Biogeochemistry **56:** 265–286, 2001.

Distribution of nitrous oxide and regulators of its production across a tropical rainforest catena in the Luquillo Experimental Forest, Puerto Rico

CLAIRE P. MCSWINEY[1]*, WILLIAM H. MCDOWELL[1] & MICHAEL KELLER[2]

[1]*University of New Hampshire, Department of Natural Resources, Durham NH 03824, U.S.A.;* [2]*International Institute of Tropical Forestry, USDA Forest Service, Rio Piedras PR 00928, U.S.A. (*Author for correspondence, current address: Kellogg Biological Station, 3700 E. Gull Lake Drive, Hickory Corners, MI 49060)*

Key words: ammonium, nitrate, nitrous oxide, oxygen, rainforest, redox

Abstract. Understanding of N_2O fluxes to the atmosphere is complicated by interactions between chemical and physical controls on both production and movement of the gas. To better understand how N_2O production is controlled in the soil, we measured concentrations of N_2O and of the proximal controllers on its production in soil water and soil air in a field study in the Rio Icacos basin of the Luquillo Experimental Forest, Puerto Rico. A toposequence (ridge, slope-ridge break, slope, slope-riparian break, riparian, and streambank) was used that has been previously characterized for groundwater chemistry and surface N_2O fluxes. The proximal controls on N_2O production include NO_3^-, NH_4^+, DOC, and O_2. Nitrous oxide and O_2 were measured in soil air and NO_3^-, NH_4^+, and DO were measured in soil water. Nitrate and DOC disappeared from soil solution at the slope-riparian interface, where soil N_2O concentrations increased dramatically. Soil N_2O concentrations continued to increase through the flood plain and the streambank. Nitrous oxide concentrations were highest in soil air probes that had intermediate O_2 concentrations. Changes in N_2O concentrations in groundwater and soil air in different environments along the catena appear to be controlled by O_2 concentrations. In general, N processing in the unsaturated and saturated zones differs within each topographic position apparently due to differences in redox status.

Introduction

Atmospheric concentrations of nitrous oxide (N_2O) are increasing at a rate of 0.2–0.3% per year (Bouwman et al. 1995). Controls on N_2O flux cited in different studies vary, sometimes within the same site, and as a result, no universal predictors exist for N_2O fluxes to the atmosphere (Hutchinson & Davidson 1993; Groffman et al. 2000). Understanding of the major controls on the production of this greenhouse gas, which also contributes to the

destruction of stratospheric ozone, is essential in order to design mitigation strategies for environments that are major producers and to calculate better global budgets.

Soils are considered one of the major sources of N_2O to the atmosphere and tropical soils are believed to be the most significant contributors (Matson & Vitousek 1990; Bouwman et al. 1993). Most of the N_2O in soils is produced by two microbial processes, denitrification and nitrification. Proximal controls on each process include substrate concentrations and environmental conditions (Robertson 1989). Organic compounds and nitrate (NO_3^-) are the substrates for denitrification and ammonium (NH_4^+) is the substrate for nitrification. Both processes are controlled by oxygen (O_2) concentration, with denitrification occurring under aerobic conditions and nitrification occurring under aerobic conditions. Production of N_2O occurs when O_2 status is not optimum for both nitrification and denitrification. During nitrification, N_2O is produced when O_2 concentrations are less than that in air (21%) and during denitrification N_2O is produced when there are small quantities of O_2 present.

Typically, studies of N_2O dynamics focus on the relationship between soil surface fluxes and extractable mineral N, net mineralization and nitrification, and water filled pore space (Davidson & Swank 1986; Groffman & Tiedje 1989; Bowden et al. 1992; Keller & Reiners 1994). The ability to predict surface N_2O fluxes based on soil and site parameters remains poor for several reasons. First, O_2 is considered a major control on the process of denitrification and nitrification, but it is rarely measured in the field in conjunction with studies of N_2O dynamics (Patrick 1977; Megonigal et al. 1993; Silver et al. 1999). Second, physical factors control gas movement out of the soil, so that the relationship between substrate concentrations in the soil and the surface flux may not be direct, particularly if production occurs at depth. Finally, after production in the soil, N_2O may be dissolved in water and moved from the site of production (Dowdell et al. 1979; Bowden & Bormann 1986; Ronen et al. 1988), further confounding the relationship between controller concentrations in the soil and surface fluxes.

In this study, we focus on the relationship between *in situ* concentrations of N_2O and concentrations of proximal controllers in soil water across a soil catena. Dissolved substrates should be more representative of availability to microbial populations than soil extracts. The catena provides a range of environments of different oxidation status. We report soil gas concentrations of N_2O and O_2, soil water concentrations of NO_3^-, NH_4^+, and dissolved organic carbon (DOC), as well as groundwater concentrations of N_2O and O_2 across a rainforest catena in the Luquillo mountains of Puerto Rico. By characterizing soil N_2O concentrations and the proximal controllers on its

production in three dimensions we can better assess where on the landscape N_2O is being produced. In addition, we can begin to account for the importance of physical factors on the patterns seen in surface fluxes across this catena and the potential for loss of N_2O through the groundwater system.

Methods and materials

Site description

This project was conducted at the Luquillo Experimental Forest, in northeastern Puerto Rico (Brown et al. 1983) in a sub-basin of the Rio Icacos watershed that has been monitored for groundwater chemistry since 1988 and characterized for surface N_2O flux (Bowden et al. 1992; McDowell et al. 1992; McSwiney et al. in prep.). The forest growing at this site has been classified as the Colorado type, with Palo colorado (*Cyrilla racemiflora*) dominant on slopes and Sierra palm (*Prestoea montana*) on the floodplains. Utuado clay soils have developed from quartz-diorite parent material (Beinroth et al. 1982). Rainfall averages from 373 to 645 cm per year and temperatures range from 19.3 to 22.7 °C (Brown et al. 1983).

The study site has been described in detail by McDowell et al. (1992). From the upland, a slope flattens into a well-developed riparian shelf, which drops steeply into a tributary of the Rio Icacos (Figure 1). Due to the highly conductive nature of the soils, distinct redox zones have developed with depth in the profile. Slope soils are red oxic clays with subangular blocky structure. In the floodplain, surface soils are brown clays, mid depth soils are mottled red and gray clays, and the deepest soils are black or gray. Specific environments studied represent a range of redox conditions, including transition zones. They were: ridge (RDG), slope-ridge break (SRD), slope (SLP), slope-riparian break (SRI), riparian shelf (RIP), and streambank (SBK). For this study, one of three catenas previously characterized for surface N_2O and CH_4 flux was used (Bowden et al. 1992; McSwiney et al. in prep).

Soil gas probe installation and sampling

Soil gases were studied to identify zones of trace gas accumulation and possible zones of production. Three randomly placed probe nests were installed in each of the six environments. Each nest sampled five different soil depths that represented different redox zones. Probes were sampled six times over the course of a year for N_2O (three wet and three dry periods) and O_2 was measured three times (dry period) (Figure 2).

