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Riparian nitrogen dynamics in two geomorphologically distinct tropical rain forest watersheds: nitrous oxide fluxes

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Abstract. Fluxes of N_2O at the soil surface, dissolved N_2O in near-surface groundwater, and potential N_2O production rates were measured across riparian catenas in two rain forest watersheds in Puerto Rico. In the Icacos watershed, mean N_2O fluxes were highest at topographic breaks in the landscape ($\sim$40—300 μg N_2O-N m^{-2} h^{-1}). At other locations in the riparian zone and hillslope, fluxes were lower ($\leqslant 2$ μg N_2O-N m^{-2} h^{-1}). This pattern of surface N_2O fluxes was persistent. In the Bisley watershed, mean suface N_2O fluxes were lower (<40 μg N_2O-N m^{-2} h^{-1}) and no identifiable spatial or temporal pattern. Although the spatial patterns and intensities of N_2O emissions differed between the two watersheds, surface soils from both sites had a high potential to reduce NO_3 to N_2O (and perhaps N_2). This potential declined sharply with depth as did soil %C, %N, and potential N-mineralization. Simple controls on denitrification (i.e. aeration, nitrate, and carbon) explained characteristics of potential N_2O production in surface and deep soils from riparian and upslope locations. In the field, spatial patterns in these controlling variables were defined by geomorphological differences between the two watersheds, which then explained the spatial patterns of observed N_2O flux.

Introduction

Riparian and hyporheic zones are areas in which soils typically exhibit strong redox transitions due to extensive saturation of the soil and intensive microbial activity (Pinay et al. 1989; Williams 1989; Howard-Williams 1991). These redox transitions provide a variety of habitats for aerobic, anaerobic, and facultative microorganisms. As a consequence, elements like N, whose microbial transformations are sensitive to redox conditions, may be strongly influenced during surface or subsurface flow through riparian zones. There is abundant evidence, for example, that nitrate concentrations in shallow groundwater are significantly reduced during transport through riparian areas and buffer strips (Davidson & Swank 1986; Schnable 1986; Pinay et al. 1989; Cooper 1990; Ambus & Lowrance 1991) and that denitrification activity is higher in fine-textured, wet, riparian soils than in loamy, moist, upland soils (Groffman & Tiedje 1989a and b; Groffman et al. 1991; Groffman & Tiedje 1991; Ambus & Lowrance 1991; Howard-Williams 1991).

Geomorphological characteristics may influence watershed nutrient dynamics on both large and small spatial scales (e.g. papers in Church et al. 1990). On a macro-scale, geomorphology influences the extent to which reducing soil conditions can form in a riparian zone, which in turn may affect N retention within and hydrologic export from the entire watershed. Several investigators have examined how riparian environments affect the relative importance of hydrologic export, gaseous flux, and plant uptake of N in a variety of ecosystems (Lowrance et al. 1984a and b; Peterjohn & Correll 1984; Jacobs & Gilliam 1985; Robertson et al. 1987).

In addition, on a micro-scale, geomorphology may influence the hydrologic characteristics of flow paths through riparian zones, which could have large effects on the nature and extent of N processing within the near-stream environment (Hynes 1983; Stanford & Ward 1988; Warwick & Hill 1988; Ford & Naiman 1989; Hill 1990; Triska et al. 1989; Triska et al. 1990a and b; Duff & Triska 1990).

We have examined this latter possibility in two geomorphologically distinct watersheds in Puerto Rico, where McDowell et al. (*this issue*) measured nitrate, ammonium, dissolved organic N, and dissolved oxygen in shallow groundwater wells across two representative riparian catenas. The magnitudes and spatial distributions of NH_4^+, NO_3^-, and dissolved oxygen (DO) concentrations in shallow groundwater corresponded to patterns in apparent soil redox levels and hydrologic flow paths that were specific to each watershed. McDowell et al. (*this issue*) concluded that these geochemical patterns were controlled by the different geomorphological characteristics of the two watersheds.

We hypothesized that these geochemical and hydrologic differences might also promote differences in both the distribution and intensity of gaseous N emissions to the atmosphere across these riparian catenas. This paper presents results of N_2O emission rates obtained with surface chambers, dissolved N_2O concentrations in near-surface groundwater, and estimates of potential N_2O production rates in soils from these sites. With the exception of potential N-mineralization, all data reported here were collected prior to Hurricane Hugo, which severely damaged parts of the Luquillo Experimental Forest in September 1989.

Site description

This study was conducted in the Bisley and Rio Icacos watersheds of the Luquillo Experimental Forest (LEF), in eastern Puerto Rico. Characteristics of the LEF are described in detail in Brown et al. (1983); the research sites are described in McDowell et al. (*this issue*). Briefly, the sampling sites in the Bisley watershed were at 240 m elevation; in the Icacos watershed they were at 625 m elevation. Average rainfall and temperature range from 373 to 645 cm and 19.3 to 22.7 °C at higher elevations (La Miña station, elevation 716 m) and from 180 to 310 cm and 23.6 to 27 °C at lower elevations (Rio Blanco, elevation 30.5 m) (Brown et al. 1983). The Icacos research site was located in the colorado forest type, dominated by palo colorado (*Cyrilla racemiflora*) on the slopes and sierra palm (*Prestoea montana* Nichols) on the floodplains. The colorado forest type covers 17% of the LEF and tends to develop above the cloud condensation level (600 m). Species diversity is modest (23 species) and understory vegetation is well developed. The palm forest type covers about 11% of the LEF and is commonly found on steep slopes in both the tabanuco and colorado forest types (Brown et al. 1983) and in the floodplains of mountain streams (Frangi & Lugo 1985). The Bisley research area is located in the tabonuco forest type, dominated by tabonuco (*Dacryodes excelsa* Vahl) on the slopes. The tabanuco forest type covers 70% of the LEF and has been intensively studied (see references in Brown et al. 1983). It tends to develop below 600 m elevation on protected and well drained slopes, has high species diversity (168 reported species), and has an open understory with little vegetation on the forest floor. Sierra palms are located on the floodplains at this site as well (McDowell et al. *this issue*). Together, the tabanuco, colorado, and palm forests cover 98% of the LEF.

Most of the LEF has developed on andesitic to basaltic volcanic sandstones, mudstones and breccia. However, the Icacos watershed has developed from a quartz diorite. The topography in the forest is steep and unstable. Soils are Ultisols and Inceptisols classified as Epiaquic and Aquic Tropohumult silty clay loams and Typic Humitropept sandy clay loams (Boccheciamp 1977; Brown et al. 1983). The soils are typically acidic with low N and P contents (Edmisten 1970; Fox 1982).

