Nitrous oxide production in riparian zones and groundwater

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Abstract

This paper addresses the question of whether riparian zones and groundwater are ‘hotspots’ of nitrous oxide (N\textsubscript{2}O) flux in the landscape. First, we describe how riparian zones and groundwater function as transformers of N, with a particular emphasis on mechanisms of N\textsubscript{2}O production in these ecosystems. We then present specific data on N\textsubscript{2}O flux in these ecosystems and attempt to reconcile these data with existing regional scale estimates of N flux for Norway and with estimates of N\textsubscript{2}O flux for Norway produced using the OECD/IPCC/IEA Phase II methodology for calculation of regional and global N\textsubscript{2}O budgets. While the OECD/IPCC/IEA approach produces estimates of riparian and groundwater N\textsubscript{2}O flux that are reasonable, given what we know about regional scale N balances and actual data on N\textsubscript{2}O flux, it does not allow us to determine if riparian zones and groundwater are ‘hotspots’ of N\textsubscript{2}O production in the landscape. The approach fails to answer this question because it is unable to account for spatially explicit phenomena such as riparian and groundwater processing of excess agricultural N. Research needs that would allow us to address this question are discussed.

Introduction

This paper addresses the question of whether riparian zones and groundwater are ‘hotspots’ of nitrous oxide (N\textsubscript{2}O) flux in the landscape. Riparian ecosystems are situated at the interface between terrestrial and aquatic components of the landscape (Figure 1) and have unique structure and function due to strong interactions between hydrologic, soil and plant processes in these areas. Many studies have documented the ability of riparian ecosystems to transform nitrogen (N) that leaves N-intensive terrestrial land uses, preventing its movement into streams (Correll, 1997; Hill, 1996). Groundwater ecosystems are of interest because they are the ‘receiving water’ for much of the excess N that is common in agricultural land uses (Keeney, 1986).

Analysis of riparian zones and groundwater as landscape-scale hotspots in the context of regional and global scale N\textsubscript{2}O budgets is complicated by the fact that hotspots are spatially explicit phenomena. Riparian zones and groundwater will have the potential to function as hotspots of N\textsubscript{2}O flux only if excess N physically interacts with the biologically active components of these areas (Schnabel et al., 1994). Analysis of these interactions requires spatially explicit data that are often not available for regional and global scale analyses (DeLong and Brusven, 1991).

Analysis of regional N balances (e.g. for Norway) suggest that there is a high potential for riparian zones and groundwater to function as hotspots of N\textsubscript{2}O flux. In Norway, there is a 128 Gg annual surplus of N at the farm level (13 g N m\textsuperscript{-2} y\textsuperscript{-1}) (Bleken and Bakken, 1997). Independent estimates suggest that 20 - 50 Gg (2 - 5 g N m\textsuperscript{-2}) of nitrate (NO\textsubscript{3}\textsuperscript{-}) leach to groundwater from agricultural fields each year. Much of the groundwater that leaves agricultural fields passes through riparian zones before it reaches streams. These are large fluxes of N. If a significant portion of this N is transformed into N\textsubscript{2}O, the flux would be important in the regional N\textsubscript{2}O budget.

In this paper, we first describe how riparian zones and groundwater function as transformers of N, with a particular emphasis on mechanisms of N\textsubscript{2}O production in these ecosystems. We then present specific data
on N₂O flux in these ecosystems and attempt to reconcile these data with regional scale estimates of N flux produced for Norway by Bleken and Bakken (1997) and with estimates of N₂O flux for Norway produced using the OECD/IPCC/IEA Phase II methodology for calculation of regional and global N₂O budgets (Mosier et al., 1996). We finish with a discussion of areas of uncertainty and needs for future research.

**N processing in riparian ecosystems**

Studies in a wide range of temperate ecosystems (northeast US, southeast US, New Zealand, Denmark, England, France, Canada) have demonstrated that riparian zones function as 'filters' for NO₃⁻ in the landscape (Haycock et al., 1997). Riparian ecosystems have been shown to absorb NO₃⁻ outputs in surface runoff (Figure 2) and groundwater (Figure 3) from upland agricultural or residential land uses, preventing NO₃⁻ movement into streams. The ability of riparian

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**Figure 1.** Conceptual diagram of a landscape showing different hydrologic flowpaths from uplands to riparian zones to streams. From Schnabel et al. (1994).

