Denitrification in riparian forests receiving agricultural discharges

D.E. Weller, D.L. Correll and T.E. Jordan

Smithsonian Environmental Research Center, Edgewater, MD 21037-0028, USA

Abstract

Riparian forests can remove large amounts of nitrate from the groundwater discharges of adjacent uphill croplands. We review the mechanisms that could account for NO_3 removal. Denitrification is hypothesized to be important, but measurement problems limit the relevant field data. We used large chambers (1–20 m^2) and tunable-diode laser infrared spectrophotometry to measure nitrous oxide (N_2O) emissions in a riparian forest and adjacent cropland. Forest N_2O emissions were very spatially heterogeneous but had clear seasonal and diurnal cycles that paralleled temperature changes. Springtime N_2O emission rates were higher in the cropland (18 μg-N m^{-2} hr^{-1}) than in the forest (6 μg-N m^{-2} hr^{-1}), but fall emission rates in both systems were similar (2 μg-N m^{-2} hr^{-1}). We also measured N_2O concentration in riparian forest groundwater. Mean groundwater N_2O was low (17 μg-N l^{-1}) and spatially heterogeneous, with no apparent relationship to groundwater NO_3 or to distance from the forest–field boundary. Estimated annual N_2O loss in soil emission (0.35 kg-N ha^{-1}) and groundwater (0.04 kg-N ha^{-1}) together accounted for <1% of the intercepted nitrogen not incorporated into wood (45–60 kg-N ha^{-1}). However, denitrification may produce mostly N_2 or NO rather than N_2O. Future experiments will measure NO emission and use the acetylene block technique to examine the balance between N_2 and N_2O in the gaseous nitrogen emissions from the cropland and forest.

INTRODUCTION

Riparian forests can intercept water, sediment, acidity, nitrogen, phosphorous, and other materials from the surface and subsurface discharges of uphill agricultural lands (Karr and Schlosser, 1978; Schlosser and Karr, 1981; Yates and Sheridan, 1983; Lowrance et al., 1984; Peterjohn and Correll, 1984; Jacobs and Gilliam, 1985b; Peterjohn and Correll, 1986; Pinay and Decamps, 1988; Correll and Weller, 1989; Correll, 1991; Haycock and Pinay, 1993; Jordan et al., 1993). Such forests modulate the effects of agriculture on the entire landscape and control nutrient delivery to downstream systems (Jordan et al., 1986; Risser, 1987; Naiman et al., 1988; Turner, 1989). Riparian forests have been advocated as a land management practice to reduce transport of pollutants from agricultural areas (Schlosser and Karr, 1981; Lowrance et al., 1984; Jacobs and Gilliam, 1985b; Lowrance et al., 1985; Cooper et al., 1986; Whigham et al., 1988; Correll et al., 1993).

In the case of nitrogen, retention of 70–90% of the total inputs to riparian forests has been observed, with most of the nitrogen entering the forest as NO_3 in subsurface discharges from cropland (Lowrance et al., 1984; Peterjohn and Correll, 1984; Jacobs and Gilliam, 1985b; Lowrance et al., 1985; Peterjohn and Correll, 1986; Lowrance, 1992). Across several studies, NO_3 concentrations in groundwater leaving fields averaged 5–15 mg l^{-1}, but dropped to <1 mg l^{-1} after 5–50 m of

travel through the forest (Peterjohn and Correll, 1984; Jacobs and Gilliam, 1985a; Pinay and Decamps, 1988; Lowrance, 1992; Haycock and Pinay, 1993). In one study, the zone of abrupt NO_3 decrease was 25–35 m inside the forest at the hillslope–flood plain boundary (Jordan et al., 1993). In all cases, declines in NO_3 were not offset by increases in other mobile forms of nitrogen (Lowrance et al., 1984; Peterjohn and Correll, 1984; Jacobs and Gilliam, 1985b; Lowrance et al., 1985; Peterjohn and Correll, 1986; Lowrance, 1992; Jordan et al., 1993).

It is important to verify groundwater flow pathways and check for dilution before concluding that concentration declines result from NO_3 removal (Warwick and Hill, 1988; Lowrance and Pionke, 1989; Hill, 1990; Denver, 1991; Simmons et al., 1992). Transport pathways have been inferred by analysis of water table elevations, detailed hydrological studies, hydrological modeling, and tracers like bromide, chloride, or ^{15}N (Lowrance et al., 1984; Jacobs and Gilliam, 1985b; Cooper et al., 1986; Peterjohn and Correll, 1986; Correll and Weller, 1989; Fustec et al., 1991; Lowrance, 1992; Simmons et al., 1992; Jordan et al., 1993). In many studies, a shallow aquiclude layer simplified the hydrological possibilities by forcing subsurface water to flow laterally through the forest and by blocking the emergence of deeper groundwater (Lowrance et al., 1984; Lowrance, 1992; Haycock and Pinay, 1993; Jordan et al., 1993). Such layers also direct groundwater through the rooting zone of riparian vegetation where the probability of plant or microbial uptake is high (Swanson et al., 1982; Lowrance et al., 1984; Peterjohn and Correll, 1984; Jacobs and Gilliam, 1985b; Peterjohn and Correll, 1986; Schnabel, 1986; Lowrance and Pionke, 1989; Pionke and Lowrance, 1991).