Methods

Soil C, N, and potential N-mineralization

Total soil C and N were analyzed by combustion on a Perkin-Elmer Model 240B CHN analyzer.

Potential N-mineralization was determined following Keeney (1982). For each soil sample, four, air-dry, sub-samples (5 g) were sealed in replicate 16 mm × 150 mm, glass, culture tubes filled to the top with distilled water (~ 13 ml). Two sub-samples were chosen at random and the soil and supernatant water were extraced in 2 *N* KCl (total volume: 50 ml), then analyzed for NH_4 and NO_3 on a Technicon Autoanalyzer II, by standard methods. The remaining two tubes were incubated at 40 °C for seven days than extracted and analyzed as for the initial sub-samples. Potential mineralization was defined as the sum of NH_4-N plus NO_3-N released per g dry (105 °C) soil.

Soil surface N_2O fluxes

Fluxes of N_2O from the soil to the atomosphere were measured in the field with closed, stirred chambers (Mathias et al. 1980; Hutchinson & Mosier 1981). Two to four chambers (5 L internal volume) were implanted within 3 m of each other at several locations along a transect from the stream bank, across the riparian zone, and up the hillslope. Special efforts were made to sample at distinct topographic breaks between these landscape components. These sampling transects crossed the well fields described by McDowell et al. (*this issue*). Each chamber location was used only once.

Headspace air samples were taken as soon as possible after the chambers were in place (1—2 min) and 10 min intervals thereafter for a total of 30 to 40 min. Samples were withdrawn through a chamber vent with a 20 cm^3 nylon, liquid-sampling syringe, modified as described by Bowden et al. (1991).

Samples were analyzed within 12 h of collection on a Shimadzu Mini-2 gas chromatograph with a Poropak Q column (80/100 mesh, 10 m × 0.32 cm stainless steel tubing, P-5 carrier gas, 40 ml/min) operated at 70 °C and an electron capture detector operated at 310 °C. Unknowns were analyzed in comparison to local air samples (310 ppb) and standard gas mixtures (Scott Environmental Products, Inc., Plumsteadville, Pennsylvania). The detector response was essentially linear over the concentration range encountered in the chamber experiments. Flux rates were calculated in μg N m^{-2} h^{-1} based on changes in headspace N_2O concentrations over the incubation period.

Dissolved N_2O

Dissolved N_2O in groundwater was measured by the dual-equilibration method of McAullife (1971, see also Bowden & Bormann 1986). Samples were obtained from capped but vented wells with a teflon bailer. A water sample (25 ml) was removed from the middle of the bailer via a thin (0.32 cm OD × 0.16 cm ID) Tygon tube attached to a 60 cm^3 glass syringe. Care was taken to exclude bubbles during sampling.

Samples were returned to the field lab where they were equilibrated with 25 ml of high-purity N_2 gas by vigorously shaking the syringe, manually, for 30 sec. The headspace was injected into the gas chromatograph through a silica gel adsorbent to remove water vapor. The water sample was extracted a second time with a fresh volume of N_2 and the equilibrated headspace gas mixture was analyzed as before. These two headspace gas concentrations were used to calculate the initial concentration of N_2O in the water sample.

Potential N_2O production rates

The potential for N_2O and N_2 production within soils from the sample sites was analyzed with laboratory incubations (Tiedje 1982). Slurries, made from 25 g soil (fresh weight) and 100 ml of water, were incubated in 0.95 L (1 qt.), glass, Mason jars with air-tight lids. In some treatments, 750 μg NO_3-N/100 ml (50 μg NO_3-N/g dry soil) was added to the slurry. Neither carbon nor chloramphenicol was added in these experiments.

The jars were evacuated to about −90 kPa, then refilled with a treatment gas mixture. This procedure was repeated three times to degas soil slurries and flush the jar headspace. The mixture used to refill the jars varied depending on the treatment. Aerobic treatments were refilled with lab air. Anaerobic treatments were refilled with high-purity N_2. For treatments requiring acetylene, 100 cm^3 were removed from the final refill volume with a syringe and replaced with acetylene generated from calcium carbide (about 10% or 10 kPa). The jars were repeatedly shaken by hand throughout the incubation.

Headspace gas was sampled and analyzed as described above. Potential N_2O plus N_2 production rates were expressed as ng N_2O-N (g dry soil)$^{-1}$ h^{-1} based on changes in headspace N_2O concentrations over the incubation period, after correcting for N_2O dissolved in the slurries.

These N_2O accumulation rates are "potentials" that are dependent upon the behavior of N_2O-producing organisms that are forced to operate under artificial conditions of aeration and substrate availability. The results from these assays are meaningful in a relative sense, e.g. a comparison of two soils assayed under identical conditions or a single soil assayed in the presence or absence of a controlling factor, such as nitrate. The absolute magnitudes of nitrification or denitrification should not be inferred from these results.

Results

Soil C, N, and potential N-mineralization

Potential N-mineralization was related to both the amount and quality of organic matter in the soil (Fig. 1). Total C and N concentrations in soils within the LEF are highest at the surface and decline sharply with depth (McDowell et al. *this issue*; Fox 1982). Figure 1 shows that potential N-mineralization in surface soils (0—10 cm) and the concentrations of C and N were directly related. Soils from 35—45 cm occasionally had high C concentrations, but under similar incubation conditions produced little mineral N. Soils from 90—100 cm produced little mineral N and had very low C and N concentrations. Thus, C and N in surface soil horizons are more abundant and, presumably, more labile than C and N in soils from deeper soil horizons. The differences among soil depths shown in Fig. 1 were similar in the Icacos watershed (which was not greatly affected by Hurricane Hugo) and in the Bisley watershed (which was heavily damaged by Hurricane Hugo).