**Figure 2.** Removal of total kjeldahl N (TKN) from surface runoff moving through grass and grass plus mixed vegetation in a riparian zone in North Carolina, USA. From Gilliam et al. (1997).
zones to process $\text{NO}_3^-$ and their widespread occurrence in agricultural landscapes suggests that they may function as 'hotspots' of $\text{N}_2\text{O}$ flux in landscape and regional $\text{N}_2\text{O}$ budgets.

The filtering capacity of riparian ecosystems is strongly regulated by hydrologic factors that control the flow path and residence time of $\text{NO}_3^-$ as it moves from upland areas into and through riparian zones (Figure 1). Surface runoff can often move rapidly through riparian zones as channelized flow, with little $\text{NO}_3^-$ processing (Hill, 1990). Groundwater flow paths can be complex and can bypass the biologically active area of the riparian zone (paths 3 and 4 in Figure 1). Landscape and regional scale assessments of the importance of riparian zones as regulators of $\text{NO}_3^-$ delivery to streams or $\text{N}_2\text{O}$ flux to the atmosphere are often hampered by a lack of understanding of landscape and regional scale controls on hydrologic flowpaths (Correll, 1997).

Filtering mechanisms for $\text{N}$ in riparian zones include sediment trapping, plant uptake, microbial immobilization and denitrification. Because our interest here is in $\text{N}_2\text{O}$ flux, the last of these mechanisms is our primary focus. The other filtering mechanisms are important to understanding the fate of excess $\text{N}$ in the landscape. These mechanisms are also important to the extent that they contribute to overall $\text{N}$ processing and denitrification within the riparian zone (discussed below).

There is abundant evidence that riparian zones dominated by inherently wet surface soils have a high capacity to consume $\text{NO}_3^-$ via denitrification.

\begin{table}[h]
\centering
\begin{tabular}{|l|c|}
\hline
\textbf{Inputs:} & (g N m$^{-1}$ yr$^{-1}$) \\
Groundwater $\text{NO}_3^-$ input & 63 \\
\hline
\textbf{Outputs:} & (g m$^{-1}$ x 31 m$^{-1}$ yr$^{-1}$) \\
\text{Denitrification} & 37 \\
\text{Hydrologic exports} & small \\
\hline
\textbf{Pools$^a$:} & (g m$^{-1}$ x 31 m$^{-1}$) \\
\text{or (g per meter width)} & \\
Inorganic N & 66 \\
Microbial biomass & <1 \\
Soil total N & 177 \\
Vegetation & ? \\
\hline
\end{tabular}
\caption{Inputs, outputs and pools of $\text{N}$ in a unit meter width of riparian zone from the upland edge to the streamside (1 m wide x 31 m length x 15 cm deep). This forested riparian zone, located in Rhode Island, USA, had been subject to approximately 30 years of $\text{NO}_3^-$-enriched groundwater loading. Outputs and pool terms for $\text{N}$ in the enriched site minus $\text{N}$ in a control (a riparian zone with similar soils and vegetation but no $\text{NO}_3^-$ loading) site. Adapted from Hanson et al. (1994b).}
\end{table}

These soils support the anaerobic conditions and high levels of organic matter necessary for denitrification (Cooper, 1990; Ambus and Lowrance, 1991; Schipper et al., 1993; Groffman, 1994). Wet riparian soils have been reported to denitrify over 100 kg N ha$^{-1}$ y$^{-1}$ (Pinay et al., 1993; Lowrance et al., 1995a; Groffman and Hanson, 1997). Unfortunately, there have been very few studies that have analyzed the relative production of $\text{N}_2\text{O}$ during this denitrification. Given the highly anaerobic nature of many riparian zone soils, it is possible that riparian zones may be areas that have high denitrification, but low $\text{N}_2\text{O}$ emission, i.e. they are not hotspots of $\text{N}_2\text{O}$ production in the landscape.