Three classes of biological processes can remove nitrogen from forest groundwater: (1) uptake and storage in the forest vegetation; (2) microbial immobilization and storage in the soil as organic nitrogen, or (3) microbial conversion to gaseous forms of nitrogen (N_2, N_2O, and NO) that are lost to the atmosphere. The role of plant uptake is variable. Storage in aboveground vegetation could account for all the nitrogen entering one forest (Lowrance et al., 1984), but only 15% of the total nitrogen retained or 30% of the NO_3 removed from groundwater in another forest (Peterjohn and Correll, 1984). Storage in vegetation should be small where net wood production is low, where only small bands of forest near the field edge experience elevated NO_3 concentrations, or where NO_3 removal continues in winter when vegetation is inactive (Jacobs and Gilliam, 1985b; Davidson and Swank, 1986).

Nitrogen storage in the soil has not been quantified in any riparian forest study. The soil nitrogen pool is large and spatially variable so that small errors in bulk density or soil nitrogen content lead to large uncertainties in total soil nitrogen (Broadbent, 1981; Hauck, 1986). Against this variability, it may be impossible to resolve the small increments in soil nitrogen necessary to account for the nitrogen removal by the riparian forest even after several years.

Gaseous nitrogen loss from denitrification is hypothesized to a major fate of the nitrate retained from groundwater (Lowrance et al., 1984; Peterjohn and Correll, 1984; Jacobs and Gilliam, 1985b; Haycock and Pinay, 1993), but much of the evidence is circumstantial (Lowrance, 1992). High denitrification has been inferred from favorable environmental conditions such as high water table, saturated soils, high organic carbon, low E_h, and reduced soil chemicals (Peterjohn and Correll, 1984; Jacobs and Gilliam, 1985b; Peterjohn and Correll, 1986; Correll and Weller, 1989; Lowrance and Pionke, 1989; Jordan et al., 1993). Direct evidence is limited by the lack of accurate field methods for measuring denitrification (Payne, 1981; Ryden and Rolston, 1983; Erich et al., 1984; Sprent, 1987; Tiedje et al., 1989) and by the enormous spatial and temporal variability of denitrification rates (Blackmer et al., 1982; Jury et al., 1982; Folorunso and Rolston, 1984; Parkin et al., 1987; Christensen et al., 1990; Lensi et al., 1991).

Soils in poorly drained riparian forest areas do often have high denitrification potentials (Davidson and Swank, 1986; Davidson et al., 1986; Duff and Triska, 1990; Groffman et al., 1991). High denitrification rates of 31.5 kg-N ha^{-1} yr^{-1} (Lowrance et al., 1984, 1985), 193.6 kg-N ha^{-1} yr^{-1} (Pinay and Decamps, 1988) have been estimated for riparian forests receiving agricultural runoff. Estimates of denitrification potentials when environmental conditions are not limiting range up to 475 kg-N ha^{-1} yr^{-1} (Fustec et al., 1991), 1278 kg-N ha^{-1} yr^{-1} (Pinay and Decamps, 1988), or 100–1000 kg-N ha^{-1} yr^{-1} (Groffman et al., 1991). In contrast, estimates of annual denitrification for non-riparian forests are generally 0–10 kg-N ha^{-1}, but do range up to 50 kg-N ha^{-1} (Davidson et al., 1990).

Three studies have found higher denitrification potentials in surface soils than beneath the water table (Ambus and Lowrance, 1991; Groffman et al., 1992; Lowrance, 1992). One concluded that plant uptake is the predominant mechanism of nitrogen removal in the growing season, when water tables are low, while denitrification and immobilization are predominant in winter, when vegetation is dormant and microbially active surface soils are saturated (Groffman et al., 1992). Another concluded that nitrate removal could not be attributed to denitrification in the saturated zone and invoked year-round root growth and nitrogen uptake as the mechanism of rapid nitrogen removal from the shallow aquifer, although nitrogen and carbon derived from litter and roots could still fuel denitrification in the surface soils (Lowrance, 1992). Other groundwater studies not done in riparian forests have found high denitrification rates in groundwater (Trudell et al., 1986; Francis et al., 1989).

Besides being a sink for nitrogen, microbial processes in the riparian forests are also possible sources of N$_2$O and NO pollution to the atmosphere. As "greenhouse" gases, both N$_2$O and NO may contribute to global warming and possible attendant problems (Abrahamson, 1989; Hileman, 1989). N$_2$O contributes to the depletion of stratospheric ozone that shields the earth from harmful ultraviolet radiation (Liu et al., 1977; Bolin et al., 1983), while NO contributes to tropospheric ozone pollution and acid deposition (Cicerone, 1989). Atmospheric N$_2$O is increasing (Pearman et al., 1986; Rasmussen and Khalil, 1986), but significant sources are either unidentified or underestimated (Cofer et al., 1991). Soil emission of NO is still a largely unknown flux (Crutzen, 1983; Conrad, 1991). Riparian forests and other ecosystems that receive nitrogen released from fertilized fields may be important N$_2$O or NO sources.

It is likely that plant uptake, soil storage and denitrification all occur in any riparian forest, and unlikely that the balance among the three processes is constant within or among forests. Determining the relative amount of nitrogen retained by each process and how that balance relates to site specific conditions are critical to understanding the capacity and limits of forest nitrogen removal. If denitrification is a relatively minor nitrogen sink, then incorporation of nitrogen into the soil and vegetation would account for most of the nitrogen consumption. Net uptake in vegetation may decrease as the forest matures (Vitousek and Reiners, 1975) unless trees are harvested (Lowrance et al., 1984; Lowrance et al., 1985), and the soil nitrogen pool could also become saturated over longer time scales and also cease to store nitrogen (Aber et al., 1989; Groffman et al., 1992). If denitrification is a major nitrogen sink, then the forest could continue to consume nitrogen without saturating (Groffman and Tiedje, 1991; Groffman et al., 1992), and the factors that affect denitrification would have an important influence on nitrogen consumption. If N$_2$O or NO are major products, then the protection of aquatic systems from NO$_3$ discharges is at the cost of increased atmospheric pollution.