Soil surface N_2O fluxes

Emissions of N_2O from the soil surface to the atmosphere were measured in January and May 1989 (prior to Hurricane Hugo), on transects along riparian catenas within both the Icacos and Bisley watersheds. At the Icacos site there was a distinct spatial pattern in N_2O fluxes with the highest fluxes at topographic breaks in the catena (Fig. 2). In January, the highest fluxes (mean 322 μg N_2O-N m^{-2} h^{-1}, $n = 6$, range 5—1150 μg N_2O-N m^{-2} h^{-1}) were measured at the upper break between the ridge and mid-slope zones. High fluxes (22—66 μg N_2O-N m^{-2} h^{-1}, $n = 3$) were observed at the break between the mid-slope and the floodplain; fluxes at the stream bank were variable (0—110 μg N_2O-N m^{-2} h^{-1}, $n = 3$). Very

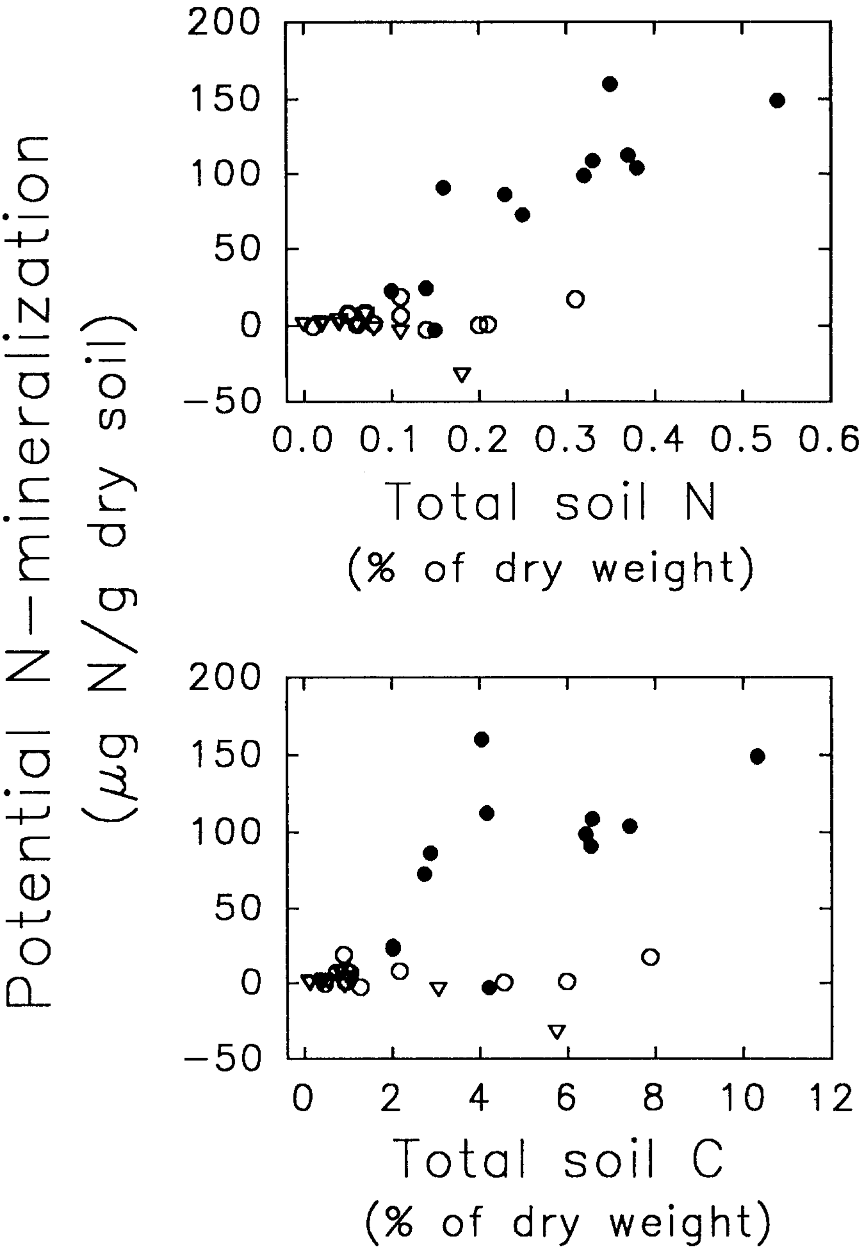

Fig. 1. Potential N-mineralization during 7-day, anaerobic incubations, as a function of soil %N (upper) and soil %C (lower). In both panels, closed circles (●) are surface soils (0—10 cm), open circles (○) are soils from 35—45 cm, and open triangles (▽) are deep (90—100 cm) soil. Soils tested included samples from both watersheds at upslope and floodplain positions in the catena.

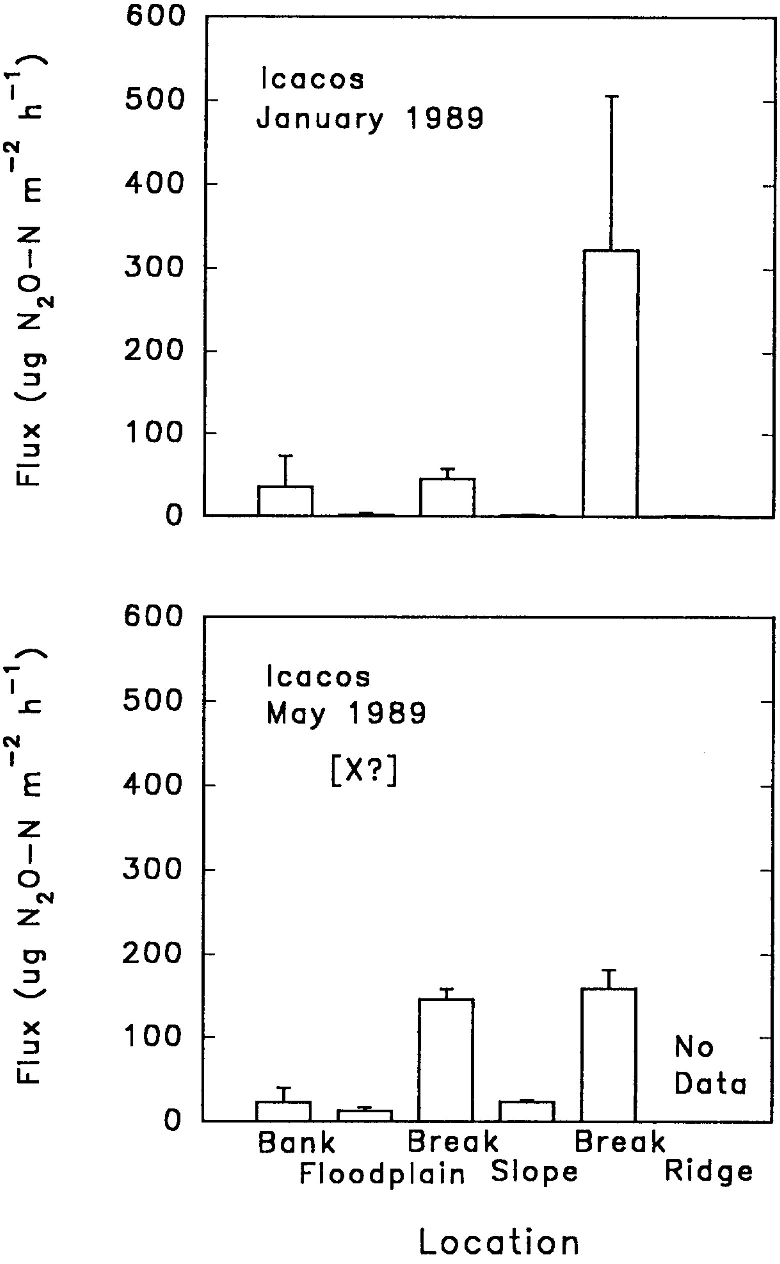

Fig. 2. Fluxes of N_2O-N at the Icacos site in January and May, 1989. The error bars indicate ± 1 standard error. The flux indicated by the "X?" was unusually high compared to others from this site and was not included in the mean flux estimate.

small fluxes (1—2 μg N_2O-N m^{-2} h^{-1}, $n = 12$) were observed at the ridge top, on the mid-slope, and within the floodplain.