Soil gas probes were constructed by first boring a hole with a soil corer while taking notes on the different redox zones based on color (Faulkner &

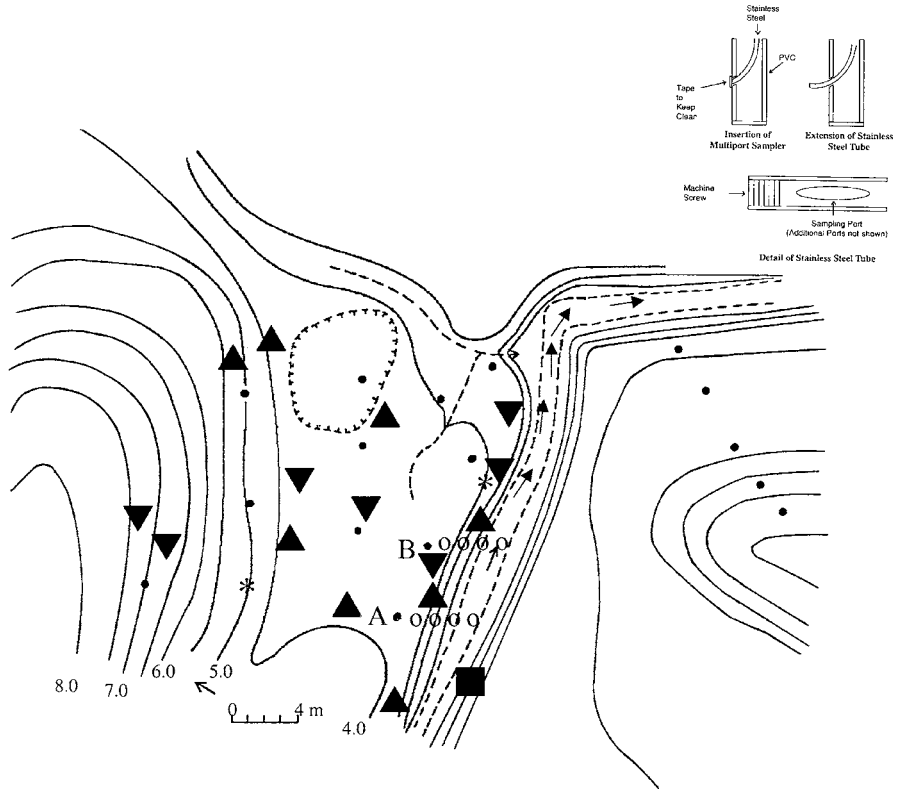

Figure 1. Location of wells (•), piezometers (o and transect designation A or B), lysimeters (*), soil gas probes (▲), sampling sites for the mineralization-nitrification study (▼), and location of potential nitrification study (■). Location of ridge, slope-ridge break, and slope soil gas probes and lysimeters are not shown. Stream channel designated by parallel dashed lines with arrows running between them. Map modified from McDowell et al. 1992.

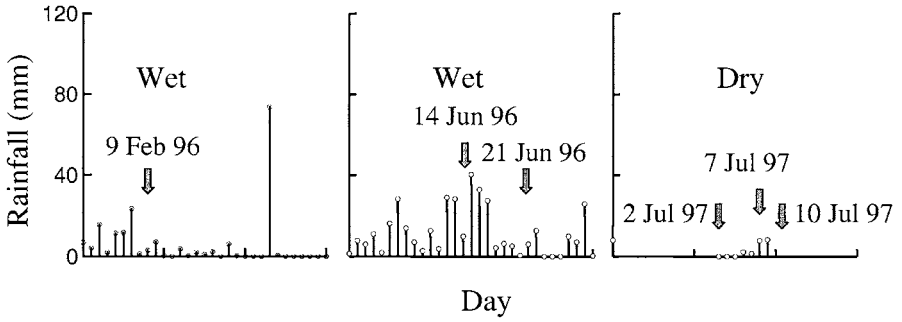

Figure 2. Rainfall for the periods when soil air probes and lysimeters were sampled. Arrows designate sampling days.

Patrick 1992; Megonigal et al. 1993; Khan & Fenton 1994). Stainless steel tubing (1/4 inch o.d.) was cut to appropriate lengths to sample each of the redox zones found when coring (Crill 1991). Slots were cut into the bottom 10 cm of the stainless steel probe and the tip was closed with a mallet (Figure 1). Holes were drilled in a 5 cm i.d. PVC pipe that corresponded with the depths of the different redox zones. Each of the holes in the PVC pipe was covered with tape to keep the probe tip clean until the pipe was fully lowered into the hole. The five stainless steel probes were placed in the appropriate positions in the PVC pipe and the pipe was lowered into the hole in the soil. Probes were then extruded 20 cm into the soil through their respective holes in the PVC pipe. Arrangement of the probes in each nest was radial so that sampling from one probe would not affect the soil gas concentrations for probes located above or below. This design, while labor intensive, allowed us to sample gases with a minimum of disturbance to the hydrology of the site.

At the time of sampling, a nylon syringe fitted with a three-way stopcock was attached to the upper end of each stainless steel tube with a short piece of silicone tubing. Ten mL of gas were drawn out and expelled to flush the stainless steel tubing and the syringe. Then, 20 mL of gas were drawn and the syringe was sealed. Syringes were returned to the laboratory at the International Institute of Tropical Forestry in Rio Piedras and analyzed within 24 hours for N_2O. Sample concentrations were determined using gas chromatographic methods similar to Keller and Reiners (1994). The system used for the analysis of N_2O is described in detail by Butler et al. (1989). This 12-port valve system was used to shorten retention times for N_2O, allowing for quicker sample turn around. Standards for N_2O analyses were calibrated against standards that had been calibrated by NOAA Climate and Monitoring Diagnostics Laboratory.

Oxygen was measured in the field by drawing 40 mL of gas from each soil air probe with a polypropylene syringe, immediately expelling it into a 2 port manifold with a small headspace (<3 mL) attached to a YSI Model 51B O_2 meter, and taking the reading when the meter equilibrated (Silver et al. 1999). Between samples the manifold was flushed with 40 mL of air to bring the meter back to 21% O_2 reading.

Lysimeter installation and sampling

Soil water was collected to determine the concentrations of the known substrates for nitrification and denitrification. Tension lysimeters constructed of quartz and teflon (Super Quartz, Prenart Equipment ApS, Fredriksberg, Denmark) were installed (n = 1) at 15, 55, and 125 cm depths in upslope environments (RDG, SRD, SLP) and at 15, 95, 135, 155 cm depths in riparian environments (SRI, RIP, SBK). Lysimeters were conditioned for two and

a half months before sampling began. Bottles were attached to the lysimeters and evacuated (620 mm Hg) the day before sampling. On the day of sampling, water was drawn from the lysimeter bottle with a clean polypropylene syringe fitted with a cannula, filtered to 0.2 μm (Sterile Acrodisc, Polysulfone, Gelman Sciences) into an autosampler vial for ion chromatography, and sealed. Another sample was drawn, filtered through a combusted glass microfiber filter (Whatman GF/F, 500 °C for 6 hours, retention to 0.7 μm) into a 60 mL acid-washed HDPE plastic bottle, and sealed for NH_4^+ and DOC analyses. Deionized water was also filtered and stored in vials and bottles to serve as blanks. At the field station the samples for ion chromatography were refrigerated and the NH_4^+ samples were frozen until the time of analysis one and a half to four months later (hold time 5 years, Avanzino & Kennedy 1993) at the University of New Hampshire. Nitrate was analyzed with an ion chromatograph (Waters Division of Millipore Corp., Milford MA, 510 Pump, 712 WISP, 431 Conductivity Detector) fitted with a Dionex (Sunnyvale CA) column (IonPak AG4A 4 mm) and suppression unit (Anion Self Regenerating Suppressor ASRS-I 4 mm). Ammonium was determined using the indophenol blue reaction and a flow injection system (Lachat Crop., Milwaukee WI). Dissolved organic carbon was determined with a Shimadzu TOC 5000 high temperature combustion instrument (680 °C, platinum catalyst, Shimadzu Scientific Instruments Inc., Columbia MD). Detection limits were 3 μg N/L for NO_3^-, 0.1 mg C/L for DOC, and 3 μg N/L for NH_4^+. Soil water was sampled six times, on the same days that soil gas samples were taken for N_2O and CH_4.