We are currently measuring gas emissions from a riparian forest and adjacent fields to quantify the sources of NO and N$_2$O in both systems, the spatial and temporal variability of gas emissions, and the role of denitrification in nitrogen removal within the riparian forest. The 16.3 ha study watershed in the Rhode River drainage (38°51′ N, 76°32′ W) on the western shore of Chesapeake
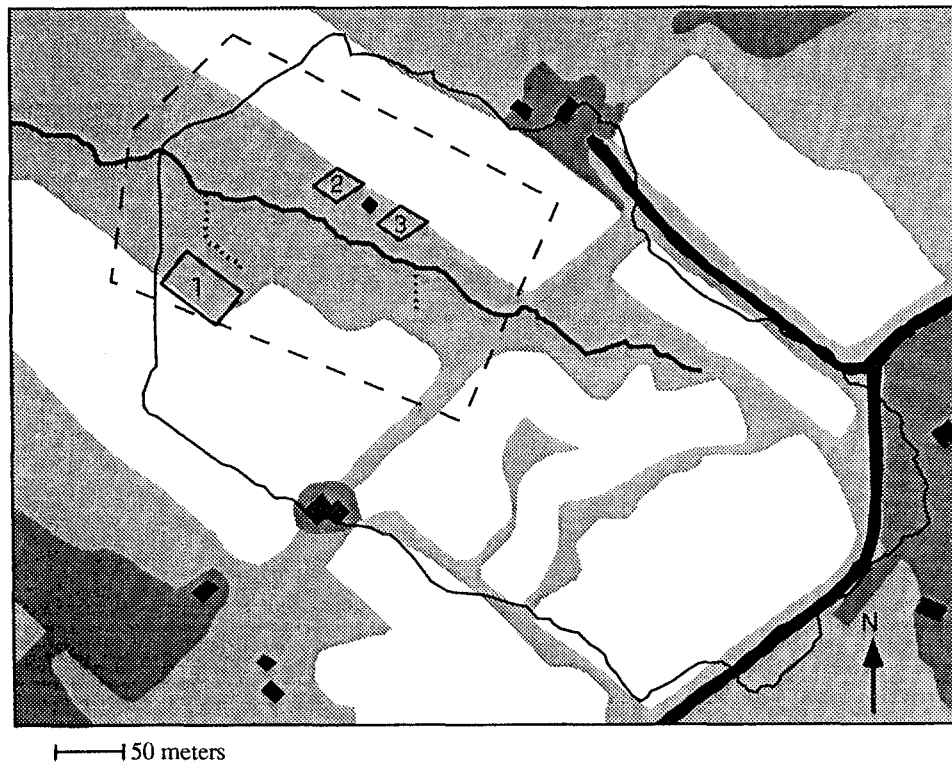
├───────┤ 50 meters

Fig. 1. The study watershed. Light gray shading indicates forest, dark gray is mowed grass, white is corn fields, and black is roads or buildings. The irregular heavy black line is the stream, and dotted lines are ephemeral tributaries. The thin line is the watershed boundary. Three grids of groundwater wells are shown by numbered boxes. Gas analysis equipment is located in the building between well grids 2 and 3. Flow-through emission chambers were located in well grids 1 and 3. A broad-scale survey of N_2O emissions was done within the dashed polygon, and a fine-scale survey was done in well grid 1.

Bay, Maryland, USA, is the site of our earlier studies of nutrient interception by riparian forests (Peterjohn and Correll, 1984; Peterjohn and Correll, 1986; Correll and Weller, 1989). The watershed is 2/3 cropland and 1/3 riparian forest (Fig. 1), and a clay aquiclude beneath the surface forces groundwater to flow laterally from the croplands through the riparian forest. Groundwater leaving the corn fields contains 2–10 mg-NO_3-N l^{-1}, but NO_3 concentrations decline to less than 1 mg-N l^{-1} in transit through the forest (Peterjohn and Correll, 1984; Peterjohn and Correll, 1986; Correll and Weller, 1989). Annual incorporation of nitrogen into woody tissues of trees (11 kg-N ha^{-1}) is insufficient to account for 45–60 kg-N ha^{-1} of annual nitrogen removal (Peterjohn and Correll, 1984). We hypothesized that the nitrate is removed by denitrification in the forest where the abundance of organic matter and saturated soils favor denitrification. Here we present some early results from this ongoing study, including measurements of dissolved N_2O in groundwater and measurements of the temporal and spatial variation in N_2O emissions from the riparian forest and adjacent cropland. We also discuss some directions for future work.

METHODS

To sample groundwater, we installed three dense grids of wells lined with perforated PVC pipe and extending to the aquiclude (Fig. 1). Well grid 1 is in the flood plain area studied earlier

(Peterjohn and Correll, 1984; Peterjohn and Correll, 1986; Correll and Weller, 1989) and two new grids (2 and 3) are across the stream on a drier hillslope. We used bromide as a tracer to ensure that the wells were arrayed parallel to the direction of groundwater flow. NaBr was introduced to the center well at the forest–field boundary, and the wells were sampled every 1–3 days to follow the movement of the downhill wells. We sampled groundwater from the well grids monthly from December 1991 through March 1992 and measured nitrate concentration with a Dionex series 4000i ion chromatograph.

