as a result of increased denitrification in the riparian buffers (e.g. Groffman and Hanson, 1997; Watts et al., 2000), it has been hypothesized that the increased denitrification may be trading a decrease in NO<sub>3</sub><sup>-</sup> transport to surface waters for increased N<sub>2</sub>O emissions (Groffman et al., 1998 and 2000), that is, trading water pollution for atmospheric pollution. In contrast, because riparian buffers efficiently decrease NO<sub>3</sub><sup>-</sup>, a source of N<sub>2</sub>O emissions, riparian buffers could provide an opportunity to decrease dissolved N<sub>2</sub>O emissions if we can develop reliable strategies for decreasing N<sub>2</sub>O 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<sub>2</sub>O in the inflowing groundwater as well as for N<sub>2</sub>O 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 and consumption of dissolved N<sub>2</sub>O in different riparian buffers and to assess

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the potential to decrease the emissions (Groffman et al., 2000).

The resulting N<sub>2</sub>O dissolves in groundwater, which flows into streams, rivers, and estuaries and is ultimately emitted into the atmosphere (Mosier et al., 1998; Nevison, 2000; IPCC, 2006). The Intergovernmental Panel on Climate Change (IPCC, 2006) defines emission of dissolved N<sub>2</sub>O as indirect N<sub>2</sub>O emissions, in contrast to direct N<sub>2</sub>O emissions from N sources such as fertilizers and crop residues in managed soils. The IPCC (1997, 2006) estimates indirect N<sub>2</sub>O emissions from N leaching in agro-ecosystems multiplying N inputs by fraction of all N lost to leaching and runoff (Frac<sub>LEACH-(H)</sub>) and emission factor for N<sub>2</sub>O emissions from N leaching and runoff (EF<sub>5</sub>). The EF<sub>5</sub> consists of emission factors for groundwater (EF<sub>5g</sub>), rivers (EF<sub>5r</sub>), and estuaries (EF<sub>5e</sub>). Owing to complexity of N cycle in agro-ecosystems and the limitation of available data, Frac<sub>LEACH-(H)</sub> and EF<sub>5</sub> have significant uncertainties. The default value of Frac<sub>LEACH-(H)</sub> currently used by IPCC (2006) is 0.3, and an uncertainty range 0.1–0.8 was reported by Seitzinger and Kroeze (1998); however, lower values of 0.15–0.2 have been substituted for the default by several countries (Nevison, 2000). Emission factors for groundwater, EF<sub>5g</sub> are derived from the ratio between dissolved N<sub>2</sub>O and NO<sub>3</sub><sup>-</sup> concentrations (IPCC 1997, 2006). Since N<sub>2</sub>O emission factor is typically defined by the ratio between N<sub>2</sub>O emission and N input (IPCC 2006), Weymann et al. (2008) proposed the ratio between dissolved N<sub>2</sub>O and initial NO<sub>3</sub><sup>-</sup> concentrations to reflect the N input and show the emission factor determined by the new concept was smaller than the emission factor determined by current EF<sub>5g</sub> concept. Since N<sub>2</sub>O concentration in groundwater does not necessarily reflect actual indirect N<sub>2</sub>O emission (Höll et al., 2005) and spatial and temporal heterogeneity of N<sub>2</sub>O concentration is high (Weymann et al., 2008), the emission factor proposed by Weymann et al. (2008) still has uncertainties for estimating indirect N<sub>2</sub>O emission. Beyond these technical issues, it has been questioned whether indirect N<sub>2</sub>O emission is a significant pathway in the N cycle (Davidson and Swank 1990; Ueda et al., 1991; Harrison and Matson, 2003; Reay et al., 2004; Höll et al., 2005; Well et al., 2005). Clearly, studies are needed to improve Frac<sub>LEACH-(H)</sub> and dissolved N<sub>2</sub>O emission factor, and evaluate the contribution

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of dissolved N<sub>2</sub>O in the N cycle.

The overarching objective of this study was to quantify dissolved N<sub>2</sub>O in groundwater moving from row-cropped fields through riparian buffers of two vegetation types and to relate these patterns to observed patterns of groundwater NO<sub>3</sub><sup>-</sup> concentration. Specific objectives were to quantify transport and fate of NO<sub>3</sub><sup>-</sup> and dissolved N<sub>2</sub>O in crop fields and riparian buffers, assess whether groundwater exported from crop fields and riparian buffers is a significant source of dissolved N<sub>2</sub>O, and evaluate the validity of Frac<sub>LEACH-(H)</sub> and the dissolved N<sub>2</sub>O emission factor.

## 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 (total length 56 km) is a third order stream with typical discharges of 0.3 to 1.4 m<sup>3</sup> s<sup>-1</sup>. The watershed drains 6810 ha of farmland, with nearly 90% 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 (Schultz et al., 2004). 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 nonpoint source pollution. This study was conducted in two riparian buffers established in 1990 on opposite sides of Bear Creek (Fig. 1). 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 pratense* L.), and Kentucky bluegrass (*Poa pratensis*

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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 a sand aquifer 2 m thick 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) (Fig. 1). At each site, 3 monitoring wells at the crop field edge of the buffers (cool-season grass filter: R1, R9, R39; multi-species riparian buffer: R16, R20, R24) and 3 monitoring wells (cool-season grass filter: R8, R12, R40; multi-species riparian buffer: R13, R17, R21) and a stilling well (cool-season grass filter: SWRN; multi-species riparian buffer: SWRS) 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<sub>3</sub><sup>-</sup> and Cl<sup>-</sup>, groundwater was collected in polyethylene bottles using a peristaltic pump. For measurement of DOC, groundwater was collected

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in glass bottles. Samples for  $\text{NO}_3^-$  and DOC were acidified with  $20 \mu\text{L}$  of concentrated  $\text{H}_2\text{SO}_4$ . Dissolved oxygen was determined in the field using a portable photometer (Oxygen 2 SAM and Vacu-vials, CHEMetrics, Virginia, USA) with a detection limit of  $0.1 \text{ mg L}^{-1}$ , and pH was measured in the field using a portable pH meter (pH tester 2, Eutech Instruments, Singapore) with a detection limit of  $0.1 \text{ pH}$ . Groundwater samples for measuring dissolved  $\text{N}_2\text{O}$  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  $0.3 \text{ mL}$   $80\% \text{ ZnCl}_2$  for preserving dissolved  $\text{N}_2\text{O}$  (Blicher-Mathiesen and Hoffman, 1999). Samples were packed in ice in the field and refrigerated ( $4^\circ\text{C}$ ) 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  $\text{NO}_3^-$  were analyzed utilizing UV- second derivative spectroscopy (Crump-ton et al., 1992) with a detection limit of  $0.1 \text{ mg L}^{-1}$ . Chloride samples were analyzed with an ion specific electrode (Orion 9617BNWP, Thermo Scientific, Massachusetts, USA) with a detection limit of  $0.1 \text{ mg L}^{-1}$ . Dissolved organic carbon samples were filtered through a  $0.45 \mu\text{m}$  filter and analyzed by persulfate oxidation on a carbon analyzer (Phoenix 8000, Tekmar-Dohrmann<sup>TM</sup>, Ohio, USA) with a detection limit of  $0.1 \text{ mg L}^{-1}$ . Vials storing groundwater samples of dissolved  $\text{N}_2\text{O}$  were warmed to room temperature ( $21\text{--}22^\circ\text{C}$ ), shaken, and brought to atmospheric pressure with He. A gas chromatograph (Model GC17A, Shimadzu, Kyoto, Japan) equipped with a  $^{63}\text{Ni}$  electron capture detector and a stainless steel column ( $0.3175 \text{ cm diameter} \times 74.54 \text{ cm}$  long) with Porapak Q ( $80\text{--}100$  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  $0.6 \mu\text{g L}^{-1}$  (Spear, 2003).