This pattern persisted in May (Fig. 2), with lower fluxes at the upper break (136 and 180 μg N_2O-N m^{-2} h^{-1}, $n = 2$) and higher fluxes at the lower break (133 and 157 μg N_2O-N m^{-2} h^{-1}, $n = 2$). In addition fluxes within the mid-slope and riparian areas were slightly higher than in January (5—25 μg N_2O-N m^{-2} h^{-1}, $n = 5$). One chamber in the floodplain (near Well 6) yielded an unusually high flux of 435 μg N_2O-N m^{-2} h^{-1}. We never observed a reduction (uptake) of N_2O in the chamber experiments done in Icacos.

Fluxes of N_2O at the Bisley site were never as large as the highest fluxes observed at the Icacos site and did not appear to follow a pattern related to landscape features (Fig. 3). In January the largest fluxes (2—42 μg N_2O-N m^{-2} h^{-1}, $n = 8$) were observed at the mid-slope, lower break, and floodplain locations. Fluxes at the ridge and stream bank locations were relatively small (< 1 μg N_2O-N m^{-2} h^{-1}, $n = 5$). A single chamber located at the upper slope break yielded a small negative flux (uptake of −7 μg N_2O-N m^{-2} h^{-1}). In May fluxes at the Bisley site were generally lower than those observed in January (< 5 mg μg N_2O-N m^{-2} h^{-1}, $n = 10$), with the exception of the upper slope break, which yielded two fluxes of 14 and 17 μg N_2O-N m^{-2} h^{-1}.

Dissolved N_2O

We measured dissolved N_2O concentrations in water from the Icacos wells four times between January and May 1989 (Fig. 4). Concentrations of dissolved N_2O followed a persistent pattern that was similar to that observed for surface N_2O emissions observed in January and May. The highest dissolved N_2O concentrations (3.0 to 9.1 μg N_2O-N L^{-1}) were observed in wells located at the interface between the mid-slope and the riparian areas (wells #9 and 23, Fig. 4). Well #10, on the floodplain side of the slope break, typically had low N_2O concentrations (< 0.4 μg N_2O-N L^{-1}). There was no wells further up the hillslope (e.g. at the upper slope break).

Dissolved N_2O concentrations were very low within the Icacos floodplain (0.05—0.50 μg N_2O-N L^{-1}, wells #5—8, Fig. 4). In many cases the concentrations of dissolved N_2O were below the concentration that would be expected for water in equilibrium with air (0.22 μg N_2O-N L^{-1} for 20 °C; Weiss & Price 1980; Bowden & Bormann 1986). Dissolved N_2O concentrations were also low in the stream bank wells (0.05—0.50 μg N_2O-N L^{-1}, wells #1—4, Fig. 4) with the exception of well #3 (0.5—1.4 μg N_2O-N L^{-1}).

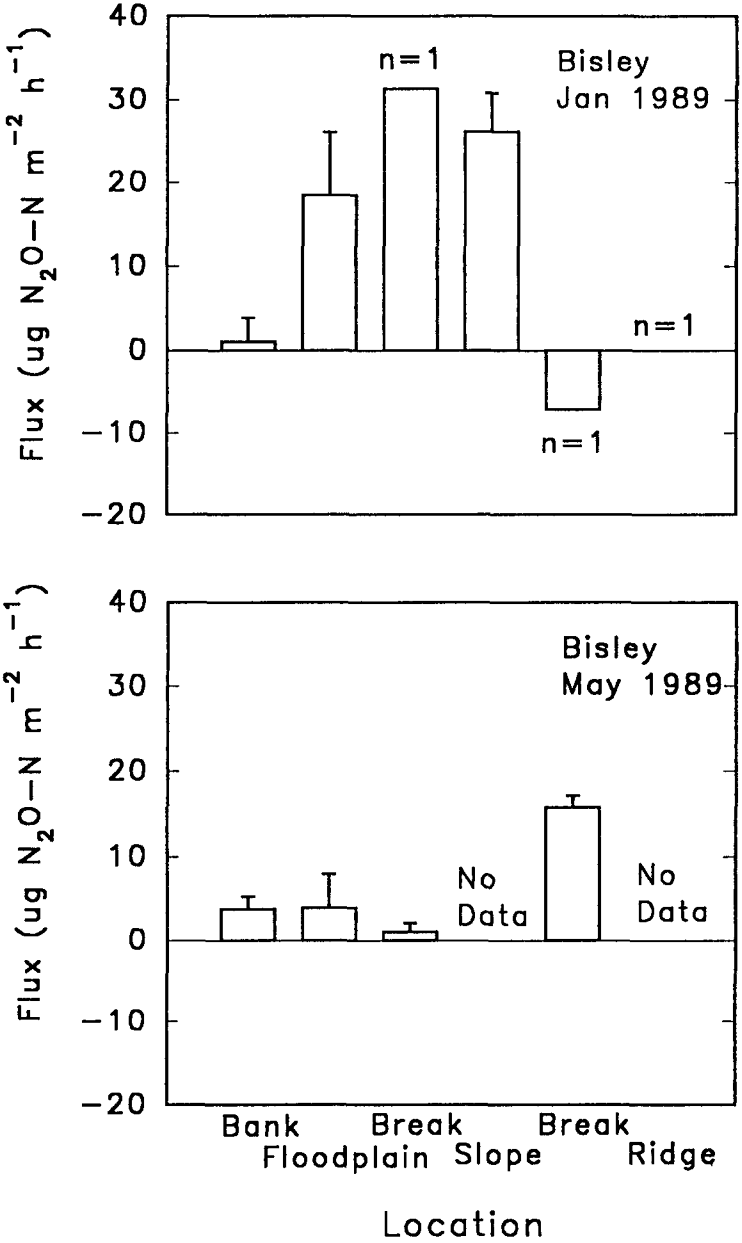

Fig. 3. Fluxes of N_2O-N at the Bisley site in January and May, 1989. The error bars indicate ± 1 standard error. Note the scale change for flux rates compared to the Icacos site (Fig. 2).