Groundwater chemistry

Concentrations of NO_3^- and NH_4^+ were determined for groundwater samples through the streambank into the hyporheic zone. Two transects of piezometers (3.8 m I.D. PVC) were installed in four (one hyporheic and three streambank) clusters of three (Figure 1). Each of the piezometers in the cluster of three was positioned at a different depth. Hyporheic piezometers had slotted screens while streambank piezometers were screened by drilling a series of 0.63 cm holes on four sides of the PVC pipe. Hyporheic piezometers were screened at depths of 5–10, 15–20 and 25–30 cm below the streambed. Streambank piezometers located 58 (Transect A) and 124 cm (Transect B) from the center of the stream were screened at depths of 43–55, 60–72 and 77–89 cm; piezometers at 109 (Transect A) and 167 cm (Transect B) from the center of the stream were screened 86–98, 103–115, and 120–132 cm depths; and piezometers at 168 (Transect A) and 238 cm (Transect B) from the center of the stream were screened at 120–132, 137–149, and 154–166 cm below the ground surface. These depths were chosen to sample just above, at, and

below the estimated water table surface. At each sampling, depth to the water table was determined and samples were drawn with a peristaltic pump or a 60 mL syringe fitted with tubing. Samples were pressure filtered to 0.45 μm (Millipore Corporation, HAWP membrane filter) at the laboratory and frozen until analysis for NO_3^- (Waters single column, non-suppressed ion chromatography, borate-gluconate mobile phase) and NH_4^+ (indophenol blue reaction measured on a Technicon AutoAnalyzer II). Ion chromatography samples were filtered to 0.2 μm (Sterile Acrosdisc, Polysulfone, Gelman Sciences) before analysis.

Nitrogen cycling

Net N mineralization/immobilization and nitrification were determined in slope and riparian surface soils, according to the techniques of Steudler et al. (1991), to further elucidate patterns seen in soil gases and soil water. Soil cores were taken at 0–2 cm and 2–20 cm depths, split, half was extracted immediately with KC1, and the remaining half was placed in a sealed plastic bag and held for incubation at 25 °C in the dark. One soil core for each depth interval was collected from each site in the slope (2 sites), riparian (3 sites), and streambank (2 sites) environments (Figure 1). Subsamples of the incubation cores were taken at 14 days and analyzed for KC1 extractable NO_3^- and NH_4^+. Soils were too wet to be sieved, so a subsample was taken and roots were removed by hand before extraction in 2M KC1. Soil moisture was determined gravimetrically, by weighing before and after drying at 60 °C. Organic matter content was determined by loss on ignition at 500 °C. Net mineralization/immobilization per day was calculated as the difference between the total mineral N (NO_3^- + NH_4^+) per gram dry weight extracted from the core that was incubated and total mineral N per gram dry weight in the core that was extracted immediately over the 14 day incubation period or (NO_3^- + NH_4^+) (gdw^{-1}) ($14\ days^{-1}$)$_{final}$ – (NO_3^- + NH_4^+) (gdw^{-1}) ($14\ days^{-1}$)$_{initial}$. Similarly, the difference between the incubation core's NO_3^- content and the initial core's NO_3^- content over the 14-day period gives an estimate for net nitrification of (NO_3^-) (gdw^{-1}) ($14\ days^{-1}$)$_{final}$ – (NO_3^-) (gdw_{-1}) ($14\ days^{-1}$)$_{initital}$. These daily estimates for nitrification and mineralization were multipled by 28 so that we could report the changes on a 28-day basis.

Nitrification potential was determined for soils excavated from the streambank, the environment where McDowell et al. (1992) proposed coupled nitrification/denitrification as the mechanism for N removal before groundwater enters the stream. Triplicate samples were removed at 2 depths above the water table (10 and 40 cm below soil surface), at the water table (60 cm below soil surface), and 2 depths below the water table (80 and 90 cm below soil surface) (Figure 1). Samples were refrigerated until the incubations were

initiated within a week of sampling. Twenty g of wet soil were combined with 200 mL of the appropriate treatment in an acid-washed jar to form a slurry. Treatments were: (1) deionized water; (2) NH_4^+ (0.5 mg/L); (3) NH_4^+ + N-serve (nitrapyrin, nitrification inhibitor at 50 μg/g dry soil). No phosphorus was added to our slurries. Duplicate jars with each of the treatment solutions (no soil) were also incubated. Jars were covered loosely with lab film during incubation and shaken by hand to ensure that the slurries remained well mixed and aerated. Slurry samples were drawn at 0, 41, 66, 114, and 138 hours, centrifuged, and syringe filtered (0.2 μm Sterile Acrodisc, Polysulfone, Gelman Sciences) for analysis of NO_3^- (hydrazine reduction) and NH_4^+ (indophenol blue) using a Technicon AutoAnalyzer II.

Statistical analyses

Soil gas data were log transformed and then analyzed using a one-way ANOVA. We also analyzed untransformed data using a Kruskall-Wallis one way analysis of variance. Due to lack of replication, soil water chemistry was not analyzed statistically. Mineralization/nitrification data did not require transformation and were analyzed using a one-way ANOVA, as well. We used SYSTAT 7.0 for all of our statistical analysis.

Results

Soil gases

Soil N_2O concentrations were low in upslope environments and higher in riparian environments. Nitrous oxide concentrations were statistically different in the six environments studied ($p < 0.05$). At most points in the profiles, N_2O concentrations were above atmospheric concentrations ($\sim$311 ppbv), even in the relatively oxic ridge, slope-ridge break, and slope environments (Figure 3). Highest concentrations were found in the riparian and streambank environments and concentrations were elevated at some points in the slope-ridge break and slope profiles. Soil surface fluxes across this catena, determined in a previous study, were low in the ridge, slope-ridge break, slope and streambank environments and higher in the slope-riparian break and riparian environments (Figure 3).

Soil O_2 concentration patterns were as expected, given the coloration of soils previously sampled across this catena (McDowell et al. 1992). In the ridge, slope-ridge break, and slope environments O_2 concentrations were near atmospheric and did not change much with depth. Oxygen concentrations were lower and changed more with depth in the slope-riparian break, riparian

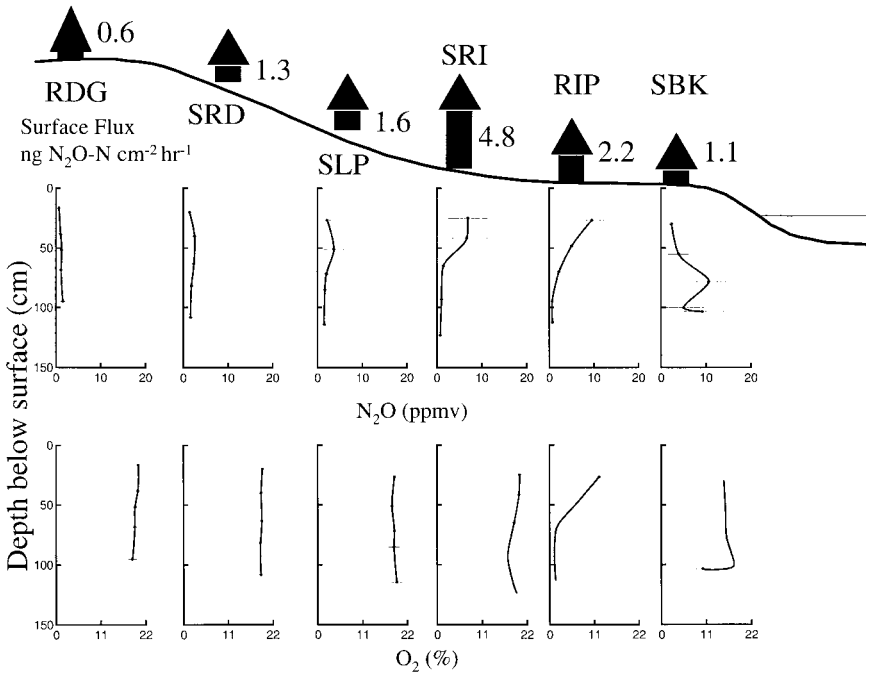

Figure 3. Soil gas depth profiles for N_2O and O_2 across the catena. Height of the arrows at the soil surface represents the average N_2O flux from each environment determined in another study (McSwiney et al. in prep). Error bars represent standard error of the mean.

