



# Nitrous oxide production in riparian zones and its importance to national emission inventories

Peter M. Groffman<sup>a,\*</sup>, Arthur J. Gold<sup>b</sup>, Kelly Addy<sup>b</sup>

<sup>a</sup> Institute of Ecosystem Studies, Box AB, Millbrook, NY 12545, USA

<sup>b</sup> Department of Natural Resources Science, University of Rhode Island, Kingston, RI 02881, USA

Received 9 August 1999; accepted 21 September 1999

*Importance of this paper: Nitrous oxide is a greenhouse gas and a contributor to stratospheric ozone depletion. Current United Nations treaties require the compilation of national emission inventories for all greenhouse gases. Riparian zones are areas that receive and process large amounts of agriculturally-derived nitrate and may be “hotspots” of nitrous oxide production in agricultural landscapes. However, the current inventory methodology for nitrous oxide does not account for these zones. Here we review the data on nitrous oxide emission from riparian zones and propose an approach for accounting for these areas in national emission inventory calculations.*

---

## Abstract

Riparian zones, which sit at the interface between terrestrial and aquatic components of the landscape, often receive and process large amounts of excess nitrogen (N) that moves out of agricultural fields towards streams. These areas thus have the potential to be “hotspots” of nitrous oxide (N<sub>2</sub>O) production in the landscape. However, current Intergovernmental Program on Climate Change (IPCC) methodologies for calculating national N<sub>2</sub>O emission inventories do not explicitly account for riparian N<sub>2</sub>O production. In this paper, we examine the nature and extent of N<sub>2</sub>O production in riparian zones, present some new data on N<sub>2</sub>O production in these areas, and propose a modification to the current IPCC methodology for quantifying N<sub>2</sub>O emissions from agriculture. We also present an example of how large-scale riparian restoration efforts to achieve agricultural water quality objectives could cause significant changes in regional N<sub>2</sub>O budgets. Although current data are inadequate to propose a quantitative emission factor for riparian N<sub>2</sub>O emissions, they suggest that these emissions are likely to be significant in many regions. Specific data on riparian N<sub>2</sub>O emissions should be collected in association with detailed watershed mass balance studies that allow for evaluation of several aspects of the IPCC methodology at once and provide constraints on the magnitude of fluxes that are difficult to measure, e.g. N<sub>2</sub>O flux, N<sub>2</sub>O:N<sub>2</sub> ratio. Riparian and wetland restoration projects to reduce NO<sub>3</sub><sup>-</sup> delivery to coastal waters are being considered in many areas of the world. These projects may affect regional and global N<sub>2</sub>O budgets, but only if they alter the N<sub>2</sub>O:N<sub>2</sub> ratio during denitrification. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Nitrogen; Nitrate; Greenhouse gas; Trace gases

---

## 1. Introduction

Riparian zones are the interface between terrestrial and aquatic components of the landscape. These areas have unique characteristics due to the mixture of terrestrial and aquatic factors that influence their structure and function (Gregory et al., 1991; Naiman and

---

\* Corresponding author. Tel.: +1-914-677-7522; fax: +1-914-677-5976.

E-mail address: groffmanp@ecostudies.org (P.M. Groffman).

Decamps, 1997). Riparian ecosystems have received attention in several contexts including biodiversity, water quality maintenance and stream ecosystem habitat protection (Gilliam, 1994; Lowrance et al., 1997).

Nitrous oxide ( $N_2O$ ) is a “greenhouse” gas which can influence the earth’s radiative budget and plays a role in stratospheric ozone destruction (Mooney et al., 1987; Prather et al., 1995). Atmospheric  $N_2O$  concentration is increasing at a rate of 0.2–0.3% a year (IPCC, 1997) and contributes approximately 5% of the global enhanced greenhouse effect (Schimel et al., 1995). Interest in  $N_2O$  production in riparian zones has arisen from the realization that these areas can be critical “hotspots” of nitrogen (N) transformation in the landscape. Many studies have found that riparian zones have the ability to intercept N moving in surface runoff and groundwater from uplands, preventing its movement into streams (Gilliam, 1994; Hill, 1996). Given that  $N_2O$  is a by-product of N processing (Firestone and Davidson, 1989), these studies suggest that rates of  $N_2O$  production in riparian zones may be quite high, especially in agricultural landscapes where there are large amounts of excess N leaving crop fields and moving towards streams (Groffman et al., 1998).

The United Nations Framework Convention on Climate Change (UNFCCC) calls for the compilation of national emission inventories for trace gases ( $CO_2$ ,  $CH_4$ ,  $N_2O$ ) that contribute to climate change. The Intergovernmental Program on Climate Change (IPCC) has developed protocols for quantifying  $N_2O$  emissions from industry, agriculture and natural ecosystems (IPCC, 1997). The methods for computing  $N_2O$  emissions from agriculture (described below) take a “cradle to grave” approach, accounting for “direct” emissions associated with fertilizer and manure inputs to crop fields as well as “indirect emissions” that occur as N is processed after it leaves the field in harvest, surface runoff or groundwater flow (Mosier et al., 1996, 1998). As N leaves crop fields in these hydrologic vectors,  $N_2O$  can be emitted as the N is processed in groundwater, riparian zones, streams, estuaries and ultimately in the ocean (Kroeze et al., 1999). In this paper, we examine the nature and extent of  $N_2O$  production in riparian zones, present some new data on  $N_2O$  production in these areas, and propose a modification to the current IPCC methodology for quantifying indirect emissions from agriculture. We also present an example of how large-scale riparian restoration efforts to achieve water quality objectives could cause significant changes in regional  $N_2O$  budgets.