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### 2.4 Nitrate and dissolved $\text{N}_2\text{O}$ flux

Cumulative annual flux of  $\text{NO}_3\text{-N}$  and dissolved  $\text{N}_2\text{O-N}$  in groundwater at the crop field edge of the buffers was estimated using  $\text{NO}_3\text{-N}$  and dissolved  $\text{N}_2\text{O-N}$  concentrations measured in the cool-season grass filter (R1, R9, R39) and the multi-species riparian buffer (R16, R20, R24) once a month in 2006–2007. Cumulative annual flux of  $\text{NO}_3\text{-N}$  and dissolved  $\text{N}_2\text{O-N}$  in groundwater at the creek edge of the buffers was estimated using  $\text{NO}_3\text{-N}$  and dissolved  $\text{N}_2\text{O-N}$  concentrations measured in the cool-season grass filter (R8, R12, R40) and the multi-species riparian buffer (R13, R17, R21) once a month in 2006–2007.

Daily mass flux was estimated using average linear velocity, effective porosity, measured concentrations and cross sectional area of the aquifer adjacent to Bear Creek (Fetter, 1999) (Eq. 1). The cross sectional area was determined by creating a hypothetical rectangle ( $35 \text{ m wide} \times 2 \text{ m height}$ ) representing the aquifer underlying the riparian buffers adjacent to Bear Creek. Monthly mass flux was estimated by multiplying the daily mass flux with days of the month (Eq. 2), and annual mass flux was sum of all monthly mass flux (Eq. 3).

$$F_{x, \text{day } i} = v_x \times n_e \times \text{Conc} \times \text{cross sectional area of aquifer} \quad (1)$$

$$F_{x, \text{month } i} = F_{x, \text{day } i} \times \text{days of month } i \quad (2)$$

$$F_{x, \text{year}} = \sum_{i=1}^{12} F_{x, \text{month } i} \quad (3)$$

where,

$F_{x, \text{day } i}$  is estimated daily mass flux ( $\text{g d}^{-1} \text{ m}^{-2}$ ) in month  $i$ ,

$v_x$  is average linear velocity ( $\text{m d}^{-1}$ ): cool-season grass filter  $0.23$  and multi-species riparian buffer  $0.13$  from Spear (2003),

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$n_e$  is effective porosity (unitless): 0.15 from Spear (2003),

Conc is concentration,  $\text{g m}^{-3}$  or  $\text{mg L}^{-1}$ ,

Cross sectional area of aquifer ( $\text{m}^2$ ) is hypothetical rectangle representing aquifer,

$F_{x, \text{month } i}$  is estimated monthly mass flux ( $\text{g month}^{-1} \text{m}^{-2}$ ) in month  $i$ ,

5  $F_{x, \text{year}}$  is estimated annual mass flux ( $\text{g y}^{-1} \text{m}^{-2}$ ) in a year.

To estimate total flux of  $\text{NO}_3\text{-N}$  and dissolved  $\text{N}_2\text{O-N}$  from all cropped fields (both sides of the creek) within the Bear Creek watershed, the above procedure (Eqs. 1–3) was used with the monthly measured  $\text{NO}_3\text{-N}$  and dissolved  $\text{N}_2\text{O-N}$  concentrations in groundwater at the crop field edge of the buffers. The concentrations measured in the cool-season grass filter (R1, R9, R39) and the multi-species riparian buffer (R16, R20, R24) represented the concentrations in the aquifers on each side of the creek (Eq. 1).  
10 Two hypothetical rectangles (56 473 m wide  $\times$  2 m height) representing the aquifers on each side of the creek were applied (Eq. 1).

### 3 Determining $\text{Frac}_{\text{LEACH-(H)}}$ , $\text{EF}_{5g}$ , and ratios of dissolved $\text{N}_2\text{O}$ flux to N inputs (EI- $\text{EF}_{5g}$ ) and dissolved $\text{N}_2\text{O}$ flux to soil $\text{N}_2\text{O}$ emission ( $\text{N}_2\text{O}_{(D)\text{-N}}/\text{N}_2\text{O}_{\text{direct}\text{-N}}$ )

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In this study, the  $\text{Frac}_{\text{LEACH-(H)}}$  was determined by the ratio of N inputs to runoff and leaching N in all crop fields (corn fields: 3404.95 ha, soybeans fields: 3404.95 ha) within the Bear Creek watershed. Nitrogen inputs included the annual amount of synthetic fertilizer N applied to crop fields (FSN) and N inputs from crop residue (FCR) and they were determined in Kim et al. (2009). Estimated  $\text{NO}_3\text{-N}$  flux in groundwater discharged from all cropped fields was used as the amount of leaching N, and runoff N was estimated using the runoff rate ( $5.23 \text{ kg N ha}^{-1} \text{ y}^{-1}$ ) determined in Kim et al. (2009).  
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In this study, the  $\text{N}_2\text{O}$  emission factor,  $\text{EF}_{5g}$  was determined by the mean of the ratio of dissolved  $\text{N}_2\text{O}$  concentration to  $\text{NO}_3\text{-N}$  concentration in groundwater discharged

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from the crop fields, the multi-species riparian buffer, and the cool-season grass filter in 2006–2007. A modified emission factor, EI- $\text{EF}_{5g}$ , was determined based on the ratio between dissolved  $\text{N}_2\text{O}$  flux ( $\text{N}_2\text{O}_{(D)\text{-N}}$ ) in groundwater discharged from all cropped fields and N inputs (FSN+FCR) in all crop fields within the watershed.

5 Soil  $\text{N}_2\text{O}$  emission ( $\text{N}_2\text{O}_{\text{direct}\text{-N}}$ ) in all cropped fields within the watershed was estimated using the measured soil  $\text{N}_2\text{O}$  emission rate (corn field:  $7.2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ , soybeans field:  $16.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) in the sites in 2006–2007 (Kim et al., 2009) and the ratio of dissolved  $\text{N}_2\text{O}$  flux to soil  $\text{N}_2\text{O}$  emission ( $\text{N}_2\text{O}_{(D)\text{-N}}/\text{N}_2\text{O}_{\text{direct}\text{-N}}$ ) was determined using the data.