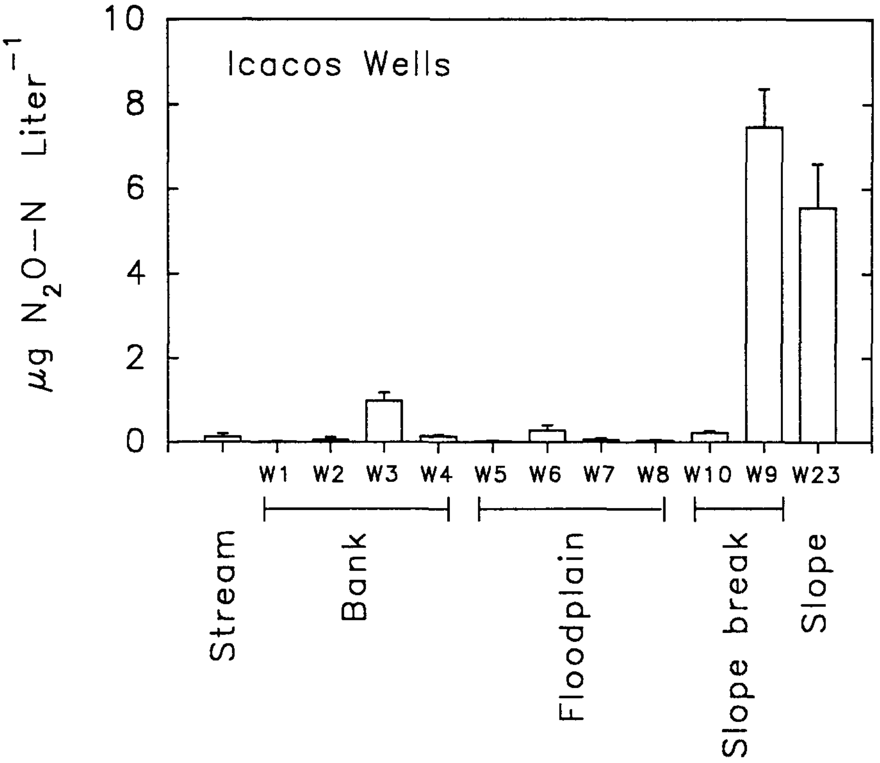

Fig. 4. Dissolved N_2O-N concentrations in shallow groundwater collected at the Rio Icacos site between January and May, 1989. Means are based on four sampling dates and error bars indicate ± 1 standard error.

The pattern of dissolved N_2O concentrations within the Bisley wells was measured only once between January and May. There was little correlation between patterns of N_2O surface emissions and dissolved N_2O in groundwater, which ranged from 0.3 to 2.4 μg N_2O-N L^{-1}.

The amount of N_2O dissolved in samples of shallow groundwater from the Icacos site was directly related to the concentration of NO_3 and inversely related to the concentration of NH_4 in the same samples (Fig. 5). The data in Fig. 5 are a subset of samples collected between January and May 1989, for which we have both N_2O or NO_3 or N_2O and NH_4 data. Based on these data alone, it is not possible to deduce whether the N_2O was produced by nitrification of NH_4 or denitrification of NO_3.

Potential N_2O production rates

The potential for N_2O plus N_2 production (in the presence of both NO_3

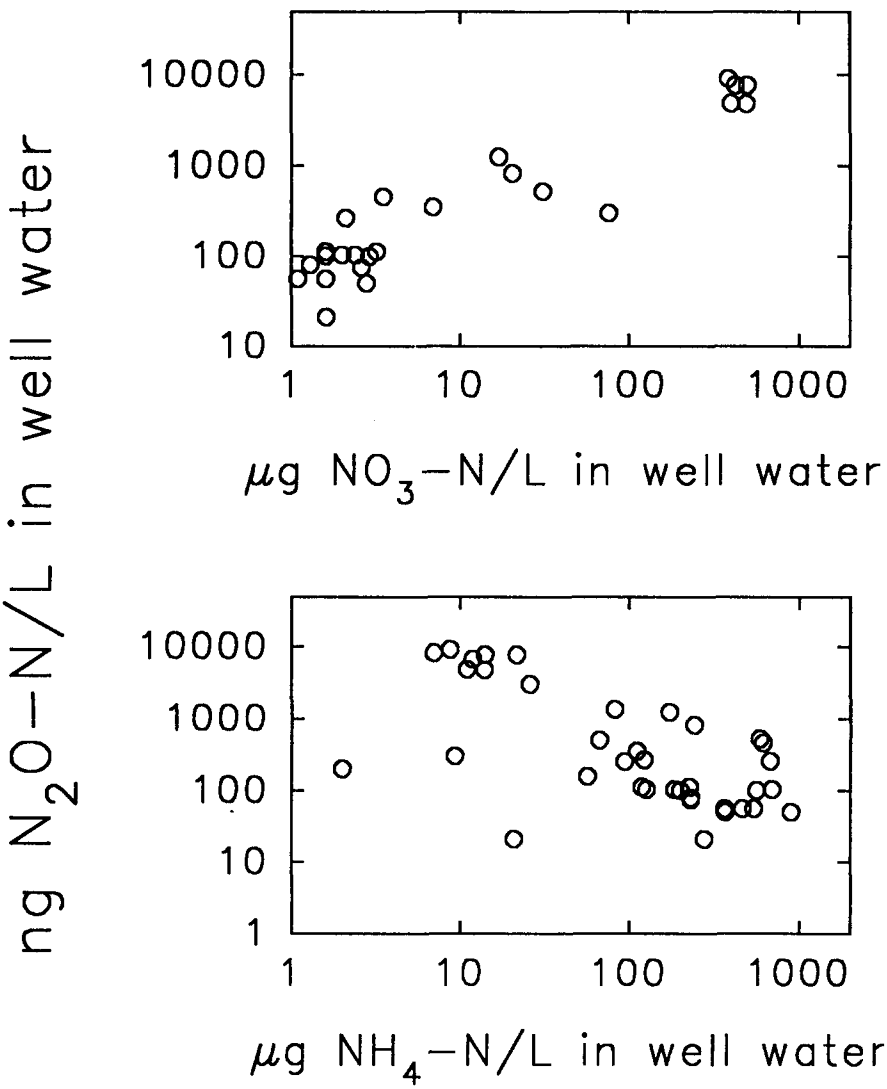

Fig. 5. Dissolved N_2O in samples from shallow groundwater at the Icacos site, as a function of NO_3 (upper panel) and NH_4 (lower panel) concentrations in the same samples. Samples were collected between January and May 1989.