## 2. Methods

We used data from several sources to achieve our objectives of (1) evaluating the nature and extent of  $N_2O$  production in riparian zones and (2) proposing a mod-

ification to the current IPCC methodology for quantifying indirect  $N_2O$  emissions from agriculture. We first make a case that riparian zones are hotspots of N transformation in agricultural landscapes. We then describe the existing IPCC methodology for quantifying indirect  $N_2O$  emissions and highlight deficiencies in the way that this methodology handles riparian dynamics. This is followed by a review of the existing literature, and a presentation of some new data on  $N_2O$  fluxes in riparian zones. We also use data from an agricultural watershed mass balance study to evaluate the IPCC methodology. Finally, we present a case study showing how large-scale riparian restoration efforts to achieve water quality objectives could cause significant changes in regional  $N_2O$  budgets.

## 3. Riparian zones as hotspots of N transformation in agricultural landscapes

### 3.1. Magnitude

Numerous studies over the last 20 years have demonstrated that riparian zones are hotspots of N transformation in agricultural landscapes (Lowrance et al., 1984; Peterjohn and Correll, 1984; Jacobs and Gilliam, 1985; Lowrance et al., 1997; Hill, 1996; Correll, 1997). There have been several attempts to propose “typical” or “default” values for N retention in these areas for use in regional assessments. Lowrance et al. (1997) suggested that 50–90% of the total load of nitrate ( $NO_3^-$ ) that leaves crop fields in the Coastal Plain of the southeastern USA is retained in the riparian zone. Gilliam et al. (1997) assumed that 30% of the N that leaves crop fields is retained in riparian zones in the same region. Of 20 studies reviewed by Hill (1996), 12 reported greater than 90% retention and only three reported less than 50%. Mitsch et al. (in press) assumed an N retention rate of  $4 \text{ g N m}^{-2} \text{ y}^{-1}$  in riparian zones in an assessment of N dynamics in the Mississippi river watershed of North America. It is important to note however, that there has been no systematic attempt to develop a community-wide “best professional judgment” estimate of riparian N processing by groups of scientists involved in regional water quality assessment and mitigation efforts. These types of estimates are critical to the development of IPCC emission inventory methodologies.

### 3.2. Mechanisms

Riparian N removal is based on complex interactions between several biological processes and hydrologic vectors. The vast majority of N movement from agricultural fields towards streams is as  $NO_3^-$  in groundwater flow (Keeney, 1986). Due to its high solubility and

negative charge,  $\text{NO}_3^-$  is readily transported to groundwater from the surface soils of agricultural fields. As  $\text{NO}_3^-$  laden groundwater moves towards riparian zones,  $\text{NO}_3^-$  can be denitrified in the subsurface or taken up by plants that have roots in the groundwater (Lowrance et al., 1984). Nitrate taken up by plants can be returned to the surface soil in litterfall where it can be denitrified, taken up again by plants, or returned to the groundwater (Hanson et al., 1994). Nitrate can also be taken up, or “immobilized” by microbes in either surface or subsurface soils (Davidson et al., 1992). Immobilized N in plant or microbial tissues can ultimately be stored, long-term, in soil organic matter (Paul and Clark, 1996). Riparian  $\text{N}_2\text{O}$  production can occur during denitrification of  $\text{NO}_3^-$  inputs or during nitrification of N that has been taken up by plants or microbes and remineralized (Firestone and Davidson, 1989).

### 3.3. Uncertainties

There are several important uncertainties and sources of variation in assessments of N removal in riparian zones. Of primary importance is the fact that riparian N processing is a spatially explicit phenomenon based on interaction of  $\text{NO}_3^-$  in agricultural drainage water with the biologically active zone of the riparian zone (Hill, 1996). Groundwater flow paths that bypass the biologically active zone eliminate riparian N processing. Bypass flow can occur when groundwater intersects with the ground surface and emerges as a “seep” across the surface. On the other hand, groundwater can move deep below the microbially active portion of soil and emerge below the river, i.e., underflow. Bypass flow can also be human caused (e.g., artificial drainage). However, there are good prospects for identifying areas of bypass flow in regional scale assessments (Winter, 1988; Hill, 1996; Lowrance et al., 1997).

In addition to groundwater flow paths, there is marked control of riparian function by soils, climate, vegetation and land use history (Correll, 1997). These factors are all topics of active research. However, the fact that high rates of riparian  $\text{NO}_3^-$  removal have been reported from a very wide range of sites suggests that as long as there is a hydrologic connection between the upland and the riparian zone, there will be active N processing.

While there is strong evidence in support of riparian zones as hotspots of N transformation in the landscape, there are very few data on  $\text{N}_2\text{O}$  flux from these areas. Conceptually, there are problems in (1) partitioning N removal between plant uptake, microbial immobilization and denitrification, (2) predicting the  $\text{N}_2\text{O}$  yield during denitrification and (3) accounting for  $\text{N}_2\text{O}$  produced during remineralization, nitrification and denitrification of N that has been taken up by plants or microbes. Practically, the fact that riparian zones are wet

and have high variation in plant, soil and hydrologic conditions has made it more difficult to measure  $\text{N}_2\text{O}$  fluxes in these areas compared to crop fields. The lack of data and synthetic models of riparian  $\text{N}_2\text{O}$  production are the most critical limitations to our ability to include riparian zones in regional and global  $\text{N}_2\text{O}$  assessments.