We also measured dissolved N_2O in groundwater. Samples for gas analysis were drawn from the bottoms of the wells using a peristaltic pump. We selected this method of sampling after testing others to identify the method least affected by N_2O outgassing during sampling. Groundwater from the wells was immediately transferred to serum vials. The vials were filled halfway with groundwater and halfway with air and then sealed. The N_2O in the sample was partitioned between the water and the air in the sealed vials at $20°$. The air in the vials was analyzed for N_2O using a Perkin–Elmer model 8500 gas chromatograph with an electron capture detector. The original concentration of N_2O dissolved in the groundwater samples was calculated from the measured volumes of air and water in the vials and the partitioning coefficient.

We used both closed and flow-through chambers to sample gases emitted from the soil. Closed chambers are easier to deploy and are more sensitive to low emission rates. However, they can only be used for short periods because temperature increase and gas buildup can change gas emission rates (Ryden and Rolston, 1983). Flow-through chambers are more difficult to set up, but the constant flow of air minimizes temperature change and gas buildup over longer periods (Jury et al., 1982; Ryden and Rolston, 1983). Thus, closed chambers are useful for exploring spatial variation in gas fluxes while flow-through chambers can be monitored for days at a time.

The flow-through chambers (Fig. 2) have an inner chamber framed with PVC pipe ($20 \times 1 \times 0.3$ m tall) within a slightly larger outer frame. Both frames are covered by polythene sheeting pressed
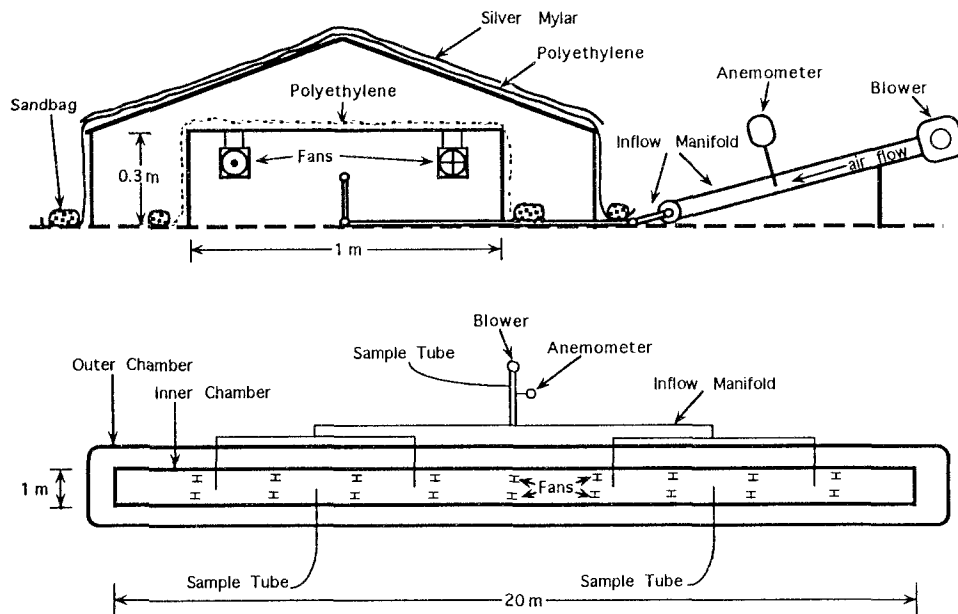

Fig. 2. Top: Cross section of flow-through chamber showing coverings of inner and outer chambers, the air inflow system, and circulation fans blowing in opposite directions. Bottom: Top view of flow-through chamber.

against the soil by 2×0.1 m sandbags. We measure gas concentration in the inner chambers. The outer chambers are wind-breaks to prevent wind-driven air exchange in the inner chamber. An external blower continuously pumps air through a manifold to four outlets in the inner chamber, and a Kurz 435 DC hot-wire anemometer linked to a Campbell 21X data logger monitors the air inflow rate. Air exits the chamber through pore spaces between the polyethylene cover and the soil surface.

Flow-through rates can be varied, but are usually 4–8 m^3 hr^{-1}, which delivers hourly a volume similar to the 6 m^3 of the inner chamber. Such rates produce small but precisely measurable differences in N$_2$O concentration between the inflowing air in the manifold and the inner chamber air. For example, N$_2$O concentration is typically about 0.31 ppmv in the air entering the chamber and about 0.34 ppmv in the air within the chamber. The chambers do not become measurably pressurized. The pressure difference between the inner chamber and the surrounding atmosphere is not sufficient to push a droplet of water through a 3 mm ID tube or cause any inflation of the chamber. Inside the chamber, several circulating fans continuously mix the air. Mixing homogenizes chamber gas concentrations, eliminating the need for replicate sampling within the chamber. Mixing also simplifies the calculation of emission rates. In a well-mixed chamber of volume V and ground area A with flow rate f, constant soil emission m, and ambient N$_2$O concentration C_a, the rate of change of N$_2$O in the chamber is

$$V(dC/dt) = -fC + fC_a + mA.$$

The solution of this differential equation yields the expression used to calculate emission rate per unit area as a function of initial concentration C_0 and final concentration C_t at time t:

$$m = \{f/[A(1 - e^{-(f/V)t})]\} \ [(C_t - C_a) - e^{-(f/V)t}(C_0 - C_a)].$$

The closed chambers also have an inner chamber ($1 \times 1 \times 0.3$ m tall) enclosed by an outer chamber ($2 \times 2 \times 0.4$ m tall), but are smaller and have no air circulating devices. They are covered by reflective mylar if a sunshade is needed to minimize solar heating. The flow-through chambers cover 20 m^2 of surface to integrate more spatial variability than the 1 m^2 closed chambers, but both designs are larger than most emission chambers. We calculated rates of emission into closed chambers from the volume and ground area of the chambers, temperature, and the initial slope of the concentration versus time relationship after closing the chamber (Matthias et al., 1980).