#### 3.1 Statistical analysis

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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  $\text{NO}_3^-$ ;  $\text{Cl}^-$ ; pH; and dissolved  $\text{N}_2\text{O}$ , 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. Differences were considered significant at the  $P < 0.05$  level. GLM was utilized to determine correlations between groundwater water quality parameters and dissolved  $\text{N}_2\text{O}$ . Statistical analyses were conducted by SAS ver 8.1 (SAS institute, 1999).  
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## 4 Results

### 4.1 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 sig-

nificantly 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 ( $318.16 \pm 0.03$  m a.s.l.,  $n=69$ ) was significantly higher than at the stream edge of buffer ( $317.43 \pm 0.02$  m a.s.l.,  $n=74$ ) over 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 ( $317.43 \pm 0.02$  m a.s.l.,  $n=74$ ) and creek elevation ( $317.35 \pm 0.04$  m a.s.l.,  $n=66$ ) 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 movement of stream water 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 ( $317.60 \pm 0.03$  m a.s.l.,  $n=73$ ) was significantly higher than the creek elevation ( $317.34 \pm 0.04$  m a.s.l.,  $n=58$ ) (Tukey's Studentized Range Test) during the entire period, indicating that there was no movement of the creek water into the riparian aquifer.

#### 4.2 Nitrate concentration, flux, and reduction rate

In the cool-season grass filter,  $\text{NO}_3\text{-N}$  concentrations in groundwater adjacent to the crop field showed a repeated seasonal trend with the highest concentrations in winter and lowest in summer (Fig. 2). However,  $\text{NO}_3\text{-N}$  concentrations in groundwater adjacent to the creek did not show any seasonal trend (Fig. 2). Average  $\text{NO}_3\text{-N}$  concentration was  $9.5 \text{ mg L}^{-1}$  in groundwater wells adjacent to crop fields and  $4.9 \text{ mg L}^{-1}$  in wells adjacent to creek, during 1997–1999 (Fig. 3), and 9 and  $3.3 \text{ mg L}^{-1}$ , respectively, during 2005–2008 (Fig. 4). In this cool-season grass filter site,  $\text{NO}_3\text{-N}$  concentrations

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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  $\text{NO}_3\text{-N}$  concentration in groundwater within the cool-season grass filter decreased by 48% in 1997–1999 and 59% in 2005–2008 when comparing wells nearest the creek with those nearest the crop field. In January 2006–December 2007,  $\text{NO}_3\text{-N}$  flux in groundwater from the crop field to the cool-season grass filter was  $14.2 \text{ kg N}$  and  $\text{NO}_3\text{-N}$  flux from the cool-season grass filter to the creek was  $5.1 \text{ kg N}$  (Fig. 4). This indicates that  $9.1 \text{ kg N}$  was removed from the groundwater as it flowed from the crop field through the cool-season grass filter. This equates to a removal rate of  $130 \text{ kg groundwater NO}_3\text{-N ha}^{-1}$  in the cool-season grass filter ( $9.1 \text{ kg N loss in length } 35 \text{ m} \times \text{width } 20 \text{ m}$ ) during the period of January 2006 to December 2007.

In the multi-species riparian buffer,  $\text{NO}_3\text{-N}$  concentrations in groundwater adjacent to the crop field showed a repeated seasonal trend with the highest concentrations in winter and lowest in summer (Fig. 2). However,  $\text{NO}_3\text{-N}$  concentration in groundwater adjacent to the creek did not show any seasonal trend (Fig. 2). Average  $\text{NO}_3\text{-N}$  concentrations were  $4.9 \text{ mg L}^{-1}$  in groundwater wells adjacent to the crop field and  $5.0 \text{ mg L}^{-1}$  in wells adjacent to the creek, respectively, during 1997–1999 (Fig. 3), and  $4.0$  and  $2.0 \text{ mg L}^{-1}$ , 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  $\text{NO}_3\text{-N}$  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 January 2006–December 2007,  $\text{NO}_3\text{-N}$  flux in groundwater from the crop field to the multi-species riparian buffer was  $4.4 \text{ kg N}$  and groundwater  $\text{NO}_3\text{-N}$  flux from the multi-species riparian buffer to the creek was  $2.1 \text{ kg N}$  (Fig. 4). This indicates the  $\text{NO}_3\text{-N}$  flux was  $2.3 \text{ kg N}$  (52.2%) lower in groundwater nearest the creek compared to near the crop field edge and the resulting groundwater  $\text{NO}_3\text{-N}$  removal was  $33.1 \text{ kg N ha}^{-1}$  ( $2.3 \text{ kg N loss in length } 35 \text{ m} \times \text{width } 20 \text{ m}$ ) in the multi-species riparian buffer in January 2006–December 2007.

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### 4.3 Chloride concentration and the ratio of nitrate to chloride

Average  $\text{Cl}^-$  concentrations in groundwater ranged between 13.2 and 13.4  $\text{mg L}^{-1}$  within the cool-season grass filter during 1997–1999 and between 20.6 and 20.9  $\text{mg L}^{-1}$  within the multi-species riparian buffer during the same period (Fig. 3).  
5 During 2005–2008, average  $\text{Cl}^-$  concentrations in groundwater ranged between 18.2 and 20.6  $\text{mg L}^{-1}$  within grass filters and between 18.2 and 20.8  $\text{mg L}^{-1}$  within the multi-species riparian buffer (Fig. 4). None of these differences in  $\text{Cl}^-$  concentrations were significant. In the cool-season grass filter, the average  $\text{NO}_3^-/\text{Cl}^-$  ratio within groundwater adjacent to crop fields was significantly higher than adjacent to the creek in both  
10 1997–1999 (Mann-Whitney rank sum test  $P < 0.0001$ ) and 2005–2008 (Mann-Whitney rank sum test  $P < 0.0001$ ) (Figs. 3, 4 and 5). Within groundwater under the multi-species riparian buffer, there was no significant difference in the average  $\text{NO}_3^-/\text{Cl}^-$  ratio of groundwater adjacent to crop fields and adjacent to the creek in 1997–1999 (Mann-Whitney rank sum test  $P = 0.41$ ) (Figs. 3 and 5). However, within this same system,  
15 the average  $\text{NO}_3^-/\text{Cl}^-$  ratio within groundwater adjacent to crop fields was significantly higher than that adjacent to the creek in 2005–2008 (Mann-Whitney rank sum test  $P < 0.0001$ ) (Figs. 4 and 5).