zone, and streambank topographic positions (Figure 3). Differences between soil O_2 in the different environments were significant ($p < 0.05$). The highest N_2O concentrations were found in soil air probes that had intermediate O_2 concentrations (Figure 4(a)).

Soil solution chemistry

Soil solution chemistry exhibited distinct changes with shifts in oxidation status. Nitrate concentrations were highest in oxic, upslope environments (ridge, slope-ridge break and slope). At the upper edge of the slope-riparian break, NO_3^- disappeared and never increased in the riparian or streambank environments (Figure 5). Ammonium concentrations were high at the top of the ridge, very low throughout the rest of the upslope environments, and increased through the slope-riparian break, riparian zone, and streambank. In soil water, as in groundwater, either NO_3^- or NH_4^+ was the dominant form of inorganic N in solution (Figure 6). Dissolved organic carbon concentrations were highest in the ridge, slope-ridge break, and slope, decreased abruptly in the slope-riparian break, and remained low in the riparian zone and the

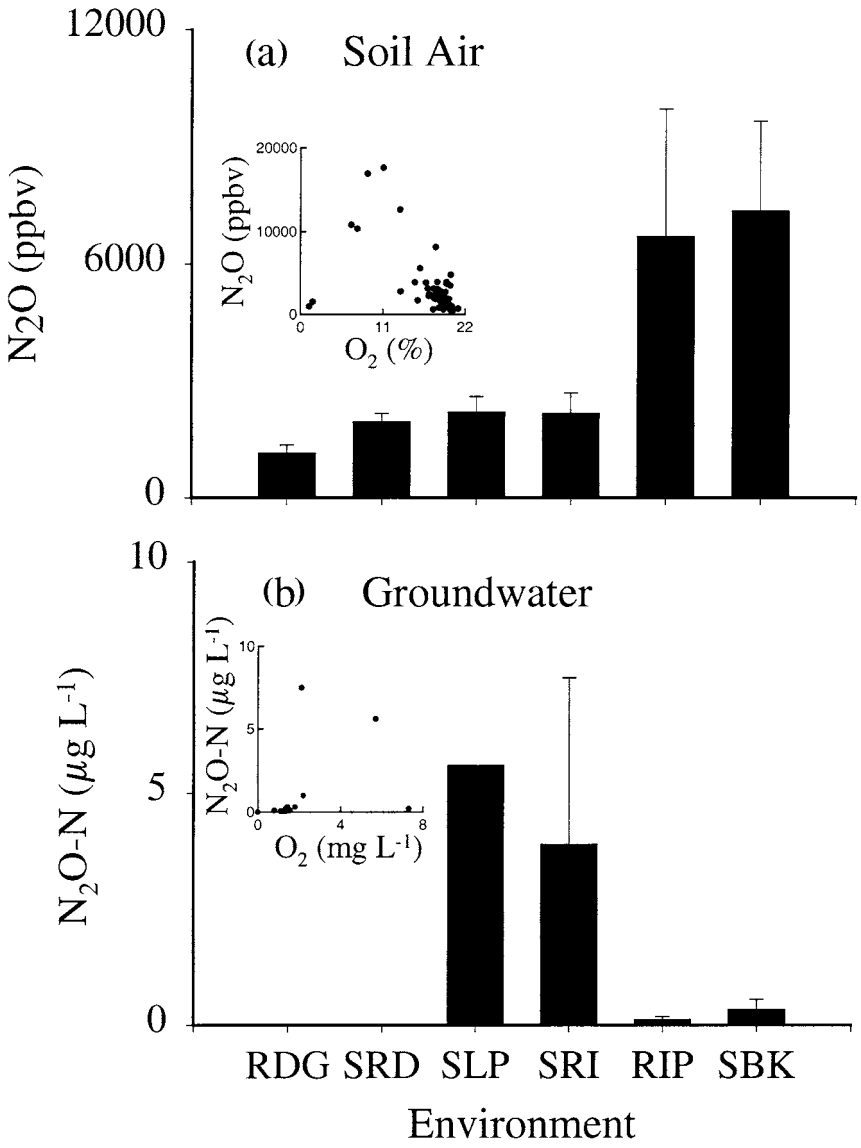

Figure 4. Nitrous oxide concentrations in soil averaged over all depths, reps, and times sampled in each environment (a) and nitrous oxide concentrations in groundwater averaged over all times and reps sampled (b). Note that there were no wells in the ridge or slope-rige break environments and that there was one well in the slope environment (no error bars). Groundwater N_2O data from Bowden et al. 1992. Error bars represent standard error of the mean.

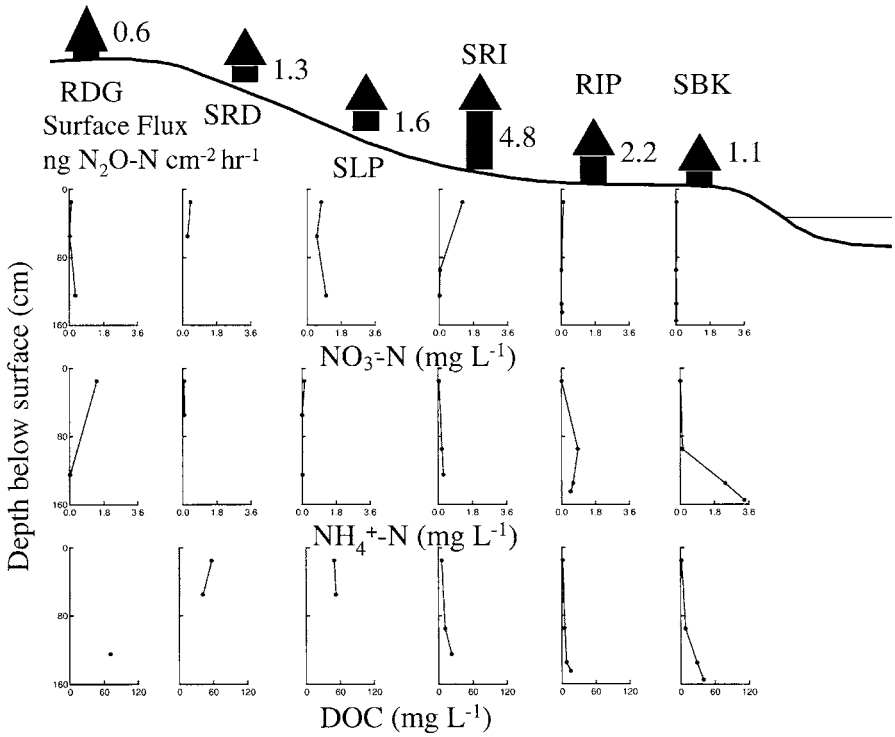

Figure 5. Soil water chemistry profiles for NO_3^-, NH_4^+, and DOC across the catena. Each point represents data from 1 lysimeter (no error bars). Height of the arrows represents the average N_2O flux from each environment determined in another study (McSwiney et al.). There is no data for DOC in the ridge environment and concentrations are low at the scale presented for NO_3^- and NH_4^+.

streambank (Figure 5). In the riparian environments, DOC concentrations increased with depth.