We used flow-through chambers for monthly intensive measurements of N$_2$O emission at two locations within groundwater well grids (Fig. 1). Measurements began in December 1991 at a site in well grid 3 and in September 1992 at a site in well grid 1 (Peterjohn and Correll, 1984). We used closed chambers to do a broad-scale spatial survey of N$_2$O emission rates at over 50 locations throughout the study watershed (Fig. 1) in May 1992 and again in September 1992. We selected four classes of locations: cornfield, field edge, forest, and stream bank. In late April 1992, we also used closed chambers to explore smaller-scale spatial variability in N$_2$O emissions among 31 locations distributed randomly within a 45 m $\times$ 20 m section of flood plain in well grid 1.

We measure N$_2$O concentrations in gas emission chambers with a custom-engineered Laser Photonics, Inc, infrared-spectrophotometry system. Several features allow the instrument to avoid interference from other gases and precisely quantify small (± 0.02 ppmv) variations around the very low ambient N$_2$O concentration (0.31 ppmv). These features include a monochromatic IR laser light source of precisely tunable wavelength, a long optical path (up to 100 m) through the gas sample cell, and measurement at low pressure to minimize peak broadening from molecular interactions.

Derivative spectroscopy is used to quantify optical absorbance and to maintain an exact wavelength by comparison to N_2O in a reference cell. The spectrophotometer continuously monitors N_2O concentration in its gas flow cell. Samples from one of 15 sampling lines or standard gases from cylinders are selected automatically by a computer-controlled sampling manifold of solenoid valves and motorized rotary valves. We calibrate the instrument with mixtures of an N_2O standard and dry N_2 prepared with high-precision MKS Instruments Type 1359C gas flow controllers.

RESULTS AND DISCUSSION

The average concentration of N_2O in riparian forest groundwater was quite variable ($n = 72$, mean $= 17.2$ μg-N l^{-1}, standard deviation $= 18.8$). High concentrations of N_2O in groundwater were interspersed among low N_2O concentrations with no clear relationship to the field–forest boundary or to NO_3 concentration (Fig. 3). If denitrification decreases NO_3 concentrations and produces N_2O, then the concentrations of N_2O and NO_3 in groundwater should be inversely related. The absence of this relationship suggests that the N_2O pool is controlled by a number of processes, not just denitrification. N_2O can be produced by nitrification, and both produced and consumed by denitrification. In addition, dissolved N_2O can be carried through the soil with groundwater flow or lost to the atmosphere.

We observed a clear seasonal cycle in N_2O emissions from the riparian forest soil. N_2O emission rates measured with flow-through chambers increased from December to May and decreased from September to December, paralleling seasonal temperature changes (Fig. 4). We also observed diurnal variations in N_2O emission rates that correlated with temperature in the surface soil (Fig. 5). Emission rates peaked after the daily peak in temperature in the litter layer but before the peak in temperature at 10 cm depth. Thus, emission rates probably correlate closest with temperature at a depth somewhere between 0 and 10 cm. The correlation of N_2O efflux with temperature may reflect
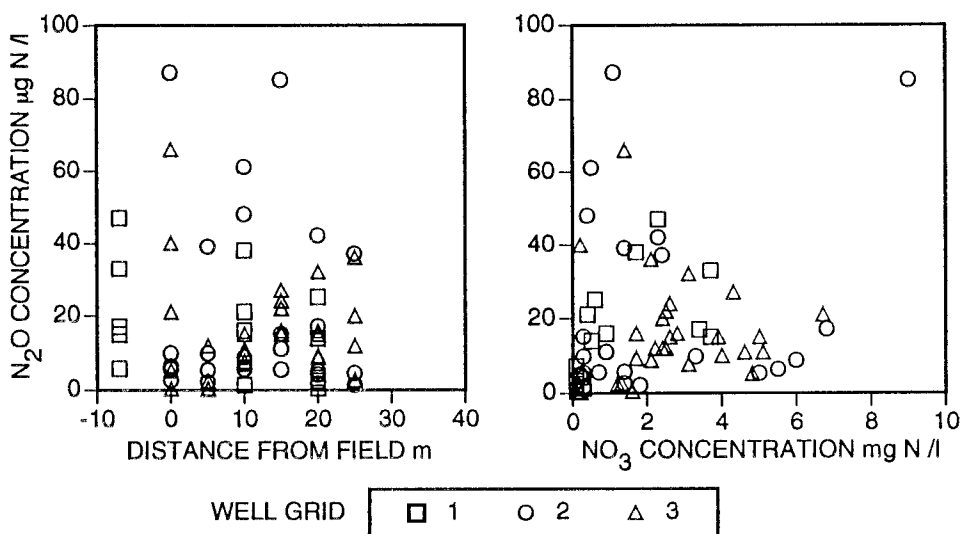