and acetylene) was higher in surface (0—12 cm) soils than in deeper ($\geqslant$ 40 cm) sub-soils (Fig. 6). This was true for both slope and floodplain soils, in both watersheds. Very deep soils ($>$ 180 cm) in the Icacos site, near the well screens, were not tested in this experiment. The potential for N_2O plus N_2 production from surface soils at the Bisley site was similar to that

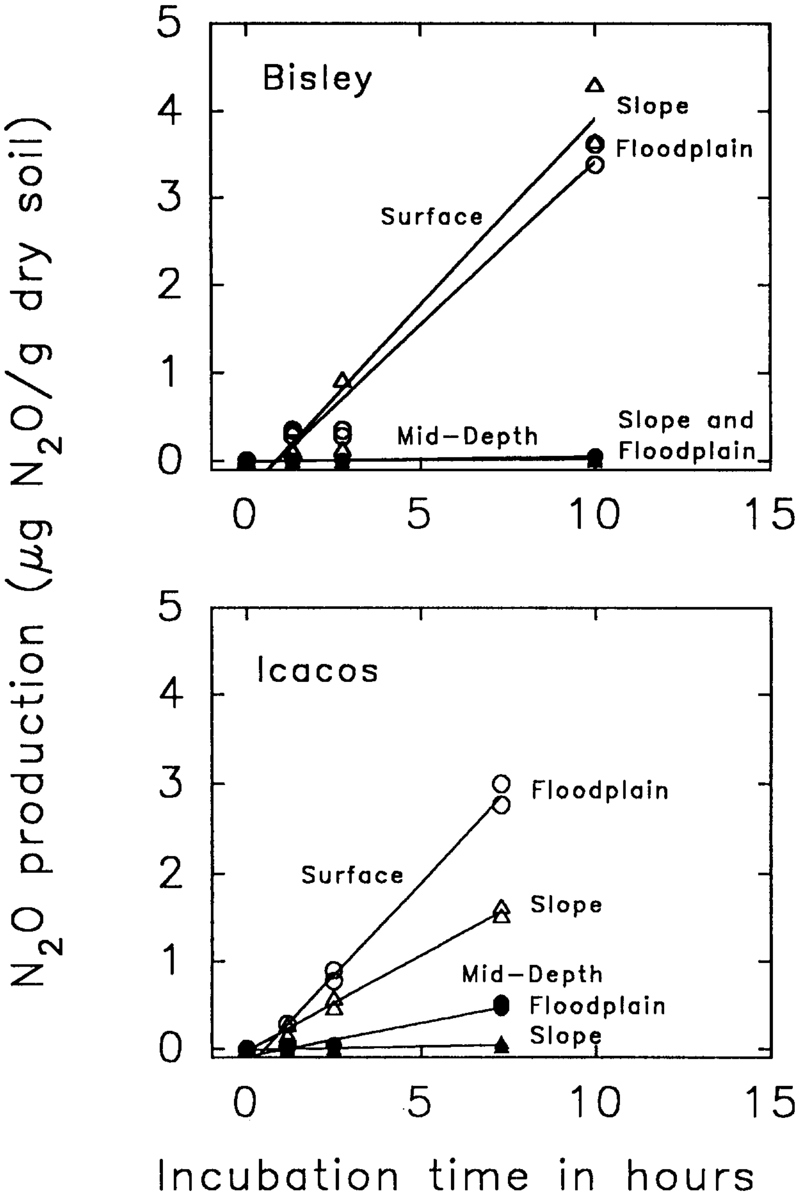

Fig. 6. Potential N_2O-N production in surface (0—10 cm, open symbols) and mid-depth (40—60 cm, filled symbols) soils from slope and floodplain positions within the Icacos and Bisley watersheds. Treatments were as follows: open triangles (Δ) surface slope soils; closed triangles (▲) mid-depth slope soils; open circles (O) surface floodplain soils; and closed circles (●) mid-depth floodplain soils. The NO_3 addition was equivalent to ~50 µg NO_3-N/g dry soil. Each treatment was replicated and all replicate determinations are plotted; however, replicates were often nearly identical and plotted as a single point.

found in surface soils from the Icacos site. However, even after 8—10 h, only small amounts of N_2O were produced from Icacos floodplain subsoils and none was produced from Icacos slope subsoils or from either of the Bisley subsoils.

Production of N_2O from Icacos soils could be stimulated by reduced aeration or by NO_3 additions, depending on the soil type. In these experiments (Fig. 7), we did not add acetylene and we used only mid-depth soils (40—60 cm), below the bulk of the rooting zone. Our intention was to test whether N_2O production in these soils responded quickly to nitrate or aeration, as would be expected if denitrifiers were abundant and active. Very little N_2O production occurred under aerated conditions without added NO_3, in either slope or floodplain sites in the Icacos watershed (Fig. 7). Nitrous oxide was produced immediately when slope soils were incubated under purified N_2, even without added NO_3. These soils appeared to be oxic (bright red-yellow) with little indication of mottling. Presumably, under anaerobic conditions, N_2O were formed from native nitrate by denitrifiers surviving in soil micro-sites. No N_2O was produced from mid-depth, floodplain soils incubated under either aerobic or anaerobic conditions (and without added NO_3, Fig. 7).

When NO_3 was added to aerobic, mid-depth, slope soils from the Icacos watershed, no N_2O was produced (Fig. 7). Because reduced aeration did stimulate N_2O production in these soil (see above), it appears that aeration alone prevents substantial N_2O production by denitrification in oxic, slope soils. Under anaerobic conditions, added NO_3 rapidly stimulated N_2O production, consistent with the previous results. Added nitrate stimulated N_2O production under both aerobic and anaerobic conditions when it was added to mid-depth, floodplain soils, but only after a lag period of about 6—7 h. This observation suggests that the Icacos floodplain environment was so persistently anaerobic that nitrifiers normally do not produce sufficient NO_3 to sustain active denitrifier populations. This interpretation is consistent with both the fluxes of N_2O measured in our chambers (Fig. 2), the concentrations of dissolved N_2O measured in our wells (Fig. 4), and the Icacos well chemistry data (McDowell et al. *this issue*).

The effects of aeration and nitrate additions were also tested on deep ($>$ 150 cm) soils at the Icacos site. Nitrate and aeration had little effect on N_2O production in soils collected from 185 cm at the upslope position; N_2O production was insignificant under all conditions (data not shown). In the floodplain position, however, deep soils (212—225 cm) behaved identically to mid-depth soils (i.e. identical to Fig. 7, lower). This depth is coincident with the depth at which the screens on the shallow, groundwater wells at the Icacos site were placed (see McDowell et al. *this issue*).