Groundwater chemistry

The chemistry of shallow groundwater in the streambank environment changed dramatically over a short distance. In contrast to mineral N concentrations observed in wells placed across the entire catena, the relationship between NO_3^- and NH_4^+ in streambank and hyporheic piezometers was not as tight (Figure 6(a)).

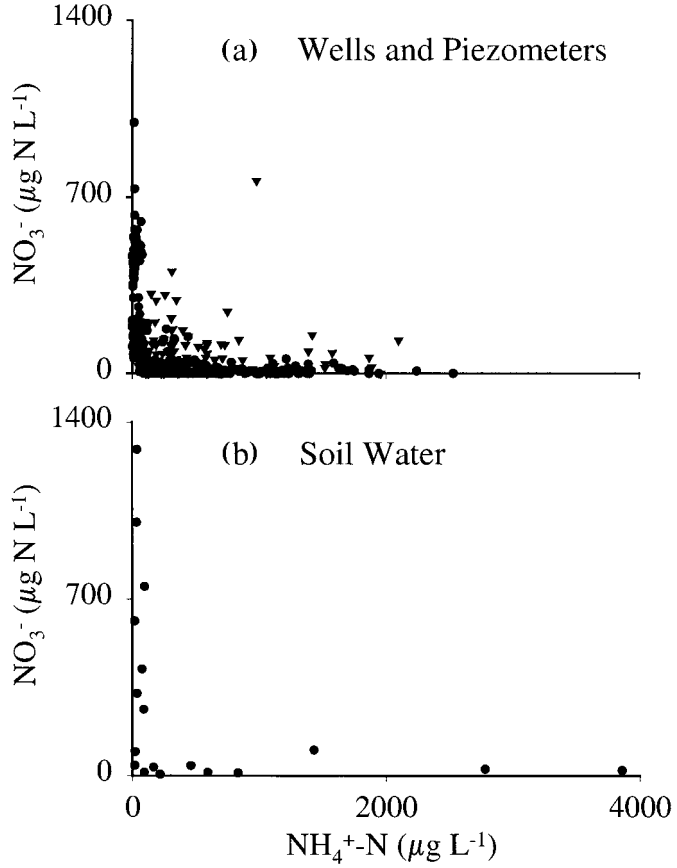

Figure 6. Relationship between groundwater NO_3^- and NH_4^+ (a) • = Groundwater wells that sample slope, slope-riparian break, riparian, and streambank environments. ▼ = Piezometers in the streambank environment. Relationship between soil water NO_3^- and NH_4^+ for the entire catena (b).

Nitrogen cycling

Net mineralization and nitrification rates were highest in environments that were not completely anaerobic. There were significant differences based on landscape position ($p < 0.05$). The lower of the slope sites, located near a groundwater well with high NO_3^- concentration, exhibited the highest rate of NO_3^- production (Figure 7). Riparian sites took up mineral N. Nitrate was not produced in the riparian soils and was produced in both streambank sites.

Soils from above the water table in the streambank were the only ones capable of NO_3^- production in the nitrification potential experiment (Figure 8). Surface soils were the only ones that produced NO_3^-. Water treated

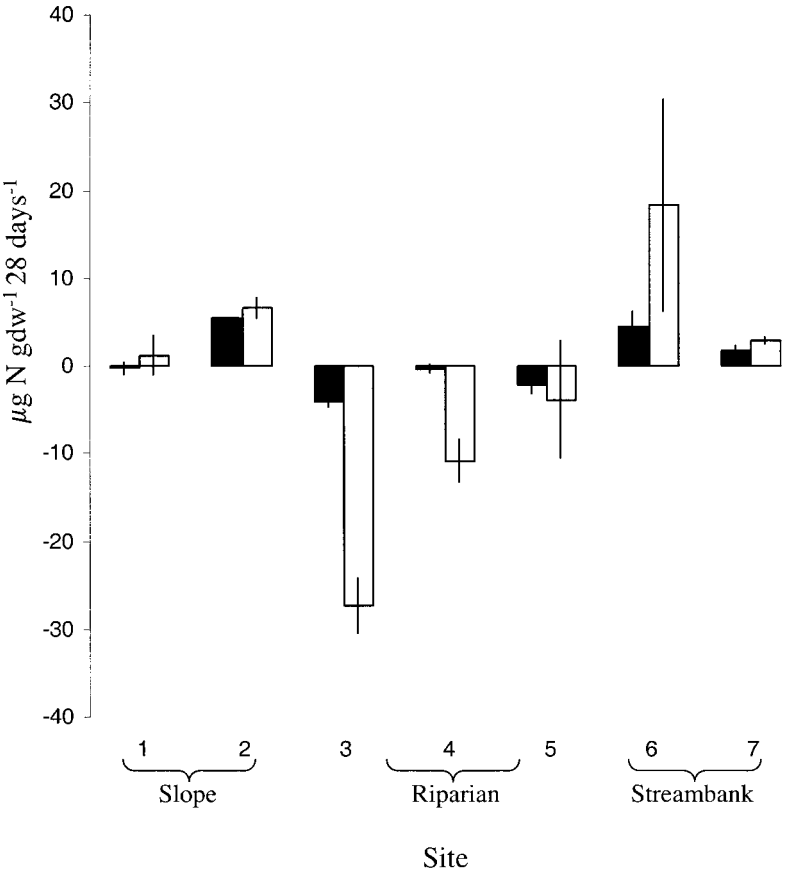

Figure 7. Net nitrification (solid bars) and net mineralization (empty bars) for surface soils across the slope, riparian, and streambank environments for the 2–10 cm depth and for both sampling times. Error bars represent the standard error of the mean.

surface soils produced a small amount of NO_3^- and NH_4^+ treated soils generated NO_3^- at the greatest rate. Addition of NH_4^+ and N-serve resulted in a short period of NO_3^- production, perhaps due to a delay in diffusion of the inhibitor, and then cessation of production (Figure 8).

Discussion

Studies of N export across topographic gradients often focus on surface N_2O flux (Davidson & Swank 1986; Groffman & Tiedje 1989; Bowden et al. 1992; Schipper et al. 1993; Reiners et al. 1998) or changes in groundwater

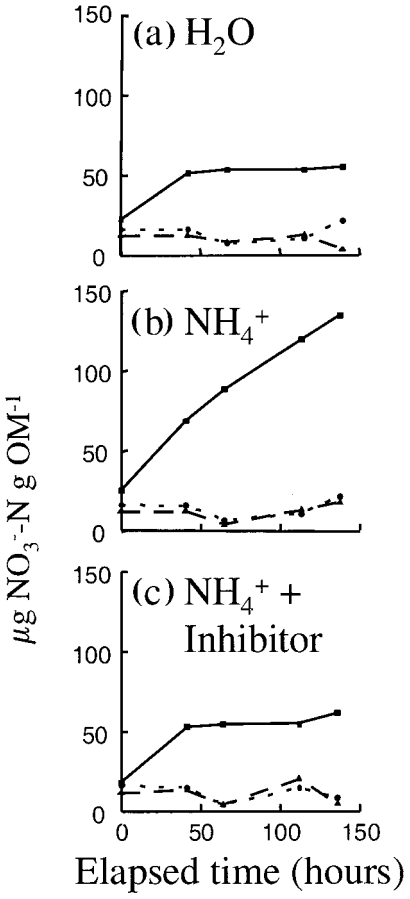

Figure 8. Nitrification potential with depth in the streambank. Solid line = above the water table. Short dashed line = at the water table. Long dashed line = below the water table. Panel a = nitrification with water treatment. Panel b = nitrification with ammonium treatment (potential). Panel c = nitrification with NH_4^+ and nitrification inhibitor.