Fig. 3. Relationship of forest groundwater N_2O concentration to distance from the agricultural field (left) and to groundwater NO_3 concentration (right).
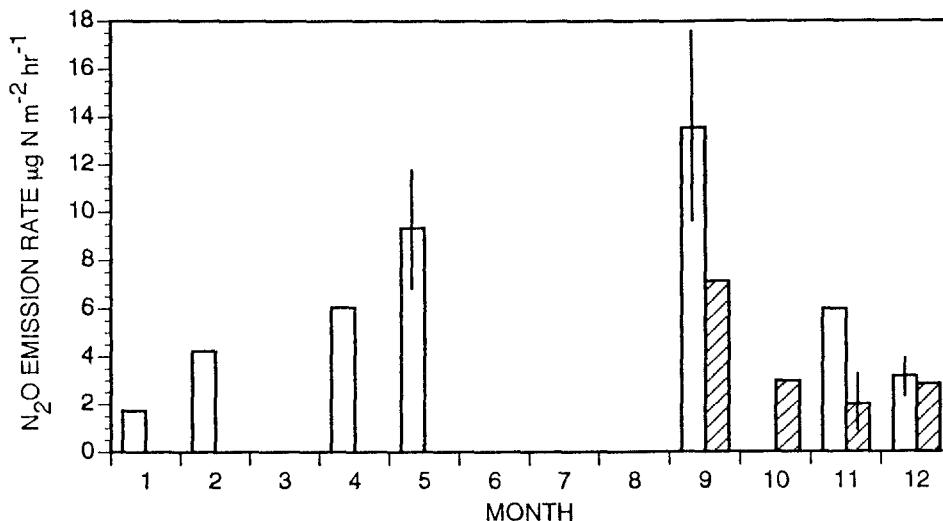
Fig. 4. N_2O-N emission ($\mu g\ m^{-2}\ hr^{-1}$) from soil at two locations measured with flow-through chambers. Vertical lines show the range of measurements when more than one measurement was made in a month. The rates are averages of 1–5 days of continuous measurements. The unshaded bars are for the site in well grid 3 and the shaded bars are for the site in well grid 1.

N_2O production by microbes in the top 10 cm of the soil or temperature-induced changes in efflux of N_2O produced deeper in the soil. N_2O produced in the surface soil may not be related to the removal of nitrate from groundwater flowing at depths greater than 10 cm. N_2O produced near the soil surface, where oxidizing conditions prevail, may result from nitrification rather than from denitrification. Recent studies of denitrification potentials have also found lower activities within the water table than in the surface soils of riparian forests (Groffman et al., 1992; Lowrance, 1992).

N_2O release rates were different at the two locations in wells grids 1 and 3 observed with flow-through chambers (Fig. 4). We expected higher emissions in the low lying flood plain site in well grid 1 (Peterjohn and Correll, 1984) where more frequently waterlogged soils and a pattern of greater change in groundwater nitrate suggest higher denitrification rates. We observed the reverse, but we measured flood plain site emissions only in the fall when the soils are dry throughout the forest. Also, N_2O emission rates do not necessarily reflect the total denitrification activity.

N_2O emissions were quite spatially variable within the flood plain area of well grid 1. Most of the sites observed with closed chambers had very low (<7 μg-N $m^{-2}\ hr^{-1}$) or high (>30 μg-N $m^{-2}\ hr^{-1}$) emission rates and few were intermediate (Fig. 6). The spatial distribution of high emission rates did not form any obvious pattern or match the distribution of N_2O or NO_3 in groundwater. Locations with high emission rates did not look different from locations with low emission rates. Most of the locations that we resampled maintained their characteristic low or high emission rates after periods of several days. The presence of high emission rates in an area where high denitrification rates are likely suggests that denitrification can be an important source of N_2O. However, the very low emission rates interspersed among the high ones suggests that there is small-scale below-ground spatial variability in factors affecting the rate of denitrification or ratio of N_2O to N_2 produced. Denitrification is notoriously variable in space (Folorunso and Rolston, 1984; Parkin et al., 1987; Christensen et al., 1990; Lensi et al., 1991).