### 4.4 Dissolved $\text{N}_2\text{O}$

Dissolved  $\text{N}_2\text{O}$ -N concentration in groundwater under both riparian buffers showed  
20 a repeated seasonal trend, with the concentrations highest in winter and lowest in summer (Fig. 6). Average dissolved  $\text{N}_2\text{O}$ -N concentrations in groundwater ranged between 6.8 and 7.8  $\mu\text{g L}^{-1}$  within the cool-season grass filter during 1997–1999 and between 6.0 and 6.1  $\mu\text{g L}^{-1}$  within the multi-species riparian buffer during the same period (Fig. 3). During 2005–2008, average dissolved  $\text{N}_2\text{O}$ -N concentrations in ground-  
25 water ranged between 11.6 and 14.4  $\mu\text{g L}^{-1}$  within the cool-season grass filters and between 9.0 and 9.1  $\mu\text{g L}^{-1}$  within the multi-species riparian buffer (Fig. 4). Within groundwater under the cool-season grass filter, there was no significant difference in

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dissolved  $\text{N}_2\text{O}$ -N concentration 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  $P = 0.29$ ). In January 2006–December 2007, dissolved  $\text{N}_2\text{O}$ -N flux was 19.7 g N in groundwater adjacent to the crop field and 20.0 g N in the  
5 cool-season grass filter near the creek (Fig. 4).

This pattern was repeated in groundwater under the multi-species riparian buffer, with no significant difference in dissolved  $\text{N}_2\text{O}$ -N concentrations in groundwater adjacent to crop fields and the creek during either 1997–1999 (Mann-Whitney rank sum test  $P = 0.96$ ) or 2005–2008 (Mann-Whitney rank sum test  $P = 0.93$ ). In January 2006–  
10 December 2007, dissolved  $\text{N}_2\text{O}$ -N flux was 8.3 g N in groundwater adjacent to the crop field and 7.7 g N in the multi-species riparian buffer near the creek (Fig. 4).

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

Average dissolved oxygen concentration in groundwater under the grass filter adjacent to crop fields ( $5.0 \pm 0.3 \text{ mg L}^{-1}$ ) was significantly higher than adjacent to the creek  
15 ( $2.6 \pm 0.3 \text{ mg L}^{-1}$ ) in 1997–1999 (two sample t-test  $P < 0.0001$ ) (Figs. 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 ( $2.7$ – $3.3 \text{ mg L}^{-1}$ ) 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  
20 adjacent to the creek either 1997–1999 ( $2.8$ – $3.4 \text{ mg L}^{-1}$ ) (two sample t-test  $P = 0.29$ ) or 2005–2008 ( $2.7$ – $3.3 \text{ mg L}^{-1}$ ) (two sample t-test  $P = 0.24$ ).

In both buffer vegetation types, the average dissolved organic carbon (DOC) concentration ( $0.6$ – $1.1 \text{ mg L}^{-1}$ ) within the groundwater was not significantly different adjacent to crop fields and adjacent to the creek during either 1997–1999 (two sample t-test  
25  $P > 0.1$ ) or 2005–2008 (two sample t-test  $P > 0.1$ ) (Figs. 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  $P > 0.1$ ).

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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  $P=0.62$ ).

#### 4.6 Relation between dissolved $N_2O$ concentrations and water characteristics

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 (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  $N_2O$  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  $N_2O$  concentrations in either the groundwater adjacent to crop fields or the creek (all  $P>0.05$ ) (Fig. 7a and b).

#### 4.7 $Frac_{LEACH-(H)}$ , $EF_{5g}$ , $EI-EF_{5g}$ , and $N_2O_{(D)}-N/N_2O_{direct}-N$ in the crop fields and riparian buffers

Estimated N leaching (TL) (estimated  $NO_3-N$  flux) from all crop fields within the Bear Creek watershed was 30 084 kg N in 2006–2007 (Table 1). Run-off N (TR) from all crop fields within the Bear Creek watershed was 71 231 kg N (North of Bear Creek: 35 615 kg N, South of Bear Creek: 35 615 kg N) in 2006–2007 (Table 2). Annual synthetic fertilizer N applications to crop fields (FSN) were estimated at 908 440 kg N and N inputs from crop residue (FCR) were estimated at 1 186 965 kg N in 2006–2007 (Table 2). Using these data, the ratio of runoff and leaching N (TR+TL, 101 315 kg N) to

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N inputs ( $F_{SN}+F_{CR}$ , 2 095 406.2 kg N),  $Frac_{LEACH-(H)}$ , was determined to be 0.05 (Table 2).

$EF_{5g}$  (mean ratio of dissolved  $N_2O$  concentration to  $NO_3-N$  concentration) in groundwater discharged from crop fields in this study ( $n=99$ ) was 0.0022 (95% C.I. 0.0013–0.0031) (Fig. 7A).  $EF_{5g}$  in groundwater discharged from riparian buffers in this study ( $n=101$ ) was 0.0041 (95% C.I. 0.0028–0.0054) (Fig. 7B).

Estimated dissolved  $N_2O$  flux ( $N_2O_{(D)}-N$ ) in all cropped fields within the Bear Creek watershed was 45.2 kg N in 2006–2007 (Table 1). Nitrogen inputs ( $F_{SN}+F_{CR}$ ) were 2 095 406 kg N in all cropped fields within the Bear Creek watershed in 2006–2007 (Table 2). Using these data, the  $EI-EF_{5g}$  (ratio of dissolved  $N_2O$  flux to N inputs,  $N_2O_{(D)}-N / F_{SN}+F_{CR}$ ) was determined to be 0.00002 in all cropped fields within the Bear Creek watershed (Table 2).  $EI-EF_{5g}$  within riparian buffers in this study was zero since there was no significant change in dissolved  $N_2O$  flux in groundwater under either riparian buffer (Fig. 4).

The estimated soil  $N_2O$  emission ( $N_2O_{direct}-N$ ) in all cropped fields within the Bear Creek watershed was 163 437 kg N (corn fields: 49 031 kg N, soybeans fields: 114 406 kg N) in 2006–2007 (Table 2). Using estimated dissolved  $N_2O$  flux ( $N_2O_{(D)}-N$ ) and soil  $N_2O$  emission ( $N_2O_{direct}-N$ ),  $N_2O_{(D)}-N/N_2O_{direct}-N$  (ratio of dissolved  $N_2O$  flux to soil  $N_2O$  emission) was determined to be 0.0003 (Table 2).  $N_2O_{(D)}-N/N_2O_{direct}-N$  in groundwater discharged from riparian buffers to soil  $N_2O$  emission in riparian buffers was zero since there was no significant change in dissolved  $N_2O$  within groundwater under either riparian buffer (Fig. 4).

## 5 Discussion

### 5.1 Transport and fate of nitrate

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

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riparian buffer in 2005–2008. Processes that may decrease  $\text{NO}_3^-$  concentration in groundwater include dilution of groundwater, uptake by vegetation, and denitrification. Andress (1999), using an isotopic method, found denitrification occurring at this cool-season grass filter site. Our data showed a decrease in the  $\text{NO}_3^-/\text{Cl}^-$  ratio in both sites, with a significant decrease in  $\text{NO}_3^-$  concentration and an insignificant change in the  $\text{Cl}^-$  concentration. These results suggest that dilution from a converging or diverging flow path was not a major factor contributing to the decrease in groundwater  $\text{NO}_3^-$  concentration (e.g. Vidon and Hill, 2004; Davis et al., 2007). Uptake of  $\text{NO}_3^-$  by vegetation was not investigated in this study but is known to occur in riparian buffers (e.g. Clément et al., 2003; Dhondt et al., 2003; Hefting et al., 2005).