NO_3^- (Peterjohn & Correll 1984; Ambus & Lowrance 1991; McDowell et al. 1992; McClain et al. 1994; Pinay et al. 1995; Hedin et al. 1998; Hill et al. 2000). From these studies we know that transition zones, upland-riparian and riparian-stream (hyporheic), can be producers of N_2O. Unfortunately, this is not true in all cases, nor even in all parts of any given transition zone. Groundwater systems have recently been described in great spatial detail for N_2O and controllers on its production (Hedin et al. 1998; Hill et al. 2000). Soils, particularly in the riparian zone, have not been considered at this level of spatial detail. Patterns of N_2O accumulation in soils are critical to understanding surface fluxes well enough to model them.

Detailed spatial analysis of *in situ* gas concentration in aquifers gives important information on features, such as organic lenses, that contribute to production or consumption of N_2O along various groundwater flowpaths (Hill et al. 2000). For the Rio Icacos topographic sequence, use of this approach for soils has helped us to identify hot environments for N_2O production, specifically the slope-riparian break and streambank, and hot points in the soil profiles, shallow soils in the slope-riparian break and deep soils in the streambank. This approach removes the frustration of lab incubations which often miss the soil features that lead to production or consumption of N_2O and the disruption of microcosm studies (Jacinthe et al. 1998; Gold et al. 1998). Zones of high concentration could be locations where production occurs or be zones of gas accumulation. This complicates interpretation but still provides information because that zone represents one end-member in a diffusion gradient that drives surface fluxes.

Consideration of controllers on N_2O production in a similar spatial context is important for understanding the patterns seen in soil gas concentrations. The relationships between N_2O and substrates for its production (DOC, NO_3^- and NH_4^+) are complicated because the concentrations measured at any point in the profile integrate production and consumption processes for the substrates. However, changes in concentrations between environments and between depths do help in the interpretation of N_2O production processes. Oxygen controls the proportion of N_2O produced by nitrification and denitrification but is not consumed or produced by the processes, so should be a better predictor of N_2O production. The relationships that we present between N_2O and O_2 in both soil and groundwater are consistent with what is seen in lab studies of nitrification and denitrification, that N_2O is produced when O_2 concentrations are not optimal for the processes (Lloyd 1993; McKenney et al. 1994; Kester et al. 1997; Bollman & Conrad 1998). At present, two models of N_2O production, PnET-N-DNDC and NLOSS, calculate O_2 concentrations in order to partition denitrification and nitrification to anaerobic and aerobic soil fractions, respectively (Li et al. 2000; Riley & Matson 2000). Models should be modified to calculate production of N_2O when O_2 concentrations are not optimum for the process of concern.

Changes between NH_4^+ and NO_3^- as the dominant form of dissolved inorganic N in other riparian sites (Stanford & Ward 1988; Ford & Naiman 1989; McDowell et al. 1992; Schipper 1993; Hedin et al. 1998) have been attributed to nitrification of NH_4^+ in the groundwater, as groundwater passes from anoxic to oxic regions. When an entire catena is considered, the changes in dominance between these two species are driven by different processes in each of the environments that make up the topographic sequence. In oxic slope soils, NH_4^+ is rapidly converted to NO_3^- during nitrification and

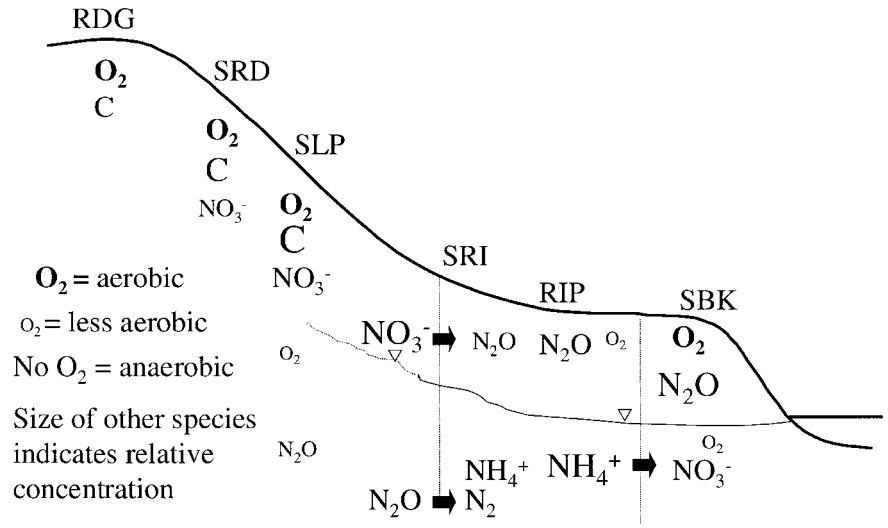

Figure 9. Conceptual model for N processing in the Rio Icacos basin.

then moved downslope in soil water that enters the groundwater system. At the break between the slope and the riparian zone, anoxic conditions lead to denitrification of NO_3^--rich waters that have entered the floodplain as groundwater at the same time that NH_4^+ concentrations begin to build due to decreases in nitrification rates (McDowell et al. 1992). As groundwater traverses the floodplain, NH_4^+ concentrations increase until the water reaches the streambank environment. In the streambank, coupled nitrification/denitrification control the balance between NO_3^- and NH_4^+. We have additional evidence for conversion of NH_4^+ to NO_3^- over a short distance from our streambank sampling at tight spatial resolution: the relationship between NO_3^- and NH_4^+ is not as tight for the streambank piezometers as it is for the groundwater wells, which sample the entire catena (Figure 6).

We propose a simple conceptual model to explain the differences in N processing at different depths across this catena in the Rio Icacos basin. For our riparian environments (SRI, RIP, SBK) we suggest the presence of saturated and unsaturated systems that appear to be decoupled from each other (Figure 9). The decoupling is most likely due to spatial segregation created by a clay lens that runs through the riparian environments. Changes in O_2 status in both zones appear to control N processing in general, and N_2O production in particular, with the greatest production of N_2O occurring at intermediate O_2 concentrations (Figure 4).

Results from the studies reported here do not allow us to distinguish between denitrification and nitrification as the sources of N_2O in the soils of

this catena. If denitrification produced the N_2O is our soils, the end product of denitrification would be N_2 under anaerobic conditions, which would result in less N_2O production, and therefore lower concentrations in bulk soil air. At near atmospheric O_2 concentrations, less N_2O production should occur because O_2 is a better electron acceptor than NO_3^-, also resulting in lower concentrations in bulk soil air (Bollman & Conrad 1998). If nitrification produced the N_2O in our soils, that would also occur at intermediate O_2 concentrations. All of the potential mechanisms described are consistent with the O_2 vs N_2O plots in Figure 4.