## 4. The IPCC methodology for calculating indirect $\text{N}_2\text{O}$ emissions from agriculture

The objective of this methodology is to provide a complete accounting of the  $\text{N}_2\text{O}$  production associated with agricultural use of N on a country by country basis (IPCC, 1997). Direct emissions from fertilized fields are assumed to be 1.25% of fertilizer and manure N applied to the field. Earlier methodologies accounted only for these direct emissions. The methodology for calculating indirect  $\text{N}_2\text{O}$  emissions from agriculture is

$$\text{N}_2\text{O} (\text{Indirect}) = \text{N}_2\text{O} (\text{G}) + \text{N}_2\text{O}(\text{L}) + \text{N}_2\text{O}(\text{S})$$

where  $\text{N}_2\text{O} (\text{G})$  – emissions associated with atmospheric deposition of agricultural N that has been transferred to the atmosphere,  $\text{N}_2\text{O} (\text{S})$  – emissions associated with human sewage,  $\text{N}_2\text{O} (\text{L})$  emissions associated with the N that leaves crop fields in leaching and runoff. This is the N that is processed in riparian zones.

$$\text{N}_2\text{O} (\text{L}) = \text{NLEACH} * \text{EF5}$$

where NLEACH – the amount of N that leaves crop fields in leaching and runoff. This is assumed to be 30% of the fertilizer and manure N that is applied to crop fields. EF5 –  $\text{N}_2\text{O}$  emission factor for N that leaves crop fields in leaching and runoff and is processed as it moves ultimately to the world ocean. This factor is assumed to be 2.5% and is partitioned as EF5-g (groundwater, 1.5%), EF5-r (rivers, 0.075%) and EF5-e (estuaries, 0.025%).

The methodology suggests that the indirect emissions account for approximately 1/3 of the total agricultural source (Mosier et al., 1998; Kroeze et al., 1999). Leaching and runoff, i.e.,  $\text{N}_2\text{O}(\text{L})$ , accounts for 75% of the indirect emissions. Groundwater, i.e., EF5-g, accounts for 60% of  $\text{N}_2\text{O}(\text{L})$ . However, the indirect emissions are considered to be the most uncertain component of the methodology because they are based on a small set of highly variable reported  $\text{N}_2\text{O}$  emission factors (Nevison, 2000).

In the current methodology, EF5-g is conceived to represent  $\text{N}_2\text{O}$  that degasses from groundwater. We suggest that this emission factor is conceptually unrealistic because it assumes that there is no N processing or  $\text{N}_2\text{O}$  production in either groundwater or riparian zones. The current factor is based on six studies from the literature that reported  $\text{N}_2\text{O}:\text{NO}_3^-$  ratios in agricultural drainage and groundwater. Nevison (2000) has

Table 1

N<sub>2</sub>O production in groundwater mesocosms (15 cm diam by 40 cm long intact horizontal sections of aquifer material) from moderately well-drained (upland/wetland transition zone) and poorly drained (wetland) locations within a forested riparian zone in Rhode Island, USA<sup>a</sup>

	Moderately well drained	Poorly drained
% of N input	0.026	3.7
kg N <sub>2</sub> O per kg N input	0.00026	0.037
N <sub>2</sub> O:N <sub>2</sub>	99:1	99:1
pH	4.8–5.3	4.8–5.3
% C	0.07	0.13

<sup>a</sup> Mesocosms were treated with natural groundwater enriched with 10 mg NO<sub>3</sub><sup>-</sup>-N L<sup>-1</sup> (99% <sup>15</sup>N) and incubated at ambient temperature and dissolved oxygen levels at a flow rate of 0.025 m d<sup>-1</sup>. N gases were collected with silicone membrane samplers (Jacinthe and Dick, 1996) and analyzed by electron capture gas chromatography (N<sub>2</sub>O) and isotope ratio mass spectrometry (N<sub>2</sub>O and N<sub>2</sub>, Mosier and Schimel, 1993). Data from Jacinthe et al. (1998). Table adapted from Groffman et al. (1998).

re-evaluated these ratios and has proposed reducing EF5-g from 0.015 to 0.001 kg N<sub>2</sub>O–N per kg of N input. We suggest that there should be a complete re-evaluation of both the conceptual basis and actual magnitude of this emission factor.

The conceptual basis for EF5-g is clearly flawed. Numerous studies have found that denitrification occurs in groundwater (Hiscock et al., 1991; Korom, 1992), especially in groundwater in riparian zones receiving NO<sub>3</sub><sup>-</sup> enriched agricultural drainage (Lowrance, 1992; Jacinthe et al., 1998; Addy et al., 1999). Moreover, the current EF5-g, which does not include riparian effects, ignores the large body of research on riparian N processing reviewed above. We suggest that EF5-g should be reformulated to encompass all N<sub>2</sub>O produced between the surface soil of the crop field and the river. This new emission factor would include N<sub>2</sub>O produced as NO<sub>3</sub><sup>-</sup> leaches through the soil profile, N<sub>2</sub>O produced in groundwater beneath the crop field and N<sub>2</sub>O produced in the riparian zone.