In our studies, there was no significant  $\text{NO}_3^-$  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 decrease groundwater residence time and reduce the potential for N loss, allowing transport of  $\text{NO}_3^-$  to the 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 groundwater  $\text{NO}_3^-$  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.

## 5.2 Transport and fate of dissolved $\text{N}_2\text{O}$

The dissolved  $\text{N}_2\text{O}$  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 or 2005–2008. The dissolved  $\text{N}_2\text{O}$  concentrations in both sites ( $6\text{--}14\ \mu\text{g L}^{-1}$ ) were similar to those ( $0\text{--}6.3\ \mu\text{g N L}^{-1}$ ) reported by Davidson and Firestone (1988), Davidson and Swank (1990), Papen and Butterbach-Bahl (1999),

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Blicher-Mathiesen and Hoffmann (1999), Höll et al. (2005), and Davis et al. (2007) and less than those reported by Weller et al. (1994) ( $17.2\ \mu\text{g N L}^{-1}$ ) and Well et al. (2001) ( $10.2\text{--}53.2\ \mu\text{g N L}^{-1}$ ). Weller et al. (1994) estimated  $0.35\ \text{kg N ha}^{-1}$  of annual  $\text{N}_2\text{O}$  loss in soil emission and  $0.04\ \text{kg N ha}^{-1}$  in groundwater (<1% of the intercepted N) and concluded that  $\text{N}_2\text{O}$  production in the riparian buffer is neither an important fate of N removed from cropland discharges nor an important source of atmospheric  $\text{N}_2\text{O}$  pollution. Blicher-Mathiesen and Hoffman (1999) reported that denitrification in a riparian soil can act as a sink for dissolved  $\text{N}_2\text{O}$  in the inflowing groundwater as well as for  $\text{N}_2\text{O}$  produced in the riparian sediment. Davis et al. (2007) reported that both dissolved  $\text{N}_2\text{O}$  and  $\text{NO}_3^-$  were significantly lower in the riparian area than in the adjacent cropping system. Clough et al. (2007) reported significant consumption of  $^{15}\text{N}_2\text{O}$  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  $\text{N}_2\text{O}$  is decreased in riparian areas.

Our results regarding  $\text{NO}_3^-$  decrease without increasing dissolved  $\text{N}_2\text{O}$  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  $\text{NO}_3^-$  to  $\text{N}_2$  without producing  $\text{N}_2\text{O}$  (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 (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  $\text{N}_2\text{O}$ . Second, produced  $\text{N}_2\text{O}$  in groundwater can be released into unsaturated soil above the groundwater table. In this study, the estimated  $\text{NO}_3^-$  losses in groundwater in the cool-season grass filter and multi-species riparian buffer was  $130.0\ \text{kg N ha}^{-1}$  and  $33.1\ \text{kg N ha}^{-1}$ , respectively, and  $\text{N}_2\text{O}$  emission measured on the soil surface was  $5.8\ \text{kg N}_2\text{O-N ha}^{-1}$  in the sites through 2006 to 2007 (Kim et al., 2009). The ratio of  $\text{N}_2\text{O}$  emission measured on the soil surface to  $\text{NO}_3^-$  loss in the groundwater in the cool-season grass filter and multi-species riparian buffer was 0.04 and 0.17, respectively. Since the  $\text{N}_2\text{O}$  emis-

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sion 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  $NO_3^-$  losses. This is consistent with the finding of Deurer et al. (2008) who estimated that upward fluxes from the exchange zone into the unsaturated zone ranged between 0.0009 to 0.3 kg  $N_2O$  ha<sup>-1</sup> y<sup>-1</sup> and the yearly downward fluxes into the exchange zone had about the same order of magnitude. Third, vegetation and microbial communities within the riparian buffers can assimilate and immobilize  $NO_3^-$  resulting in  $NO_3^-$  decrease without increasing dissolved  $N_2O$  in the groundwater. Since this study did not investigate  $NO_3^-$  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.

### 5.3 Determined $Frac_{LEACH-(H)}$ , $EF_{5g}$ , $EI-EF_{5g}$ and $N_2O_{(D)}-N/N_2O_{direct}-N$ and their implication

In this study,  $Frac_{LEACH-(H)}$ , N lost to leaching and runoff, was determined to be 0.05 a value is 6-fold lower than the current IPCC's default value (0.3). Thoms et al. (2005) suggested a value of 0.07 (0.03–0.1) as an appropriate  $Frac_{LEACH-(H)}$  for New Zealand conditions. Our  $Frac_{LEACH-(H)}$  is similar to the value suggested for New Zealand (Thomas et al., 2005).

Our results determine  $EF_{5g}$  (emission factor for  $N_2O$  emissions from N leaching and runoff) of groundwater leached from the crop fields at 0.0022 (95% C.I. 0.0013–0.0031). The Intergovernmental Panel for Climate Change (2006) reported that the previously used  $EF_{5g}$  for groundwater leached from crop fields (0.015) (IPCC, 1997) was too high and they modified  $EF_{5g}$  to 0.0025 based on several studies (Hiscock et al., 2003; Reay et al., 2004; Sawamoto et al., 2005). Our  $EF_{5g}$  is similar to the new IPCC  $EF_{5g}$ . However, since 1) the  $N_2O$  emission factor is typically defined by the ratio of  $N_2O$  emission and N input (IPCC, 2006; Weymann et al., 2008), 2)  $N_2O$ -N concentration in groundwater does not necessarily reflect actual dissolved  $N_2O$  emission (Höll

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et al., 2005), and 3) insignificant correlation between  $NO_3^-$ -N and dissolved  $N_2O$ -N concentrations was observed in this study (Fig. 7), it is suggested that  $EI-EF_{5g}$  is suitable for the emission factor of dissolved  $N_2O$  emission in the sites. The  $EI-EF_{5g}$  (0.00002) in the crop fields is 35-fold less than the value of  $Frac_{LEACH-(H)}$  (0.3) ×  $EF_{5g}$  (0.0025) and this indicates the current IPCC methodology using  $Frac_{LEACH-(H)}$  and  $EF_{5g}$  substantially overestimates dissolved  $N_2O$  flux at this site. It is suggested that  $EI-EF_{5g}$  be determined in various regions and environments and these values be evaluated as improvements to current IPCC methodology.