There are often complex interactions between hydrologic, soil, plant and microbial processes in riparian ecosystems, e.g. plants can remove $\text{NO}_3^-$ from groundwater, this $\text{N}$ can be transferred to surface soils via litterfall, and then mineralized, nitrified and denitrified. Hanson et al. (1994a,b) observed increases in surface soil $\text{NO}_3^-$ pools, potential net $\text{N}$ mineralization and nitrification and denitrification in a forested riparian buffer zone subjected to long-term (30 year) groundwater $\text{N}$ loading relative to a 'control' riparian zone (Figure 4). More than 50% of the groundwater $\text{NO}_3^-$ that entered this site left via surface soil denitrification (Table 1). This groundwater loading effect on surface soil processes was facilitated by the
ability of riparian zone trees to remove NO$_3^-$ from groundwater. These results underscore the importance of understanding hydrologic flowpaths as regulators of the nature and extent of N processing in riparian zones. These results also show that there can be significant 'storage' of excess N in riparian zone soils (Table 1). This storage may be important for understanding the fate of the large farm-scale excess N in the Norwegian (and other) regional N budget.

N processing in groundwater

Groundwater ecosystems are often assumed to have very low biological activity. This assumption is based on the low C content of groundwater sediments and the fact that NO$_3^-$ tends to accumulate in aquifers in many locations. The OECD/IPCC/IEA Phase II methodology for calculation of regional and global N$_2$O budgets assumes that there is no biological processing of NO$_3^-$ in groundwater. The methodology calculates N$_2$O emissions associated with leaching and runoff of agricultural N by assuming that 30% of the N added to crop fields is leached to groundwater as NO$_3^-$. Production of N$_2$O is calculated to occur as this NO$_3^-$ moves through rivers and coastal marine areas. The methodology assumes that there is some degassing of N$_2$O carried in groundwater, but no biological production in groundwater itself.

In contrast to this assumption, several studies have shown active NO$_3^-$ processing in the subsurface. If a source of energy (either organic C or inorganic energy sources such as reduced sulfur) is present, biological activity can be sufficient to consume enough oxygen to make groundwater anaerobic, allowing denitrification to occur (Desimone and Howes, 1996; Hiscock et al., 1991; Johnson and Wood, 1992; Korom, 1992; Lind and Eilander, 1989; McCarty and Bremner, 1992; Spalding and Parrott, 1994; Starr and Gillham, 1993; Weier and MacRae, 1993). Some studies have found high potential and/or actual denitrification in subsurface material (Francis et al., 1989; Haycock and Pinay, 1993; Obenhuber and Lowrance, 1991; Slater and Capone, 1987; Smith and Duff, 1988; Trudell et al., 1986), while others have found little or no activity (Bradley et al., 1992; Groffman et al., 1992; Groffman et al., 1996; Lowrance, 1992; Parkin and Meisinger, 1989; Starr and Gillham, 1993; Yeomans et al., 1992). The latter studies often found strong energy limitation of denitrification.

Figure 4. Soil nitrate, potential net N mineralization and nitrification in surface soil (0 – 15 cm) from four different soil drainage classes in NO$_3^-$-enriched and 'control' riparian forests in Rhode Island USA. MWD = moderately well drained, SPD = somewhat poorly drained, PD = poorly drained, VPD = very poorly drained. The NO$_3^-$ enriched site had been exposed to high groundwater NO$_3^-$ loading for approximately 30 years. The control site had similar soils and vegetation as the enriched site, but no NO$_3^-$ loading. Data from Hanson et al. (1994b).
It is important to note that given the slow flow rates of groundwater in many areas, even low rates of denitrification can consume significant amounts of NO$_3^-$ and produce significant amounts of N$_2$O (Groppman et al., 1996). For example, consider a parcel of groundwater with 10 mg of NO$_3^-$ N L$^{-1}$ moving through an aquifer with a bulk density of 1.6 x 10$^3$ kg m$^{-3}$ at a rate of 0.037 m d$^{-1}$ (a very realistic groundwater flow rate). A denitrification rate of 4.0 ug N kg$^{-1}$ d$^{-1}$ (a very low denitrification rate) would remove 85% of the NO$_3^-$ in this water over 20 m (540 days of travel time). This denitrification would represent 2.7 g N m$^{-2}$ y$^{-1}$ of N gas production.