## 5. Data on N<sub>2</sub>O emissions from riparian zones

Comprehensive data on N<sub>2</sub>O production from a riparian forest in Maryland, USA were presented by Weller et al. (1994). This forest has been demonstrated to remove between 4.5 and 6.0 g N m<sup>-2</sup> y<sup>-1</sup> of agriculturally-derived NO<sub>3</sub><sup>-</sup>. Flux of N<sub>2</sub>O from the soil surface was measured with large (1–20 m<sup>2</sup>) flux chambers and a tunable diode laser over the course of a year. Of the 4.5–6.0 g N m<sup>-2</sup> y<sup>-1</sup> of groundwater NO<sub>3</sub><sup>-</sup> that was transformed in this riparian zone, 0.039 g N m<sup>-2</sup> y<sup>-1</sup> was converted to N<sub>2</sub>O. The investigators assume that a much larger amount of N left as N<sub>2</sub>. The N<sub>2</sub>O flux was 0.65–0.87% of the N input to the riparian zone, or 0.0065–0.0086 kg N<sub>2</sub>O–N produced per kg of N input.

Production of N<sub>2</sub>O was measured in mesocosms of groundwater material taken from two positions (moderately well-drained soils at the upland edge of the riparian zone and poorly drained soils at the wetland end of

the riparian zone) in a riparian forest in Rhode Island, USA (Jacinthe et al., 1998; Table 1). Emissions of N<sub>2</sub>O ranged from 0.02% of N input at the upland edge of the riparian zone (0.0002 kg N<sub>2</sub>O–N per kg of N input) to 3.7% (0.037 kg N<sub>2</sub>O–N per kg of N input) of N input in the wetland transition zone. These results and other studies (Groffman et al., 1992, 1996; Simmons et al. 1992; Nelson et al., 1995) clearly show that riparian N<sub>2</sub>O emission depends fundamentally on the abundance of specific soil types at specific sites. Ratios of N<sub>2</sub>O:N<sub>2</sub> were very high in this study.

Nitrate removal and denitrification rates were measured in two poorly drained sites in Rhode Island using the same mesocosm technique used by Jacinthe et al. (1998) by Addy et al. (1999), except that mesocosms were dosed with NO<sub>3</sub><sup>-</sup> at 5, rather than 10 mg N L<sup>-1</sup>. Here we report N<sub>2</sub>O production from this same study (Table 2). Emissions of N<sub>2</sub>O ranged from 0.085% (0.00085 kg N<sub>2</sub>O per kg of N input) of N input to 0.449% (0.0045 kg N<sub>2</sub>O–N per kg of N input) of N input and averaged 0.163% (0.00163 kg N<sub>2</sub>O–N per kg of N input) of N input. There were significant relationships between the N<sub>2</sub>O:N<sub>2</sub> ratio and pH (Fig. 1,  $r^2 = 0.49$ ,  $p < 0.01$ ) and total denitrification rate (Fig. 2,  $r^2 = 0.71$ ,  $p < 0.001$ ). The N<sub>2</sub>O:N<sub>2</sub> ratio ranged from 0.002 (1:500) to 0.047 (1:21) with a mean of 0.02 (1:50).

High variation in the N<sub>2</sub>O:N<sub>2</sub> ratio during denitrification has complicated assessment of N<sub>2</sub>O production in many cases (Firestone and Davidson, 1989). Data from our Rhode Island studies, where this ratio varied from 1:500 to 99:1 suggest that this ratio is a critical controller of riparian N<sub>2</sub>O emission. During denitrification, NO<sub>3</sub><sup>-</sup> and N<sub>2</sub>O are used as electron acceptors during respiration, with reduction of N<sub>2</sub>O to N<sub>2</sub> the last step in the process. The reduction of N<sub>2</sub>O has been found to be strongly influenced by low pH and high soil O<sub>2</sub> levels that can denature the N<sub>2</sub>O reductase enzyme. The reduction can also be affected by the demand for electron acceptors, i.e., if NO<sub>3</sub><sup>-</sup> levels are low and denitrification rates are high, N<sub>2</sub>O is more likely to be reduced. Multifactor control by pH, NO<sub>3</sub><sup>-</sup> concentration and

Table 2

Fluxes of N in groundwater mesocosms (15 cm diam by 40 cm long intact horizontal sections of aquifer material) from two sites (six mesocosms each) with poorly drained soils in Rhode Island, USA<sup>a</sup>

Core	Nitrate removal ( $\mu\text{g N kg}^{-1} \text{d}^{-1}$ )	Denitrification	N <sub>2</sub> O production	N <sub>2</sub> O production (% of N input)	pH
1	16.4	13.2	0.467	0.449	4.7
2	-0.1	6.5	0.181	0.174	4.3
3	4.6	4.0	0.182	0.175	4.6
4	3.7	4.0	0.148	0.142	6.0
5	-4.3	4.0	0.185	0.178	6.0
6	20.3	20.5	0.190	0.183	5.8
7	38.1	6.0	0.107	0.10	6.8
8	36.5	32.1	0.111	0.107	7.1
9	39.7	32.5	0.127	0.122	7.0
10	54.5	51.0	0.154	0.148	6.4
11	50.1	46.3	0.088	0.085	6.5
12	24.5	29.1	0.090	0.087	6.3

<sup>a</sup> Mesocosms were treated with natural groundwater enriched with 5 mg NO<sub>3</sub>-N L<sup>-1</sup> (0.5% <sup>15</sup>N) and incubated at ambient temperature and dissolved oxygen levels. N gases were collected with silicone membrane samplers (Jacinthe and Dick, 1996) and analyzed by electron capture gas chromatography (N<sub>2</sub>O) and isotope ratio mass spectrometry (N<sub>2</sub>O and N<sub>2</sub>, Mosier and Schimel, 1993). Nitrate removal and denitrification data from Addy et al. (1999).