In this study,  $N_2O_{(D)}-N/N_2O_{direct}-N$  (the ratio of dissolved  $N_2O$  flux to soil  $N_2O$  emission) in the crop fields was 0.0003 indicating that the mass of dissolved  $N_2O$  leaving the crop field was negligible in comparison to soil  $N_2O$  emission. This is consistent with the findings of Davidson and Swank (1990), Ueda et al. (1991), Harrison and Matson (2003), Reay et al. (2004), Höll et al. (2005), and Well et al. (2005) who suggested that indirect  $N_2O$  emission is an insignificant pathway in the N cycle. However, in this study, it was recognized that a monthly sampling interval of dissolved  $N_2O$  measurements may not be frequent enough to observe increases of dissolved  $N_2O$ -N concentration and peaks of dissolved  $N_2O$  emission affected by dry-wet events (Höll et al., 2005) and that estimating  $NO_3^-$ -N and dissolved  $N_2O$ -N flux of the whole watershed using results from measurements in two sites embodies significant uncertainties.

## 6 Conclusions

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  $NO_3^-$  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  $NO_3^-$  concentration decrease provides evidence that dilution from a converging

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or diverging flow path was not a major factor contributing to the decreased  $\text{NO}_3^-$  concentration in groundwater. Our results indicated that determined  $\text{Frac}_{\text{LEACH-(H)}}$  (0.05) is 6-fold less than the current IPCC's default value (0.3) and the  $\text{N}_2\text{O}$  emission factor ( $\text{EF}_{5g}$ ) based on the ratio between dissolved  $\text{N}_2\text{O}$ -N and  $\text{NO}_3$ -N concentrations was not suitable in the site. The modified emission factor ( $\text{EI-EF}_{5g}$ ) based on the ratio between dissolved  $\text{N}_2\text{O}$  flux and N input (0.00002) was determined in the crop fields and indicates the current IPCC methodology overestimates dissolved  $\text{N}_2\text{O}$  flux in the site. A low ratio between dissolved  $\text{N}_2\text{O}$  flux and soil  $\text{N}_2\text{O}$  emission (0.0003) was observed in the crop fields. Based on these results, we suggest that the riparian buffers established adjacent to crop fields to decrease  $\text{NO}_3^-$  did not increase dissolved  $\text{N}_2\text{O}$  in groundwater and dissolved  $\text{N}_2\text{O}$  flux from the crop fields was negligible in comparison to soil  $\text{N}_2\text{O}$  emission.

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**Table 1.** Summarizing the procedures (Eqs. 1, 2, and 3) used to estimate total NO<sub>3</sub>-N and dissolved N<sub>2</sub>O-N flux in groundwater discharged from whole crop fields (North of Bear Creek and South of Bear Creek) in the Bear Creek watershed to Bear Creek in 2006–2007. Conc. is concentration,  $V_x$  is average linear velocity (North of Bear Creek: 0.23 and South of Bear Creek: 0.13 from Spear, 2003),  $n_e$  is effective porosity (0.15 from Spear, 2003), and  $F_{x, \text{day}}$  and  $F_{x, \text{month}}$  are estimated daily and monthly mass flux, respectively.

	Date	Conc.	$V_x$	$n_e$	$F_{x, \text{day}}$	Aquifer	days	$F_{x, \text{month}}$	Total flux
		mg L <sup>-1</sup>	m day <sup>-1</sup>	no unit	g N day <sup>-1</sup> m <sup>-2</sup>	m <sup>2</sup>		kg N month <sup>-1</sup>	kg N
NO <sub>3</sub> -N, North of Bear Creek	Jan 2006	11.7	0.23	0.15	0.4037	112 946	31	1413.3	
	Dec 2007	6.7	0.23	0.15	0.2312	112 946	31	809.3	
	2006–2007								22 957.9
NO <sub>3</sub> -N, South of Bear Creek	Jan 2006	3.5	0.13	0.15	0.0689	112 946	31	241.2	
	Dec 2007	3.4	0.13	0.15	0.0657	112 946	31	229.9	
	2006–2007								7126.1
NO <sub>3</sub> -N, Whole crop fields	2006–2007								30 084.0
N <sub>2</sub> O-N, North of Bear Creek	Jan 2006	0.0039	0.23	0.15	0.000134	112 946	31	0.5	
	Dec 2007	0.0179	0.23	0.15	0.000618	112 946	31	2.2	
	2006–2007								31.8
N <sub>2</sub> O-N, South of Bear Creek	Jan 2006	0.0073	0.13	0.15	0.000143	112 946	31	0.5	
	Dec 2007	0.0106	0.13	0.15	0.000206	112 946	31	0.7	
	2006–2007								13.4
N <sub>2</sub> O-N, Whole crop fields	2006–2007								45.2

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**Table 2.** Summarizing parameters used to calculate the ratios of N inputs to runoff and leaching N ( $\text{Frac}_{\text{LEACH-(H)}}$ ), dissolved N<sub>2</sub>O flux to N inputs ( $\text{EI-EF}_{5g}$ ), and dissolved N<sub>2</sub>O flux to soil N<sub>2</sub>O emission ( $\text{N}_2\text{O}_{(D)}\text{-N}/\text{N}_2\text{O}_{\text{direct-N}}$ ) in crop fields in Bear Creek watershed in 2006–2007.  $F_{SN}$  is annual amount of synthetic fertilizer N applied to crop fields and  $F_{CR}$  is N inputs from crop residue.