More direct evidence for the potential importance of groundwater ecosystems to regional and global N$_2$O budgets comes from widespread observations of very high (supersaturated) concentrations of N$_2$O in groundwater in many locations, especially in areas with NO$_3^-$ contamination (Dowdell et al., 1979; Minami and Fukushima, 1984; Minami and Oshawa, 1990; Ronen et al., 1988; Ueda et al., 1991, 1993). Ronen et al. (1988) suggested that N$_2$O flux from NO$_3^-$ contaminated aquifers was a very large flux in the global N$_2$O budget. This analysis was highly uncertain, however, due to difficulty in determining the global extent of NO$_3^-$ contaminated aquifers and the source of the N$_2$O present in groundwater (i.e. was the N$_2$O produced in the subsurface or did it leak there from the surface?).

### Data on N$_2$O flux in riparian forests and groundwater

There have been very few studies that have quantified N$_2$O flux from riparian forests and groundwater in a way that is useful for assessment of the importance of these areas to landscape and regional N$_2$O budgets. However, the few studies that have been done are useful for illustrating the complexity of riparian zone and groundwater processes and for highlighting needs for research.

The most comprehensive study of N$_2$O flux in a riparian forest was done in Maryland, USA (Weller et al., 1994). In this study, N$_2$O flux from the soil surface was measured with large (1 – 20 m$^2$) flux chambers and a tunable diode laser over the course of a year. Of the 4.5 – 6.0 g N m$^{-2}$ y$^{-1}$ that entered this riparian zone, 0.039 g N m$^{-2}$ y$^{-1}$ left as N$_2$O. The investigators assume that a much larger amount of N left as N$_2$. The N$_2$O flux was 0.65 – 0.87% of the N input, or 0.0065 – 0.0086 kg N$_2$O-N produced per kg of N input. For comparison, the OECD/IEPS/IEA Phase II methodology for calculation of regional and global N$_2$O budgets assumes an N$_2$O yield of 0.015 kg N$_2$O-N production per kg of N leached to groundwater. There is a strong need for further studies of this type, with a particular focus on the relative importance of N$_2$O versus N$_2$ production as NO$_3^-$ is denitrified as it traverses the riparian zone.

A major source of uncertainty around the importance of groundwater N$_2$O flux has been the source of the high concentrations of N$_2$O that have been observed in groundwater in many locations, i.e. was the N$_2$O produced in the subsurface or did it leak there from the surface? Recent direct measurements of N$_2$O production in groundwater mesocosms show that N$_2$O production does occur in the subsurface, and that this production varies strongly with aquifer characteristics (Table 2, Jacinthe et al. 1998). In these studies, which were done with aquifer material from Rhode Island, USA, N$_2$O production ranged from 0.026 – 3.7% of N input. There was significant variation in production within the riparian zone. Rates of production were two orders of magnitude higher in groundwater material taken from the wetland end of the riparian zone than in material taken from the upland end, less than 30 m away. These differences in production are consistent with higher levels of C and lower levels of oxygen at the wetland end of the riparian zone. The N$_2$O:N$_2$ ratio

<table>
<thead>
<tr>
<th>% of N input</th>
<th>Moderately well drained</th>
<th>Poorly drained</th>
</tr>
</thead>
<tbody>
<tr>
<td>kg N$_2$O per kg N input</td>
<td>0.00026</td>
<td>0.037</td>
</tr>
<tr>
<td>N$_2$O:N$_2$</td>
<td>99:1</td>
<td>99:1</td>
</tr>
<tr>
<td>pH</td>
<td>4.8 - 5.3</td>
<td>4.8 - 5.3</td>
</tr>
<tr>
<td>% C</td>
<td>0.07%</td>
<td>0.13%</td>
</tr>
</tbody>
</table>

*These patches of highly organic material, primarily decomposed roots embedded within the matrix of the poorly drained soil. These patches appear to function as ‘hotspots’ of NO$_3^-$ removal in the aquifer of this soil.*
was very high in this study, likely due to the low pH of the aquifer sediments. Studies in nearby sediments with higher pH (K. Addy, unpublished data) showed much lower N$_2$O:N$_2$ ratios.