The upland portion of this watershed (RDG, SRD, and SLP) was an active zone for coupled mineralization and nitrification. Soils were clearly oxic based on O_2 concentrations, soil colors, and the fact that groundwater draining the slope environment was still relatively oxic and carried high concentrations of NO_3^- (McDowell et al. 1992). Some N_2O was produced in these upslope soils, either by nitrification or denitrification. Dentrification can occur under oxic conditions so we cannot rule it out as a potential source of N_2O (Robertson et al. 1984, 1990; Ottow & Fabig 1985) or it could have occurred in anaerobic microsites. Nitrification was most likely the source of N_2O in these environments because there was an increase in NO_3^- that parallels the increase in N_2O moving downslope and the bulk soil conditions were oxic. The steady downslope increase of NO_3^- and N_2O may be explained by accumulation of these soluble species as water moves downslope or by increasing rates of production from the ridge to the slope environments. In these environments, there should be a hydrologic connection between soil water and groundwater because NO_3^- concentrations were high at all depths in the soil water chemistry profiles and in the groundwater measured in previous studies (McDowell et al. 1992). Tracer studies would be required to demonstrate vertical and horizontal hydrologic transport of N_2O and NO_3^-.

Abrupt decreases in soil water NO_3^-, DOC, and O_2 along with an increase in soil N_2O at the slope-riparian break lead us to conclude that denitrification was the main source of N_2O at this topographic position. While soil conditions were reduced enough for N_2O production, groundwater conditions became so reduced that dissolved N_2O disappeared, presumably converted to dinitrogen (Bowden et al. 1992). Other studies have shown a disproportionately high denitrification enzyme activity (DEA) for organic soils at slope-floodplain interfaces when compared to organic soils across the entire riparian zone, lending further support for this interpretation (Cooper 1990; Schipper et al. 1993).

The streambank, a landscape position that is a transition between a reduced zone and an oxidized zone, was an area of active N processing in both the unsaturated and the saturated systems. Surface soils in the streambank had

the potential for nitrification, but NO_3^- concentrations were not elevated in the soil water. Nitrification probably occurred *in situ* because soils from above the water table had the potential to nitrify and net nitrification occurred in incubated soils from this landscape position. Most likely, NO_3^- was immediately denitrified to produce the high N_2O concentrations seen in this environment. In the groundwater system, NH_4^+ that was produced in the riparian zone was rapidly nitrified as groundwater entered the streambank. Further study will be required to determine whether NO_3^- is converted to N_2O in the streambank as seen by Hedin et al. (1998) in a site in Michigan and also proposed by McDowell et al. (1992) for this site.

Physical factors and surface N_2O flux

The streambank environment has the highest soil N_2O concentrations of all the landscape positions considered, but has surface fluxes that are as low those in the ridge, slope-ridge break, and slope environments (Figure 2). One possible explanation would be that the convex structure of the streambank would have more surface area and lead to more diffuse fluxes. Another possibility is that clay lenses or pockets of soil water impede movement of gas out of the soil, generating the high concentrations in these soils without correspondingly high surface fluxes. Worms are especially active in the streambank and their burrows may provide pathways of preferred transport for N_2O in both the gaseous and dissolved phases. Finally, the zone with the highest N_2O concentration lies deep within the soil profile, which would result in longer transport times to the soil surface and a greater likelihood for advection via the groundwater system or along the top of the clay lens. We would have missed higher fluxes closer to the stream margin because random placement of the chambers resulted in all of the chambers being located at the top of the streambank. Physical controls on movement may be as important as the production processes in regulating the flux of N_2O to the atmosphere in this wet ecosystem and need to be considered.

Conclusions

The results of this study support the hypothesis that redox status controls production and consumption of N_2O and the balance between NO_3^- and NH_4^+ in soils at different landscape positions along a cetena in the Rio Icacos basin in Puerto Rico. Oxygen concentrations in soils and groundwater are good indicators of where on the topographic sequence N_2O production will occur, with environments that are intermediate in O_2 status, most often occurring at transition zones, having the highest N_2O concentrations. When the entire

catena is considered, disappearance of DOC and NO_3^- in soil solution helps in prediction of sites of N_2O production. For modeling of some systems, consideration of substrate concentrations and redox status as controls on N_2O production should allow good prediction of surface flux. In other systems, like this rainforest, physical factors may control N_2O movement out of the soil profile and advection away from sites of production and will have to be considered in addition to the chemical controls on *in situ* production in order to predict N_2O fluxes across landscapes.

Acknowledgements

We acknowledge María Milagros Rivéra, Carlos Rubén Ortiz, Brynne Bryan, Dan Kent, and Rebecca Chaplin for help in the field and laboratory. Rainfall data was provided by Matt Larson of the USGS. We appreciate the comments from three anonymous reviewers that improved our manuscript immensely. This work was done in cooperation with the University of Puerto Rico. Support for this project was from the NASA-IRA and NSF-LTER grants to the University of Puerto Rico, NSF grants BSR 8718396, BSR 8718395, and BSR 9007498 awarded to WH McDowell and WB Bowden, a cooperative agreement between WH McDowell and the U.S. Forest Service, Southern Research Station, and a NASA Fellowship for Global Change awarded to CP McSwiney. This is Kellogg Biological Station Contribution no. 968.

References

Avanzino RJ & Kennedy VC (1993) Long-term frozen storage of stream water samples for dissolved orthophosphate, nitrate plus nitrite, and ammonia analysis. Water Resour. Res. 29(10): 3357–3362

Ambus P & Lowrance R (1991) Comparison of denitrification in two riparian soils. Soil Sci. Soc. of Amer. Jnl 55: 994–997

Beinroth FH (1982) Some highly weathered soils of Puerto Rico I: Morphology and Classification. Geoderma 27: 1–74

Bollmann A & Conrad R (1998) Influence of O_2 availability on NO and N_2O release by nitrification and denitrification. Global Change Biology 4: 387–396

Bouwman AF, Fung I, Matthews E & John J (1993) Global analysis of the potential for N_2O production in natural soils. Global Biogeochem. Cycles 7: 557–597

Bouwman AF, Van der Hoek KW & Olivier JGJ (1995) Uncertainties in the global source distribution of nitrous oxide. Jnl of Geophys. Res. 100: 2785–2800

Bowden WB & Bormann FH (1986) Transport and loss of nitrous oxide in soil water after forest clear-cutting. Science 233: 867–869

Bowden WB, McDowell WH, Asbury CE & Finley AM (1992) Riparian nitrogen dynamics in two geomorphologically distinct tropical rain forest watersheds: nitrous oxide fluxes. Biogeochem. 18: 77–89

Brown S, Lugo AE, Silander S & Liegel L (1983) Research history and opportunities in the Luquillo Experimental Forest. In USDA-Forest Service Southern Forest Experimental Station, General Technical Report SO-441 28 pp

Butler JH, Elkins JW, Thompson TM & Egan KB (1989) Tropospheric and dissolved N_2O of the West Pacific and East Indian oceans during the EI Niño southern oscillation event of 1987. Jnl of Geophys. Res. 94: 14865–14877

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

Crill PM (1991) Seasonal patterns of methane uptake and carbon dioxide release by a temperate woodland soil. Global Biogeochem. Cycles 5: 319–334

Davidson EA & Swank WT (1986) Environmental parameters regulating gaseous nitrogen losses from two forested ecosystems via nitrification and denitrification. Applied and Environmental Microbiology 52: 1287–1292

Dowdell RJ, Burford JR & Crees R (1979) Losses of nitrous oxide dissolved in drainage water from agricultural land. Nature 278: 342–343

Faulker SP & Patrick WH Jr (1992) Redox processes and diagnostic wetland soil indicators in bottomland hardwood Forests. Soil Sci. Soc. of Amer. Jnl 56: 856–865