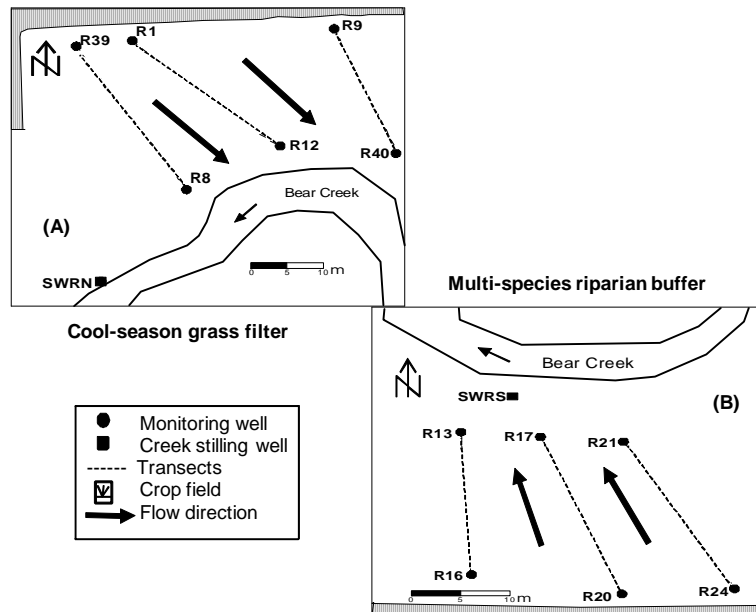
Factor	Unit	Bear Creek watershed		
		Corn fields	Soybean fields	Total
Area <sup>a</sup>	ha	3404.95	3404.95	6809.9
N Fertilizer application rate <sup>b</sup>	kg N ha <sup>-1</sup> y <sup>-1</sup>	133.4	0	–
FSN	kg N	908 440.7	0	908 440.7
N residue rate <sup>c</sup>	kg N ha <sup>-1</sup> y <sup>-1</sup>	92.2	82	–
FCR	kg N	627 872.8	559 092.8	1 186 965.6
FSN+FCR	kg N	1 536 313.4	559 092.8	2 095 406.2
Runoff rate <sup>d</sup>	kg N ha <sup>-1</sup> y <sup>-1</sup>	5.23	5.23	5.23
Total runoff (TR)	kg N	35 615.8	35 615.8	71 231.6
Total leaching (TL) <sup>e</sup>	kg N	–	–	30 084.1
TR+TL	kg N	–	–	101 315.6
$\text{Frac}_{\text{LEACH-(H)}}$ <sup>f</sup>	kg N (kg N of N input) <sup>-1</sup>	–	–	0.05
$\text{N}_2\text{O}_{(D)}\text{-N}$ <sup>g</sup>	kg N	–	–	45.2
$\text{EI-EF}_{5g}$ <sup>h</sup>	kg N (kg N of N input) <sup>-1</sup>	–	–	0.00002
$\text{N}_2\text{O}_{\text{direct-N}}\text{ rate}$ <sup>i</sup>	kg N ha <sup>-1</sup> y <sup>-1</sup>	7.2	16.8	–
$\text{N}_2\text{O}_{\text{direct-N}}$	kg N	49 031.3	114 406.3	163 437.6
$\text{N}_2\text{O}_{(D)}\text{-N}/\text{N}_2\text{O}_{\text{direct-N}}$	kg N (kg N) <sup>-1</sup>	–	–	0.0003

<sup>a</sup> Assumed 50% corn fields and 50% soybean fields. <sup>b</sup> Kim et al. (2009). <sup>c</sup> Kim et al. (2009). <sup>d</sup> Calculated from Lee et al. (2003). <sup>e</sup> Total NO<sub>3</sub>-N flux in groundwater from crop fields in the Bear Creek watershed (Table 1).

<sup>f</sup>  $\text{TR}+\text{TL}/\text{FSN}+\text{FCR}$ . <sup>g</sup> Total dissolved N<sub>2</sub>O-N flux in groundwater from crop fields in the Bear Creek watershed (Table 1).

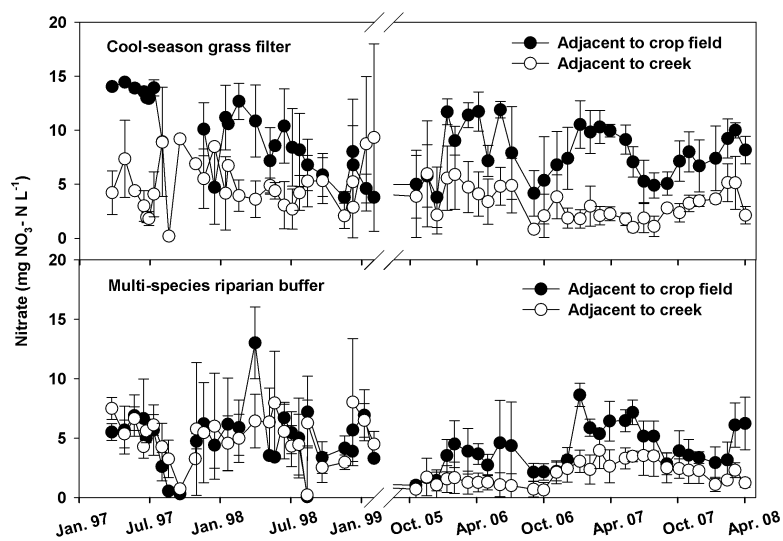
<sup>h</sup> Ratio of dissolved N<sub>2</sub>O flux to N inputs,  $\text{N}_2\text{O}_{(D)}\text{-N}/\text{FSN}+\text{FCR}$ . <sup>i</sup> Soil N<sub>2</sub>O emission in the crop field in 2006–2007 (Kim et al., 2009).

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**Fig. 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 the creek and monitoring wells R39, R1, and R9 are adjacent a crop field. In a multi-species riparian buffer (B), monitoring wells R13, R17, and R21 are adjacent to the creek and monitoring wells R16, R20, and R24 are adjacent a crop field. Figures (A and B) are from Spear (2003).

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**Fig. 2.** Seasonal variation of groundwater NO<sub>3</sub>-N concentration in groundwater under a cool-season grass filter and a multi-species riparian buffer in 1997–1999 (data from Spear, 2003) and 2005–2008.

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	Crop field	Multi-species riparian buffer	Bear Creek	Cool-season grass filter	Crop field	
Groundwater flow direction	→ →	→ →		← ←	← ←	Groundwater flow direction
Cl <sup>-</sup>	20.6 (1.2)	20.9 (1.0)		13.4 (1.0)	13.2 (0.9)	Cl <sup>-</sup>
NO <sub>3</sub> -N	4.9 (0.5)	5 (0.4)		4.9 (2.4)*	9.5(0.7)*	NO <sub>3</sub> -N
NO <sub>3</sub> <sup>-</sup> /Cl <sup>-</sup>	0.3 (0.1)	0.2 (0.0)		0.4(0.0)*	0.8(0.1)*	NO <sub>3</sub> <sup>-</sup> /Cl <sup>-</sup>
Dissolved N <sub>2</sub> O-N	6.1(1.0)	6 (0.7)		6.8(0.8)	7.8(1.2)	Dissolved N <sub>2</sub> O-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

**Fig. 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<sup>-</sup>, NO<sub>3</sub>-N, DOC, and DO is mg L<sup>-1</sup> and unit of dissolved N<sub>2</sub>O-N is μg L<sup>-1</sup>. The value inside parenthesis is standard error of the mean and an asterisk (\*) indicates  $P < 0.05$ . The number of measurements: Cl<sup>-</sup> ( $n=21-23$ ), NO<sub>3</sub>-N ( $n=26-29$ ), NO<sub>3</sub><sup>-</sup>/Cl<sup>-</sup> ( $n=17-22$ ), dissolved N<sub>2</sub>O-N ( $n=26-27$ ), DOC ( $n=3$ ), DO ( $n=19-21$ ), and pH ( $n=3$ ).