In our broad-scale spatial survey, N_2O emission rates from forest and cornfield sites were nearly equal in the fall, but springtime emission rates were roughly three times higher in the cornfield than
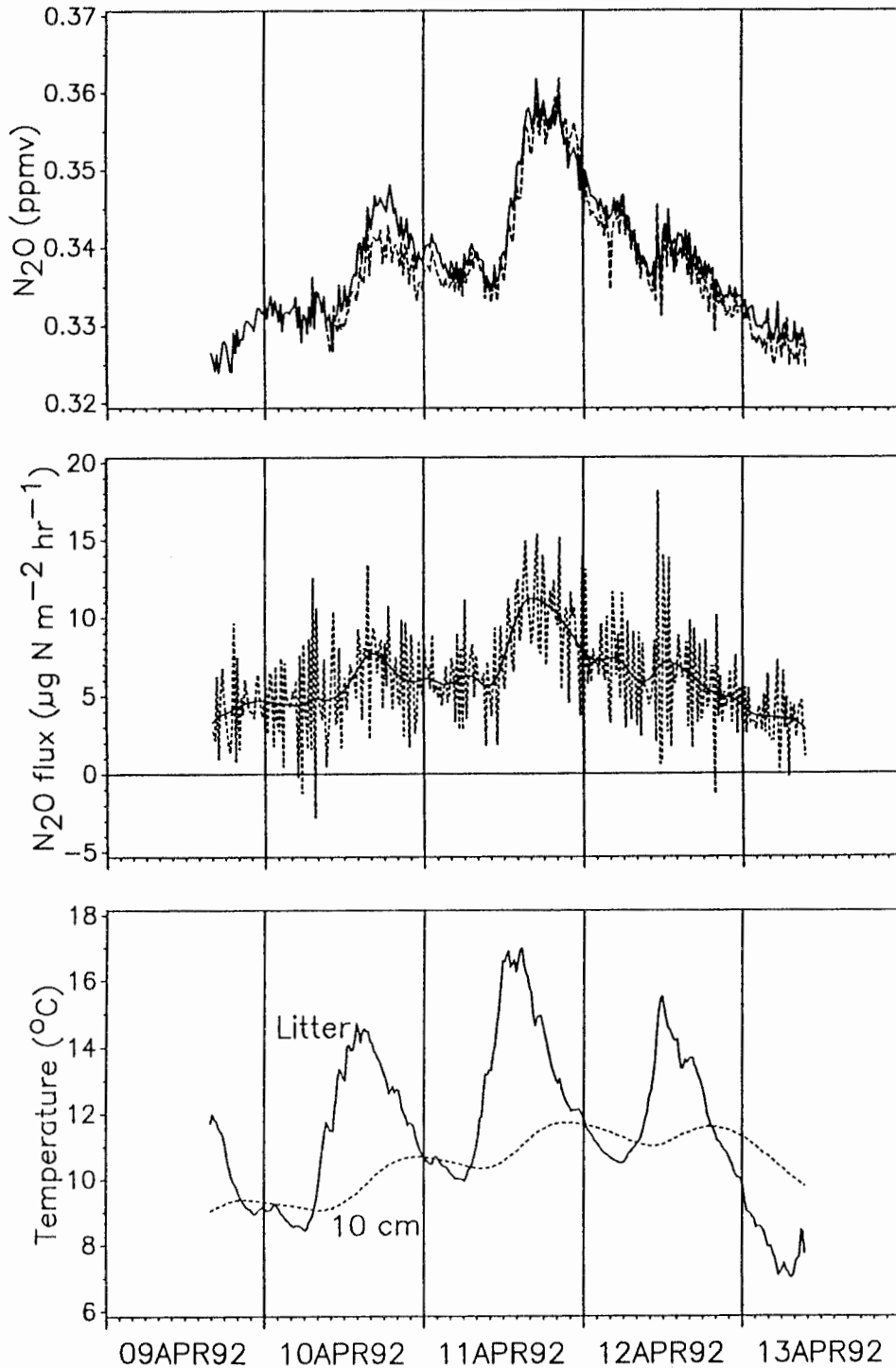
Fig. 5. Top: Concentrations of N_2O (ppmv) in a flow-through chamber monitored over a 4 day period. Dotted line connects raw data. Solid line is a smoothed fit. Concentration in inflowing air is 0.31 ppmv. Middle: N_2O flux ($\mu g\ m^{-2}\ hr^{-1}$) from the soil calculated from the concentration data and the rate of air inflow. Dotted and dashed lines as above. Bottom: Temperature in the litter layer and at 10 cm depth.
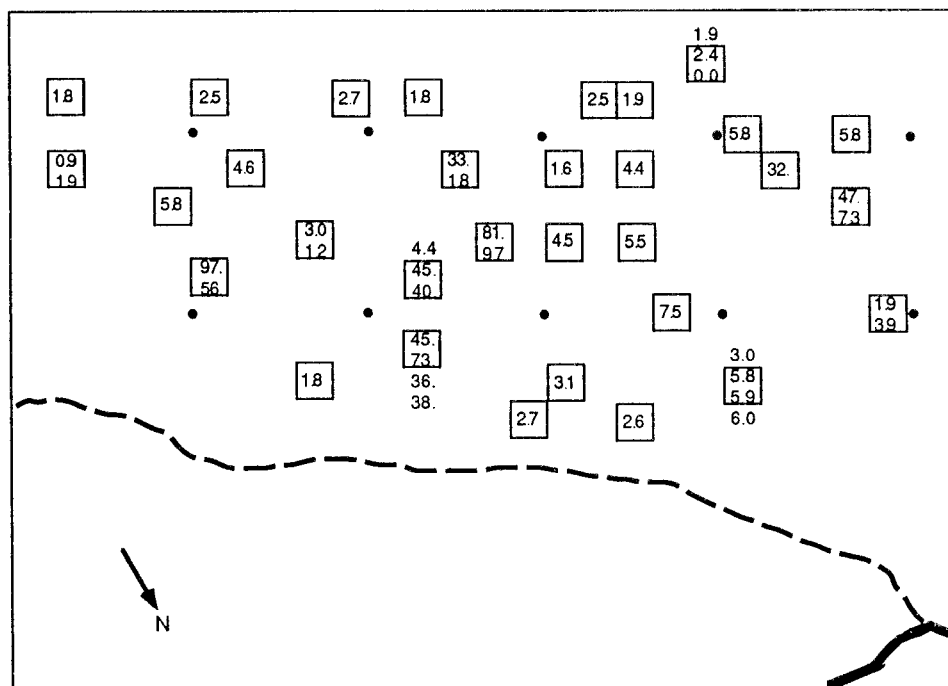
Fig. 6. N_2O emission (μg m^{-2} hr^{-1}) at 31 sites in well grid 1 measured with closed chambers. Multiple rates are repeated measurements on different days. Wells (•) are on a 10×10 m grid. Irregular lines are streams (Fig. 1), including an ephemeral tributary (dashed line).

at locations near or within the riparian forest (Table 1). This result contradicted our hypothesis that most of the N_2O emitted from the watershed would come from denitrification in the riparian forest. The N_2O emitted from the cornfield may be produced by nitrification, which is likely to predominate over denitrification in the well-drained N-enriched cornfield soils. Since the cornfield has high emission rates and covers 2/3 of the watershed, it accounts for more of the total N_2O emitted from the watershed than does the riparian forest. Cornfield N_2O emissions were lower in fall than in spring, possibly because soil ammonium and nitrification rates are both elevated after fertilizer application in the spring. N_2O release at the edge of the cornfield was similar in the spring and fall. N_2O release near the stream bank was quite variable. Some stream bank locations where emergence of groundwater was evident released N_2O at extremely high rates, but such areas comprise a very small proportion of the total area of riparian forest. Our cornfield N_2O emission rates of 0.5–1.6 kg-N ha^{-1} yr^{-1} are slightly lower than the ranges of 2–152 kg-N ha^{-1} yr^{-1} cited in recent reviews of N_2O emissions (Eichner, 1990; Matson and Vitousek, 1990; Williams et al., 1992), but our forest rates of 0.16–0.53 kg-N ha^{-1} yr^{-1} are higher than cited ranges of 0.001–0.1 kg-N ha^{-1} yr^{-1} among forests that are not receiving agricultural nitrogen inputs.