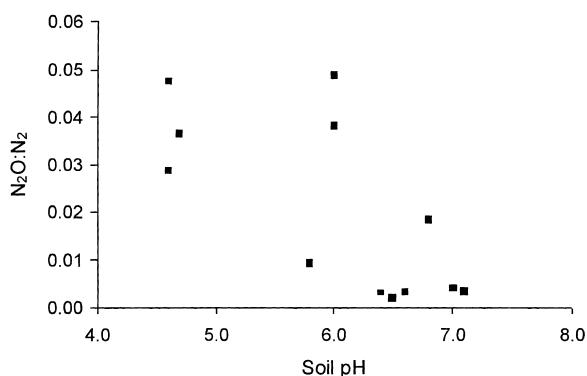


Fig. 1. N<sub>2</sub>O:N<sub>2</sub> ratio versus pH in groundwater mesocosms from two riparian sites with poorly drained soils in Rhode Island, USA.

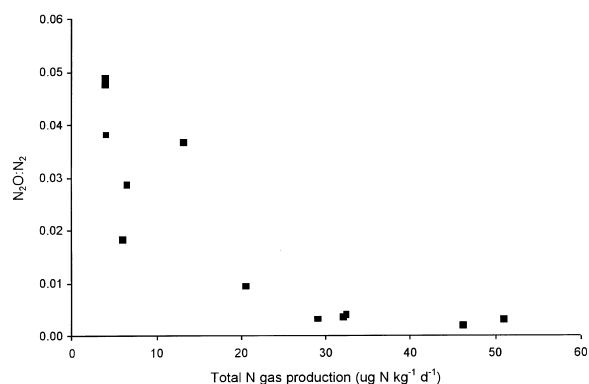


Fig. 2. N<sub>2</sub>O:N<sub>2</sub> ratio versus total N gas production in groundwater mesocosms from two riparian sites with poorly drained soils in Rhode Island, USA.

denitrification rate can explain the variation in N<sub>2</sub>O:N<sub>2</sub> in our Rhode Island studies (Figs. 1 and 2) and likely causes high variation in nature.

Clearly, there are not enough data to make a new, well-justified EF5-g (Table 3). The few data that are available range over three orders of magnitude, with some exceeding the current IPCC value and others even lower than the much lower value proposed by Nevison (2000). There is a strong need for more data on riparian N<sub>2</sub>O emissions given the importance of these areas as hotspots of anthropogenic, agriculturally-derived N flux in the landscape.

An alternative approach to evaluating N<sub>2</sub>O emission from riparian zones (and other aspects of the IPCC methodology for indirect N<sub>2</sub>O emissions) is to analyze long-term N budgets from small agricultural water-

sheds with intact riparian zones. For example, Steinheimer et al. (1998) report a 23 year N budget for an intensively monitored, 40 ha agricultural watershed in Iowa, USA with continuous maize production. Over the 23 year period, approximately half of the applied fertilizer was removed as grain, 16% of the applied N was transported to the adjacent stream and 31% was considered to be “lost” or “stored” in the watershed (Table 4).

The IPCC methodology for calculating indirect N<sub>2</sub>O emissions from agriculture assumes that 30% of N fertilizer leaves the field in leaching and runoff. However, there is great uncertainty and much active research on N leaching losses. For example, for the Iowa watershed described above, Steinheimer et al. (1998) report only 16% leaching. It is important to note that this watershed

Table 3  
N<sub>2</sub>O emission factors for riparian zones

Study	Emission factor (kg N <sub>2</sub> O–N per kg of N input)
Current IPCC methodology, groundwater emission factor (EF5-g)	0.015
Proposed new EF5-g (Nevison, 2000)	0.001
Weller et al. (1994)	0.0065–0.0086
Jacinthe et al. (1998)	0.0002–0.037
This study	0.00085–0.0049

Table 4  
Fate of 23 years of nitrogen fertilizer added to a 40 ha watershed in Iowa cropped to continuous maize. All data other than N<sub>2</sub>O from Steinheimer et al. (1998)

Fate of added fertilizer	Percent of fertilizer input
Grain harvest	50
Loss to stream in groundwater	16
Loss as sediment	2
Loss as surface runoff	1
“Lost” or “stored” <sup>a</sup>	31
N <sub>2</sub> O – IPCC <sup>b</sup>	1.7
N <sub>2</sub> O – Mass balance <sup>c</sup>	0.9 (0.06–30)

<sup>a</sup> “Lost” refers primarily to gaseous loss, “stored” refers to storage in soil organic matter.

<sup>b</sup> Includes direct production (1.25% of input) and N<sub>2</sub>O (L), the indirect production associated with leaching and groundwater. This indirect production equals 0.45% of input, assuming that 30% of N input leaches to groundwater and an EF5-g of 0.015.

<sup>c</sup> Calculated assuming that all “lost and stored” N was denitrified with the mean N<sub>2</sub>O:N<sub>2</sub> ratio from the data in Table 2 (0.020) and the range of all our Rhode Island data (1:500–99:1).

includes an intact riparian zone that might have absorbed much of the N that leached from the fertilized soils. It is also important to note that excess N (input–harvest) was approximately 50%, which is consistent with many previous studies (National Research Council, 1993; Karlen et al., 1998). Cambardella et al. (1999) reported 29% of applied fertilizer was leached over a four year period from maize-soybean rotations, also in Iowa, USA. However, their analysis did not account for N input by symbiotic fixation associated with the soybeans so leaching as a percent of total N input was lower than 29%. Vinten (1999) found that percent leaching of fertilizer ranged from >30% to <10% over a seven-year period on a clay loam soil cropped to spring and/or winter barley in Scotland, UK. On a sandy loam soil with similar cropping in the same region, losses were much higher, ranging from 40% to greater than 50%

over the same period. In contrast, Toth and Fox (1998) found close to the predicted average of 30% of fertilizer leached over a four year period of continuous maize cropping in Pennsylvania, USA. These results suggest that the IPCC estimates of N leaching should likely be revisited (Nevison, 2000), and that riparian zone processing may be a critical controller of variability in this process.