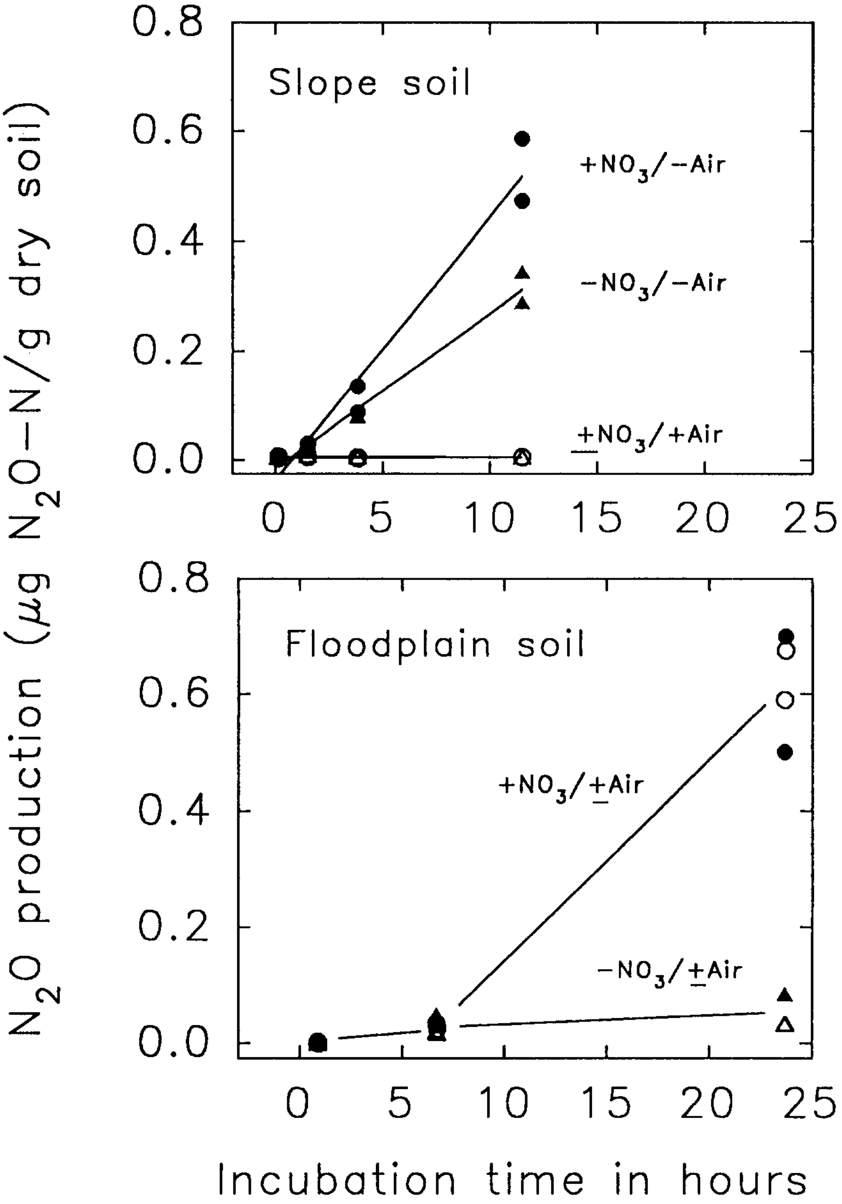

Fig. 7. Effects of aeration and nitrate on N_2O production from mid-depth (40—60 cm) slope and floodplain soils in the Icacos watershed. Treatments were as follows: open triangles (Δ) +air/—NO_3; close triangles (▲) —air/—NO_3; open circles (O) +air/+NO_3; and closed circles (●) —air/+NO_3. The NO_3 addition was equivalent to ~50 μg NO_3-N/g dry soil. Acetylene was not used in these incubations. Similar incubations with soils from 215 cm at both slope positions yielded essentially identical results. See Fig. 6 legend regarding replicates.

When similar amounts of NH_4 were added to mid-depth slope and floodplain soils from Icacos, there was little production of N_2O from either soil under aerobic conditions without added acetylene (Fig. 8). When acetylene was added, under aerobic conditions, N_2O accumulation increased in both soil types. No incubations were done with ammonium under anaerobic conditions.

Discussion

Controls on N_2O production at the Icacos and Bisley sites

Our observations that potential N_2O production (in the presence of acetylene) was closely linked to anaerobic conditions and the availability

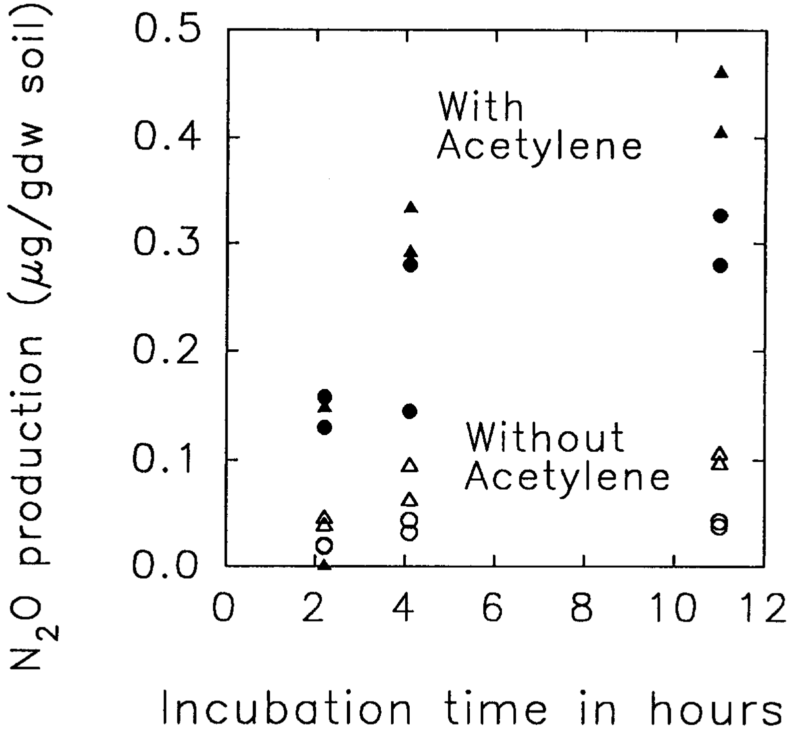

Fig. 8. Effects of ammonium and acetylene on N_2O production from surface slope and floodplain soils in the Icacos watershed. Treatments were asl follows: open triangles (Δ) slope soil/no acetylene; closed triangles (▲) slope soils/+acetylene; open circles (O) floodplain soils/no acetylene; and closed circles (●) floodplain soils/+acetylene. All treatments started with ~50 µg NH_4-N/g dry soil and were incubated with lab air. Acetylene was added as indicated at 10% (10 kPa). See Fig. 6 legend regarding replicates.

of NO_3 (Fig. 7) suggest that N_2O was produced by denitrification. Due to the amount and frequency of rainfall at these sites, soil moisture is typically high and aeration is low, conditions that favor denitrifiers. In fact, the Epiaquic and Aquic soil moisture regimes used to describe these soils indicate soils with reducing conditions due to high moisture conditions.