Ford TE & Naiman RJ (1989) Groundwater-surface water relationships in boreal forest watersheds: dissolved organic carbon and inorganic nutrient dynamics. Canadian Journal of Fisheries and Aquatic Science 44: 1948–1956

Gold AJ, Jacinthe PA, Groffman PM, Wright WR & Puffer RH (1998) Patchiness in groundwater nitrate removal in a riparian forest. Jnl of Environ. Qual. 27: 146–155

Groffman PM & Tiedje JM (1989) Denitrification in north temperate forest soils: spatial and temporal patterns at the landscape and seasonal scales. Soil Biol. and Biochem. 21: 613–620

Groffman PM & Tiedje JM (1991) Relationships between denitrification, CO_2 production and air-filled porosity in soils of different texture and drainage. Soil Biol. and Biochem. 23: 299–302

Groffman PM, Brumme R, Butterbach-Bahl K, Dobbie KE, Mosier AR, Ojima D, Papen H, Parton WJ, Smith KA & Wagner-Riddle C (2000) Evaluating annual nitrous oxide fluxes at the ecosystem scale. Global Biogeochem. Cycles 14(4): 1061–1070

Hill AR, Devito KJ, Campagnolo S & Sanmugadas K (2000) Subsurface denitrification in a forest riparian zone: interactions between hydrology and supplies of nitrate and carbon. Biogeochem. 51: 193–223

Hutchinson GL & Davidson EA (1993) Processes for production and consumption of gaseous nitrogen oxides in soil. In: Rolston DE, Harper LA, Mosier AR & Duxbury JM (Eds) Agricultural Ecosystem Effects on Trace Gases and Global Climate Change (pp 79–93). American Society of Agronomy, Madison WI

Hedin LO, von Fischer JC, Ostrom NE, Kennedy BP, Brown MG & Robertson GP (1998) Thermodynamic constraints on nitrogen transformations and other biogeochemical processes at soil-stream interfaces. Ecology 79(2): 684–703

Jacinthe PA, Groffman PM, Gold AJ & Mosier A (1998) Patchiness in microbial transformations in goundwater in a riparian forest. Jnl of Environ. Qual. 27: 156–164

Jacobs TC & Gilliam JW (1985) Headwater stream losses of nitrogen from two coastal plain watersheds. Jnl of Environ. Qual. 14: 467–472

Keller M & Reiners WA (1994) Soil-atmosphere exchange of nitrous oxide, nitric oxide, and methane under secondary succession of pasture to forest in the Atlantic lowlands of Costa Rica. Global Biogeochem. Cycles 8: 399–409

Kester RA, de Boer W & Laanbroek HJ (1997) Production of NO and N_2O by pure cultures of nitrifying and denitrifying bacteria during changes in aeration. Appl. and Environ. Microbiol. 63(10): 3872–3877

Khan FA & Fenton TE (1994) Saturated zones and soil morphology in a mollisol catena of central Iowa. Soil Sci. Soc. of Amer. Jnl 58: 1457–1464

Li C, Aber J, Stange F, Butterbach-Bahl K & Papen H (2000) A process-oriented model of N_2O and NO emissions from forest soils: 1. Model development. Jnl of Geophys. Res. 105(D4): 4369–4384

Lowrance R, Todd R, Fail J Jr, Hendrickson O Jr, Leonard R & Asmussen L (1984) Riparian forests as nutrient filters in agricultural watersheds. Biosci. 34: 374–377

Lloyd D (1993) Aerobic denitrification in soils and sediments: from fallacies to facts. Trends in Ecology and Evolution 8(10): 352–356

Matson PA & Vitousek PM (1990) An ecosystem approach to the development of a global nitrous oxide budget. Bioscience 40: 667–672

McClain ME, Richey JE & Pimentel TP (1994) Groundwater nitrogen dynamics at the terrestrial-lotic interface of a small catchment in the Central Amazon basin. Biogeochem. 27: 113–127

McDowell WH, Bowden WB & Asbury CE (1992) Riparian nitrogen dynamics in two geomorphologically distinct tropical rain forest watersheds: subsurface solute patterns. Biogeochem. 18: 53–75

McDowell WH, McSwiney CP & Bowden WB (1996) Effects of hurricane disturbance on groundwater chemistry and riparian function in a tropical rain forest. Biotropica 28(4a): 577–584

McKenney DJ, Drury CF, Findlay WI, Mutus B, McDonnell T & Gajda C (1994) Kinetics of denitrification by *Pseduomonas fluorescens*: oxygen effects. Soil Biol. and Biochem. 26(7): 901–908

McSwiney CP, Keller M, McDowell WH & Scatena FN. Spatial variability in nitrous oxide and methane flux across tropical rainforest catenas. In prep

Megonigal JP, Patrick WH Jr & Faulker SP (1993) Wetland identification in seasonally flooded forest soils: soil morphology and redox dynamics. Soil Sci. Soc. of Amer. Jnl 57: 140–149

Ottow JCG & Fabig W (1985) Influence of aeration on denitrification and redox level in different bacterial batch cultures. In: Caldwell DE, Brierley JA & Brierley CL (Eds) Planetary Ecology (pp 427–440). Van Nostrand Reinhold Company, New York

Patrick WH Jr (1977) Oxygen content of soil air by a field method. Soil Sci. Soc. of Amer. Proceedings 41: 651–652

Peterjohn WT & Correl DL (1984) Nutrient dynamics in an agricultural watershed observations on the role of a riparian forest. Ecology 65: 1466–1475

Pinay G, Decamps H, Arles C & Lacassin-Seres M (1989) Topographic influence on carbon and nitrogen dynamics in riverine woods. Archiv Fur Hydrobiologie 114: 401–414

Reiners WA, Keller M & Gerow KG (1998) Estimating rainy season nitrous oxide and methane fluxes across forest and pasture landscapes in Costa Rica. Water, Air, and Soil Pollution 105: 117–130

Riley WJ & Matson PA (2000) NLOSS: A mechanistic model of denitrified N_2O and N_2 evolution from soil. Soil Science 165(3): 237–249

Robertson GP (1989) Nitrification and denitrification in humid tropical systems In: Procotor J (Ed.) Mineral Nutrients in Tropical Forest and Savanna Ecosystems (pp 55–69). British Ecological Society Special Publication Number 9

Robertson LA & Kuenen JG (1984) Aerobic denitrification: a controversy revived. Archive of Microbiology 139: 351–354

Robertson LA & Kuenen JG (1990) Combined heterotrophic nitrification and aerobic denitrification in *Thiosphaera pantotropha* and other bacteria. Antonie Van Leeuenhoek 57: 139–152

Ronen D, Magaritz M & Almon E (1988) Contaminated aquifers are a forgotten component in the global N_2O budget. Nature 335: 57–59

Schipper LA, Cooper AB, Harfoot CG & Dyck WJ (1994) An inverse relationship between nitrate and ammonium in an organic riparian soil. Soil Biol. and Biochem. 26(6): 799–800

Schipper LA, Cooper AB, Harfoot CG & Dyck WJ (1993) Regulators of denitrification in an organic riparian soil. Soil Biol. and Biochem. 25: 925–933

Stanford JA & Ward JV (1988) The hyporheic habitat of river ecosystems. Nature 335: 64–66

Steudler PA, Melillo JM, Bowden RD, Castro MS & Lugo AE (1991) The effects of natural and human distrubance on soil nitrogen dynamics and trace gas fluxes in a Puerto Rican wet forest. Biotropica 23: 356–363

Silver WL, Lugo AE & Keller M (1999) Soil oxygen availability and biogeochemistry along rainfall and topographic gradients in upland wet tropical forest soils. Biogeochem. 44: 301–328