In addition to evaluating some of the basic assumptions of the IPCC methodology, we can also use the Steinheimer et al. (1998) data to make some estimates of N<sub>2</sub>O flux. If we assume that their watershed is not gaining or losing N, then we can assume that the 31% of fertilizer that was lost or stored was lost as gas by denitrification. Assuming that long-term agricultural soils are not gaining or losing N has a solid basis in the literature (Paul and Clark, 1996). On the other hand, there are no measurements to support the high rates of denitrification that would be required to account for 31% of the added N being lost to this process. The enigma of “missing N” is common in many agricultural studies (National Research Council, 1993). However, if we apply the mean N<sub>2</sub>O:N<sub>2</sub> ratio observed in the Rhode Island studies presented in Table 2 (0.020 or 1:50) to this 31%, then 0.6% of the total fertilizer input would have gone off as N<sub>2</sub>O (Table 4). Using the full range of ratios observed in our Rhode Island studies would produce estimates of N<sub>2</sub>O emission ranging from 0.062% to 30% of fertilizer input. The standard IPCC methodology described above would predict that 1.25% would be emitted as N<sub>2</sub>O in direct emissions from the crop field and another 0.45% would go off as indirect emissions associated with leaching and groundwater, i.e., N<sub>2</sub>O(L), for a total of 1.7% (Table 4).

The above analysis suggests that N<sub>2</sub>O flux studies and evaluations of the IPCC methodology should be carried out in association with detailed watershed mass balance studies. These balances allow for evaluation of several aspects of the methodology at once and provide constraints on the magnitude of fluxes that are difficult to measure, e.g. N<sub>2</sub>O flux, N<sub>2</sub>O:N<sub>2</sub> ratio. The analysis also reinforces the idea that the N<sub>2</sub>O:N<sub>2</sub> ratio during denitrification is a critical controller of N<sub>2</sub>O emission in agricultural landscapes.

## 6. Riparian restoration and N<sub>2</sub>O flux in the Mississippi river watershed

The Gulf of Mexico is characterized by a large area of hypoxic bottom water that is thought to be caused by high N outputs from the Mississippi River (Turner and Rabalais, 1991). Proposed solutions to the hypoxia problem include the restoration of up to 50,000 km<sup>2</sup> of wetlands and riparian zones in the Mississippi watershed (Mitsch et al., 1999). The objective of this restoration

would be to reduce N delivery to the Gulf by 50%, or 784,000 metric tons of N, by denitrification. With an  $N_2O$  ratio of e.g. 1:20, this would produce approximately 4.5 Gg of  $N_2O-N$ , or 0.045 Tg. For comparison, Potter et al. (1996) estimate a global temperate grassland (the natural vegetation of much of the Mississippi watershed)  $N_2O$  source of 0.09 Tg. It is important to note that large-scale wetland and riparian restoration projects to reduce  $NO_3^-$  delivery to coastal waters are being considered in many parts of the world.

While these calculations suggest that riparian restoration could produce significant amounts of  $N_2O$ , it is important to consider that restoration may just alter the location of  $N_2O$  production and not change the total amount of production. The IPCC methodology suggests that as agriculturally-derived N moves from fields to groundwater to rivers to estuaries,  $N_2O$  is produced at each step along the way. The methodology suggests that  $N_2O$  emission is controlled only by the amount of N added as fertilizer and would thus not be affected by restoration, i.e., the  $N_2O$  would be produced in restored riparian buffers rather than in rivers or estuaries.

Restoration can only affect (positively or negatively) regional  $N_2O$  budgets if it alters the  $N_2O:N_2$  ratio during denitrification. For example, if wetlands are created to facilitate denitrification in watersheds to prevent delivery of  $NO_3^-$  to the Gulf of Mexico, and if the  $N_2O:N_2$  ratio during denitrification is higher in these wetlands than it is in Gulf sediments, then restoration will result in an increase in  $N_2O$  emissions to the atmosphere. Conversely, restoration could represent an opportunity to decrease indirect  $N_2O$  emissions if we can develop reliable strategies for reducing the  $N_2O$  yield during denitrification in created/restored wetlands in the watershed. Clearly, there is a strong need for evaluating how the  $N_2O:N_2$  ratio varies in different environments and for exploring the potential for manipulation of this ratio to reduce indirect  $N_2O$  emissions.

## 7. Conclusions

- Riparian zones are hotspots of N transformation in the landscape, converting large amounts of agriculturally-derived N into N gas.
- The current IPCC methodology does not account for riparian N processing and  $N_2O$  production, conceptually or practically.
- There is currently not enough data to propose a new quantitative emission factor for riparian  $N_2O$  emissions. Studies to date suggest that riparian  $N_2O$  production is strongly influenced by site hydrologic conditions, soil type and denitrification rate. There is a strong need for more measurements of riparian  $N_2O$  production. These measurements should be carried out in association with detailed watershed mass balance studies that allow for evaluation of several components of the IPCC methodology at once and provide quantitative constraints on measured fluxes.
- Riparian and wetland restoration projects to reduce  $NO_3^-$  delivery to coastal waters are being considered in many areas of the world. These projects may affect regional and global  $N_2O$  budgets, but only if they alter the  $N_2O:N_2$  ratio during denitrification. There is a strong need for determining if management practices can alter this ratio or if agricultural  $N_2O$  emissions can only be reduced by reducing the amount of fertilizer applied to crop fields.