We can apply the OECD/IPCC/IEA Phase II methodology for calculation of regional N budgets to the Norwegian N balances produced by Bleken and Bakken (1997) to see if we can produce regional scale estimates of N$_2$O flux that are reasonable given the specific data on N$_2$O flux in riparian zones and groundwater that are available. This methodology produces an estimate of ‘N leached’ to groundwater by multiplying total N input (155 Gg in Norway) by 0.3 and then produces an estimate of groundwater N$_2$O flux by multiplying the N leached (46.5 Gg) by 0.015. This procedure produces an estimate of 0.6975 Gg y$^{-1}$ of groundwater N$_2$O flux in Norway. This estimate is consistent with estimates of N leaching (20 – 50 Gg of N) independently calculated by Bleken and Bakken (1997) using data from Uhlen (1989).

Another estimate of Norwegian N$_2$O flux can be produced by assuming that approximately 50% of the N that is leached is denitrified in riparian forests and groundwater. This estimate of denitrification is based on results from the range of riparian NO$_3^-$ consumption studies in the literature, and in particular, the analysis by Hanson et al. (1994b, Table 1). Thus, if we have 20 Gg (approximately 50% of the N leaching calculated by either Bakken and Bleken (1997) or the OECD/IPCC/IEA Phase II methodology) of denitrification per year, we would need an N$_2$O yield of 6% (N$_2$O:N$_2$ = 1:16) to reconcile with the estimate produced by the OECD methodology. This yield is quite reasonable given previous studies of N$_2$O:N$_2$ ratios.

**Conclusions, uncertainties and needs for future research**

While the OECD/IPCC/IEA Phase II methodology for calculation of regional and global N$_2$O budgets produces estimates of riparian and groundwater N$_2$O flux that are reasonable, given what we know about regional scale N balances and actual data on N$_2$O flux, they do not allow us to answer the question posed at the beginning of this paper, i.e., are riparian zones and groundwater ‘hotspots’ of N$_2$O production in the landscape? The regional scale analyses do not allow us to determine if highly NO$_3^-$ enriched groundwater is interacting with the biologically active zones of groundwater and riparian ecosystems resulting in production of amounts of N$_2$O that could be much greater than suggested by these non-spatially explicit analyses.

Clearly, several types of data collection and analysis are necessary if we are going to be able to answer the question posed by this paper. First, there is a need to reduce the uncertainty in the regional N balances, e.g., why is the estimate of leaching so low relative to the very large farm scale N surplus? We see this uncertainty in the Norwegian N balance as well as in other regional N balances that have been computed (Robertson, 1990). Second, there is a need for more measurements of N$_2$O flux in riparian zones and groundwater. Given the large amount of work on NO$_3^-$ removal in riparian zones, it is somewhat surprising that there are not more data on N$_2$O production. The assumption in the OECD/IPCC/IEA methodology that there is no biological processing of NO$_3^-$ in groundwater clearly should be discarded. The methodology produces ‘reasonable’ estimates of N$_2$O flux, but clearly neglects some important mechanisms of N processing and N$_2$O flux. A more mechanistically sound methodology is more likely to be useful as it is applied in a variety of spatial and temporal contexts.

Finally, there is a more fundamental need to develop approaches to evaluation of spatially explicit phenomena in regional and global scale analyses. We need to determine landscape-scale controllers of riparian and groundwater N$_2$O flux (e.g. soil type, geologic materials, hydrologic pathways) and develop regional-scale databases on these controllers. We then need to carry out extrapolation and modeling exercises to produce regional and global scale assessments of the importance of these ‘hotspot’ phenomena. It is important to note that the development of approaches to evaluate spatially explicit landscape and regional scale hotspot phenomena would be relevant to many topics in earth system science and global change research.

**References**


Cooper AB (1990) Nitrate depletion in the riparian zone and stream channel of a small headwater catchment. Hydrobiol 202: 13–26


Keeney DR (1986) Sources of nitrate to ground water. CRC Crit Rev Environ Cont 16: 257–304


Robertson GP (1990) Nitrogen: Regional contributions to the global budget. Environment