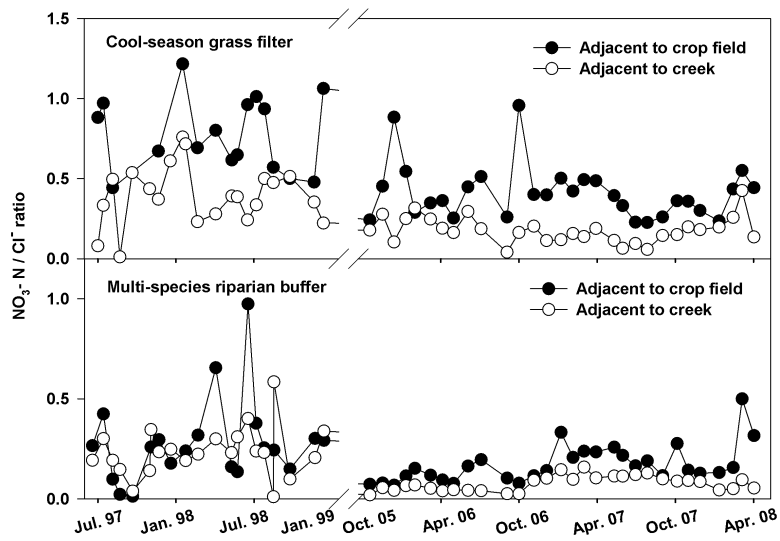
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	Crop field	Multi-species riparian buffer	Bear Creek	Cool-season grass filter	Crop field	
Groundwater flow direction	→ →	→ →		← ←	← ←	Groundwater flow direction
Cl <sup>-</sup>	20.8 (1.2)	18.2 (0.6)		18.2 (0.6)	20.6 (1.2)	Cl <sup>-</sup>
NO <sub>3</sub> -N	4.0 (0.3)*	2.0 (0.2)*		3.3 (0.3)*	7.9 (0.5)*	NO <sub>3</sub> -N
NO <sub>3</sub> -N flux	4.4	2.1		5.1	14.2	NO <sub>3</sub> -N flux
NO <sub>3</sub> <sup>-</sup> /Cl <sup>-</sup>	0.2 (0.1)*	0.1 (0.0)*		0.2 (0.0)*	0.4 (0.0)*	NO <sub>3</sub> <sup>-</sup> /Cl <sup>-</sup>
Dissolved N <sub>2</sub> O-N	9.0 (1.1)	9.1 (1.3)		14.4 (2.2)	11.6 (1.5)	Dissolved N <sub>2</sub> O-N
Dissolved N <sub>2</sub> O-N flux	8.3	7.7		20.0	19.7	Dissolved N <sub>2</sub> O-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

**Fig. 4.** Groundwater characteristics (in 2005–2008) and NO<sub>3</sub>-N and dissolved N<sub>2</sub>O-N fluxes (in January 2006–December 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<sup>-</sup>, NO<sub>3</sub>-N, DOC, and DO is mg L<sup>-1</sup>, dissolved N<sub>2</sub>O-N is μg L<sup>-1</sup>, NO<sub>3</sub>-N flux is kg N (2006 and 2007 years)<sup>-1</sup>, and dissolved N<sub>2</sub>O-N flux is g N (2006 and 2007 years)<sup>-1</sup>. The value inside parenthesis is standard error of the mean and an asterisk (\*) indicates  $P < 0.05$ . The number of measurements: Cl<sup>-</sup> ( $n=29$ ), NO<sub>3</sub>-N ( $n=29$ ), NO<sub>3</sub><sup>-</sup>/Cl<sup>-</sup> ( $n=29$ ), dissolved N<sub>2</sub>O-N ( $n=25-26$ ), DOC ( $n=8$ ), DO ( $n=26-27$ ), and pH ( $n=21$ ).

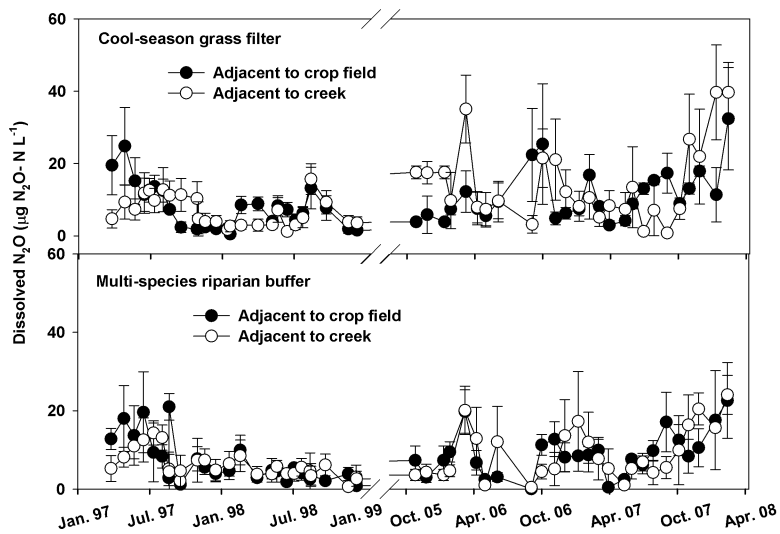
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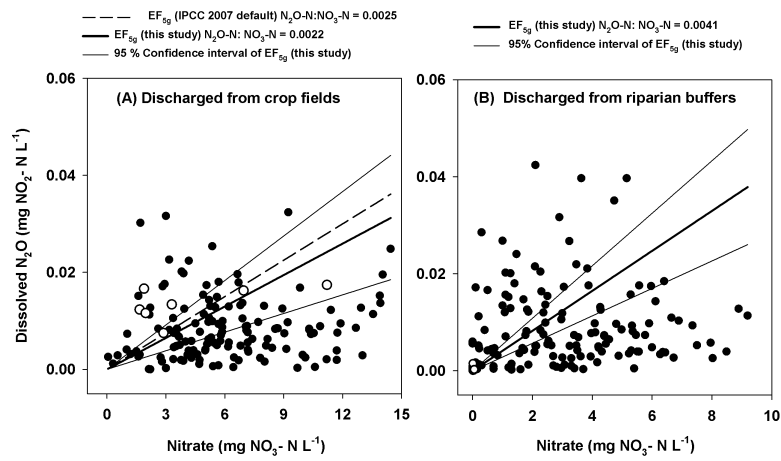
**Fig. 5.** Seasonal variation of the  $\text{NO}_3^-/\text{Cl}^-$  ratio in groundwater under a cool-season grass filter and a multi-species riparian buffer in 1997–1998 (data from Spear, 2003) and 2005–2008.

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**Fig. 6.** Seasonal variation of dissolved  $\text{N}_2\text{O-N}$  concentration in groundwater under a cool-season grass filter and a multi-species riparian buffer in 1997–1999 (data from Spear, 2003) and 2005–2008.

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**Fig. 7.** Relationship between NO<sub>3</sub>-N and dissolved N<sub>2</sub>O-N concentration in groundwater discharged from crop fields **(A)** and riparian buffers (a cool-season grass filter and a multi-species riparian buffer) **(B)** in 1997–1999 (data from Spear, 2003) and 2005–2008 in this study (●,  $n=99-101$ ) and data from Davis et al. (2007) (○,  $n=7$ ). Default of EF<sub>5g</sub> (IPCC, 2007) (---), and EF<sub>5g</sub> of this study (—) and 95% confidence interval of the EF<sub>5g</sub> of this study (---).