## References

- Addy, K.L., Gold, A.J., Groffman, P.M., Jacinthe, P.A., 1999. Groundwater nitrate removal in forested and mowed riparian buffer zones. *Journal of Environmental Quality* 28, 962–970.
- Cambardella, C.A., Moorman, T.B., Jaynes, D.B., Hatfield, J.L., Parkin, T.B., Simpkins, W.W., Karlen, D.L., 1999. Water quality in Walnut Creek watershed: Nitrate-nitrogen in soils, subsurface drainage water, and shallow groundwater. *Journal of Environmental Quality* 28, 25–34.
- Correll, D.L., 1997. Buffer zones and water quality protection: General principles. In: Haycock, N.E., Burt, T.P., Goulding, K.W.T., Pinay, G. (Eds.), *Buffer Zones: Their Processes and Potential in Water Protection*. Harpenden, UK, Quest Environmental, pp 7–20.
- Davidson, E.A., Hart, S.C., Firestone, M.K., 1992. Internal cycling of nitrate in soils of a mature coniferous forest. *Ecology* 73, 1148–1156.
- Firestone, M.K., Davidson, E.A., 1989. Microbiological basis of NO and  $N_2O$  production and consumption in soil. In: Andreae, M.O., Schimel, D.S. (Eds.), *Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere*. Wiley, Chichester, pp. 7–22.
- Gilliam, J.W., 1994. Riparian wetlands and water quality. *Journal of Environmental Quality* 25, 896–900.
- Gilliam, J.W., Osmond, D.L., Evans, R.O., 1997. Selected agricultural best management practices to control nitrogen in the Neuse River Basin. North Carolina Agricultural Research Service Technical Bulletin #311. North Carolina State University, Raleigh, NC.
- Gregory, S.V., Swanson, F.J., McKee, W.A., Cummins, K.W., 1991. An ecosystem perspective of riparian zones. *BioScience* 41, 540–551.
- Groffman, P.M., Gold, A.J., Simmons, R.C., 1992. Nitrate dynamics in riparian forests: Microbial studies. *Journal of Environmental Quality* 21, 666–671.
- Groffman, P.M., Gold, A.J., Jacinthe, P.A., 1998. Nitrous oxide production in riparian zones and groundwater. *Nutrient Cycling in Agroecosystems* 52, 179–186.
- Groffman, P.M., Howard, G., Gold, A.J., Nelson, W.M., 1996. Microbial nitrate processing in shallow groundwater in a riparian forest. *Journal of Environmental Quality* 25, 1309–1316.