Our observations to date do not confirm the hypothesis that denitrification removes 45–60 kg-N ha^{-1} yr^{-1} of nitrogen from groundwater traversing the riparian forest (Peterjohn and Correll, 1984). If we extrapolate the average rate of N_2O release from the riparian forest (Table 1) to an entire year, we estimate that about 0.35 kg-N ha^{-1} yr^{-1} of N_2O-N is lost by soil emission. This number is perhaps a lower bound because it does not account for higher emissions of stream bank locations within the forest (Table 1). If the groundwater flows in our earlier study (Peterjohn and Correll, 1984) carried N_2O concentrations similar to the average of 17.2 μg-N l^{-1} observed here (Fig. 3) then about 0.04

TABLE 1

Spatial surveys of N$_2$O-N emissions (μg m^{-2} hr^{-1}) measured with closed chambers

	May–June			September–October		
	Mean	Std. err.	Locations(n)	Mean	Std. err.	Locations (n)
Corn Field	18.1	4.5	16	1.7	0.5	28
Field Edge	4.6	1.7	15	5.0	1.1	15
Forest	6.1	1.4	16	1.8	0.5	9
Stream Bank	5.5	1.1	14	10.0	2.4	18

Note: 1 μg m^{-2} hr^{-1} = 0.088 kg ha^{-1} yr^{-1}.

kg-N$_2$O-N were lost in annual groundwater discharge. This rate is low compared to an estimate of 0.22 kg-N$_2$O-N ha^{-1} yr^{-1} in groundwater leaving a clear-cut forest (Bowden and Bormann, 1986), but similar to an estimate of 0.06 kg-N$_2$O-N ha^{-1} yr^{-1} for an intact forest (Davidson and Swank, 1990). N$_2$O loss by soil emission and groundwater transport together can account for roughly 1% of the apparent removal of nitrogen within our riparian forest.

However, our analysis of gaseous nitrogen loss from the forest is incomplete because we have only accounted for N$_2$O. Denitrification also produces N$_2$ and NO, and the proportion of N$_2$O varies from 0–100% depending on substrate concentrations and environmental conditions. The interactions are complex, but the proportion of N$_2$O is generally thought to decrease with lower redox potential or lower NO$_3$ concentration and with higher soil moisture or pH (Firestone et al., 1980; Letey et al., 1980b; Weier and Gilliam, 1986; Drury et al., 1992; Kralova et al., 1992). Denitrification has produced only N$_2$ in some studies, particularly when measured some time after the onset of denitrification (Rolston et al., 1978; Firestone and Tiedje, 1979; Letey et al., 1980a). Also, denitrification deeper in the soil may produce a smaller proportion of N$_2$O than in the surface soil (Gilliam et al., 1978).

To estimate the total nitrogen loss from denitrification, we will measure N$_2$O and NO production after introducing acetylene into the unsaturated soil (McConnaughey and Duxbury, 1986) and shallow groundwater (Duff and Triska, 1990) to block the reduction of N$_2$O to unmeasurable N$_2$ (Yoshinari et al., 1977; Ryden and Rolston, 1983; Terry and Duxbury, 1985; Hauck, 1986; Terry et al., 1986; Nagele and Conrad, 1990a; Nagele and Conrad, 1990b; Remde and Conrad, 1991a). N$_2$O emissions and groundwater N$_2$O transport from "acetylene blocked" soils and will be much higher than our present measurements if denitrification is indeed important and produces mostly N$_2$. Careful interpretation of environmental conditions and emissions from blocked soils may also help resolve the contributions of nitrification and denitrification to N$_2$O and NO production (Bremner and Blackmer, 1978; Davidson et al., 1986; Robertson and Tiedje, 1987; Remde and Conrad 1991a; William et al., 1992).

Laboratory studies show that NO can also be a significant product of denitrification (Nagele and Conrad, 1990b; Nagele and Conrad, 1990a; Remde and Conrad, 1990; Tortoso and Hutchinson, 1990; Remde and Conrad, 1991a; Remde and Conrad, 1991b) favored by high NO$_3$ and carbon concentrations (Baumgartner and Conrad, 1992), but field data remain limited. A recent review found soil NO emissions of 3–30 kg-N ha^{-1} yr^{-1} for fields and 0.09–0.4 kg-N ha^{-1} yr^{-1} for forests (Williams et al., 1992). Such rates would not account for much of our 45–60 kg-N ha^{-1} yr^{-1} in forest nitrogen removal, but the range is based on only three forests and we may find much higher rates in our riparian forest with its agricultural nitrogen input.

Our low measurements of N_2O loss in soil emissions and groundwater transport indicate that N_2O production in the riparian forest is neither an important fate of nitrogen removed from cropland discharges nor an important source of atmospheric N_2O pollution. Ongoing studies of acetylene blocked soils and NO emissions will determine if denitrification is a major mechanism of forest nitrogen removal forest despite the low rates of N_2O loss. If not, storage in the soil may be the fate of nitrogen not incorporated into wood or lost in gaseous forms.

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GLOBAL WETLANDS
OLD WORLD AND NEW

EDITED BY

WILLIAM J. MITSCH

School of Natural Resources, The Ohio State University
2021 Coffey Road, Columbus, OH 43210, U.S.A.

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