- Hanson, G.C., Groffman, P.M., Gold, A.J., 1994. Symptoms of nitrogen saturation in a riparian wetland. *Ecological Applications* 4, 750–756.
- Hill, A.R., 1996. Nitrate removal in stream riparian zones. *Journal of Environmental Quality* 25, 743–755.
- Hiscock, K.M., Lloyd, J.W., Lerner, D.N., 1991. Review of natural and artificial denitrification of groundwater. *Water Research* 9, 1099–1111.
- IPCC, 1997. (Intergovernmental Panel on Climate Change/ Organization for Economic Cooperation and Development). Guidelines for National Greenhouse Gas Inventories. OECD/OCDE, Paris.
- Jacinto, P.A., Dick, W.A., 1996. Use of silicone rubber tubing to sample nitrous oxide in the soil atmosphere. *Soil Biology and Biochemistry* 28, 721–726.
- Jacinto, P.A., Groffman, P.M., Gold, A.J., Mosier, A., 1998. Patchiness in microbial nitrogen transformations in groundwater in a riparian forest. *Journal of Environmental Quality* 27, 156–164.
- Jacobs, T.C., Gilliam, J.W., 1985. Riparian losses of nitrate from agricultural drainage waters. *Journal of Environmental Quality* 22, 467–473.
- Karlen, D.L., Kramer, L.A., Logsdon, S.D., 1998. Field-scale nitrogen balances associated with long-term continuous corn production. *Agronomy Journal* 90, 644–650.
- Keeney, D.R., 1986. Sources of nitrate to ground water. *CRC Critical Reviews in Environmental Control* 16, 257–304.
- Korom, S.F., 1992. Natural denitrification in the saturated zone: A review. *Water Resources Research* 28, 1657–1668.
- Kroeze, C., Mosier, A., Bouwman, L., 1999. Closing the global N<sub>2</sub>O budget: A retrospective analysis 1500–1994. *Global Biogeochemical Cycles* 13, 1–8.
- Lowrance, R., 1992. Groundwater nitrate and denitrification in a coastal plain riparian forest. *Journal of Environmental Quality* 21, 401–405.
- Lowrance, R., Todd, R., Fail Jr., J., Hendrickson Jr., O., Leonard, R., Asmussen, L., 1984. Riparian forests as nutrient filters in agricultural watersheds. *BioScience* 34, 374–377.
- Lowrance, R., Altier, L.S., Newbold, J.D., Schnabel, R.R., Groffman, P.M., Denver, J.M., Correll, D.L., Gilliam, J.W., Robinson, J.L., Brinsfield, R.B., Staver, K.W., Lucas, W., Todd, A.H., 1997. Water quality functions of riparian forest buffers in Chesapeake Bay watersheds. *Environmental Management* 21, 687–712.
- Mitsch, W.J., Day Jr., J.W., Gilliam, J.W., Groffman, P.M., Hey, D.L., Randall, G.W., Wang, N., 1999. Reducing nutrient loads, especially nitrate nitrogen, to surface water, groundwater, and the Gulf of Mexico. Topic 5 Report for the Integrated Assessment on Hypoxia in the Gulf of Mexico. NOAA Coastal Ocean Program, Decision Analysis Series No. 19 US Department of Commerce, National Oceanic and Atmospheric Administration, Silver Spring, Maryland. Available at [http://www.nos.noaa.gov/Products/pubs\\_hypox.html](http://www.nos.noaa.gov/Products/pubs_hypox.html).
- Mooney, H.A., Vitousek, P.M., Matson, P.A., 1987. Exchange of materials between terrestrial ecosystems and the atmosphere. *Science* 238, 926–932.
- Mosier, A.R., Schimel, D.S., 1993. Nitrification and denitrification. In: Knowles, R., Blackburn, T.H. (Eds.), *Nitrogen Isotope Techniques*. Academic press, New York, pp. 181–208.
- Mosier, A.R., Duxbury, J.M., Freney, J.R., Heinemeyer, O., Minami, K., 1996. Nitrous oxide emission from agricultural fields: Assessment, measurement and mitigation. *Plant and Soil* 181, 95–108.
- Mosier, A., Kroeze, C., Nevison, C., Oenema, O., Seitzinger, S., Cleemput, O., 1998. Closing the global atmospheric N<sub>2</sub>O budget: Nitrous oxide emissions through the agricultural nitrogen cycle. *Nutrient Cycling in Agroecosystems* 52, 225–248.
- Naiman, R.J., Decamps, H., 1997. The ecology of interfaces: Riparian zones. *Annual Review of Ecology and Systematics* 28, 621–658.
- National Research Council, 1993. *Soil and Water Quality: An Agenda for Agriculture*. National Academy Press, Washington, DC.
- Nelson, W.M., Gold, A.J., Groffman, P.M., 1995. Spatial and temporal variation in groundwater nitrate removal in a riparian forest. *Journal of Environmental Quality* 24, 691–699.
- Nevison, C., 2000. Review of the IPCC methodology for estimating nitrous oxide emissions associated with agricultural leaching and runoff. *Chemosphere – Global Change Science*, this issue.
- Paul, E.A., Clark, F.E., 1996. *Soil Microbiology and Biochemistry*, second ed. Academic Press, New York.
- Peterjohn, W.T., Correll, D.L., 1984. Nutrient dynamics in an agricultural watershed. Observations on the role of a riparian forest. *Ecology* 65, 1466–1475.
- Potter, C.S., Matson, P.A., Vitousek, P.M., Davidson, E.A., 1996. Process modeling of controls on nitrogen trace gas emissions from soils worldwide. *Journal of Geophysical Research* 101, 1361–1377.
- Prather, M., Derwent, R., Ehhalt, D., Fraser, P., Sanhueza, E., Zhou, X., 1995. Other trace gases and atmospheric chemistry. In: Houghton, J., Meira, L.G., Haites, E., Harris, N., Maskell, K. (Eds.), *Climate Change 1995: Radiative Forcing of Climate Changes and an Evaluation of the IPCC IS92 Emission Scenarios*. Cambridge University Press, New York.
- Schimel, D.S., et al. 1995. Radiative forcing of climate change. In: Houghton, J.T., Meira Fihlo, L.G., Callender, B.A., Harris, N., Kattenberg, A., Maskell, K. (Eds.), *IPCC Climate Change 1995*. Cambridge University Press, New York (Chapter 2).
- Simmons, R.C., Gold, A.J., Groffman, P.M., 1992. Nitrate dynamics in riparian forests: Groundwater studies. *Journal of Environmental Quality* 21, 656–665.
- Steinheimer, T.R., Scoggin, K.D., Kramer, L.A., 1998. Agricultural chemical movement through a field-size watershed in Iowa: Surface hydrology and nitrate losses in discharge. *Environmental Science and Technology* 32, 1048–1058.
- Toth, J.D., Fox, R.H., 1998. Nitrate losses from a corn-alfalfa rotation: Lysimeter measurement of nitrate leaching. *Journal of Environmental Quality* 27, 1027–1033.
- Turner, R.E., Rabalais, N.N., 1991. Changes in Mississippi River water quality this century. *BioScience* 41, 140–147.
- Vinten, A.J.A., 1999. Predicting nitrate leaching from drained arable soils derived from glacial till. *Journal of Environmental Quality* 28, 988–996.

- Weller, D.E., Correll, D.L., Jordan, T.E., 1994. Denitrification in riparian forests receiving agricultural discharges. In: Mitsch, W.J. (Ed.), *Global Wetlands: Old World and New*. Elsevier, Amsterdam, pp 117–131.
- Winter, T.C., 1988. Conceptual framework for assessment of cumulative impacts on hydrology of non-tidal wetlands. *Environmental Management* 12, 605–620.

**Peter M. Groffman** is a Scientist with interests in soil microbial ecology at the Institute of Ecosystem Studies, Millbrook, NY, USA. **Arthur J. Gold** is a Professor and **Kelly Addy** is a Research Associate with interests in Water Resources at the University of Rhode Island, Department of Natural Resources Science, Kingston, RI, USA.