Alternatively, autotrophic nitrifiers may produce N_2O under microaerobic conditions (Blackmer et al. 1980; Bremner & Blackmer 1981; Lipschultz et al. 1981; Poth & Focht 1985). Certainly, under the conditions of our incubations, most of the N_2O production was due to denitrification of nitrate rather than nitrification of ammonium. When we added only ammonium during an aerobic incubation, acetylene increased rather than decreased N_2O production compared to a similar incubation without acetylene (Fig. 8). If N_2O were produced by nitrification, we should have obtained the opposite result (Bremner & Black 1979; Davidson et al. 1986). This increase in the presence of acetylene suggests that denitrification occurred even under the "aerobic" conditions of this incubation. We can not rule out, however, that under field conditions (as opposed to our incubation conditions) some N_2O is produced by nitrification.

We observed that potential N_2O production was higher in surface than in deep soils at both the Bisley and Icacos sites. This is consistent with similar measurements in other riparian systems (Ambus & Lowrance 1991; Henrich & Haselwandter 1991; Struwe & Kjøller 1991). This decrease with depth is also consistent with an observed decrease in total soil C, total soil N, and N-mineralization potentials in these soils (Fox 1982; McDowell et al. *this issue*, Fig. 1).

Spatial and temporal patterns of N_2O flux

We used dissolved N_2O in groundwater as a surrogate for surface N_2O emissions measured in chambers, to establish that our flux measurements in January and May persisted both spatially and temporally. Nitrous oxide, like carbon dioxide, is readily soluble in water (Weiss 1974; Weiss & Price 1980). Thus, patterns of dissolved N_2O in near-surface groundwater should be correlated with ambient gas-phase concentrations in the open soil interstices (Bowden & Bormann 1986) which may, in turn, be correlated with observed fluxes of N_2O from the soil surface.

While it is not possible to calculate quantitative losses of N_2O from an ecosystem based on dissolved N_2O data alone, persistent, high concentrations of N_2O in soil water do suggest that there may be a sustained potential for surface emissions of N_2O. Because the dissolved N_2O pattern was similar in January and May and at sampling times between, we concluded that the surface N_2O flux pattern was a persistent feature of this landscape.

The N_2O production rates reported here are equal to or greater than results of similar measurements from two other studies done in non-riparian (upland) areas of the LEF. Keller et al. (1986) reported N_2O emission rates equivalent to 42 μg N_2O-N m^{-2} h^{-1} for a Tabonuco forest site, 11 μg N_2O-N m^{-2} h^{-1} for a elfin forest site, and 3 μg N_2O-N m^{-2} h^{-1} for a Colorado/sierra palm site. Steudler et al. (1991) report values of about 2 to 15 μg N_2O-N m^{-2} h^{-1} for undisturbed (pre-Hurricane Hugo) sites in upland sites of the Bisley watershed.

Although the potential for N_2O production appeared to be quite high in surface soils from Bisley, this potential was not expressed in a clear pattern of surface N_2O emissions correlated with topography, as at the Icacos site. This difference may be due to geomorphological differences between the two watersheds, which promote different dominant subsurface flow paths and, as a consequence, different redox conditions and substrate NO_3 concentrations in shallow groundwater (McDowell et al. *this issue*).

Matson & Vitousek (1987) showed that N_2O production and soil N-mineralization in a number of tropical soils are directly related. Similarly, we found that in both watersheds, potential N_2O production was directly correlated with the depth distribution of soil potential N-mineralization, soil %C, and soil %N. Both of these results are a logical expectation where local mineralization is the dominant source of mineral N for nitrification and denitrification. However, in portions of the landscape where large amounts of NH_4 or NO_3 may be imported, as in riparian areas, actual N_2O production rates may be higher than expected; i.e. sites of mineral N production and reduction may be separated in space and time. This probably explains the unusually high N_2O emission rates observed at topographic (and redox) breaks within the Icacos watershed.

Hydrologic versus gaseous export of N

Riparian zones and the redox transition zones within them, typically account for only a small portion of the total area within most watersheds. Therefore, these areas may have a disproportionately large influence on both volatile and hydrologic export of N from watersheds. When the landscape can be stratified into zones of high and low processing activity (e.g. N_2O production in riparian zones), it is misleading to state annual estimates of N_2O-N loss on a per hectare basis, without also stating the portion of the watershed area to which this flux applies (Schimel et al. 1986; Cooper 1990; Matson et al. 1990). However, when the zones of high activity are narrow and the processing activity is inherently variable, it can be difficult to quantify the watershed-scale (ha) effect based on chamber-scale ($< m^2$) measurements.

For example, in the Icacos watershed the highest average N_2O fluxes we observed were about 100 to 300 μg N_2O-N m^{-2} h^{-1}. If such rates persisted over an entire year, as they might at this tropical site, the annual N_2O loss rate would be 8.7 to 26.3 kg N ha^{-1}. These rates would be among the highest reported for any undisturbed temperate or tropical system (Bowden 1986; Matson & Vitousek 1990). However, if the high rates at Icacos were characteristic of only 10% of the watershed and the other 90% supported little or no N_2O flux, then the N_2O flux rate would be 10 times lower on a watershed basis.

Nevertheless, even these lower emission rates are important. McDowell and Asbury (*in review*) measured nitrate, ammonium, particulate N (PN) and dissolved organic N (DON) export from three watersheds in this same forest. They reported the following hydrologic export rates (kg N ha^{-1} yr $^{-1}$): nitrate, 0.9 to 2.8; ammonium, 0.2 to 0.8; PN, 0.3 to 2.2; and DON, 2.3 to 5.2. Thus, an annual export of 0.9 to 2.6 kg N_2O-N ha^{-1} could be at least as large as the hydrologic export of inorganic N and might be similar to either the PN or DON export.

These results are similar to other reports which compare the relative importance of hydrologic and gaseous N exports from ecosystems. Robertson et al. (1987) reported that gaseous N loss from their undisturbed loblolly pine site was 0.4—0.7 kg N ha^{-1} yr^{-1} while literature estimates of hydrologic N export might be 0.5 to 1.5 kg N ha^{-1} yr^{-1}. They suggested that disturbance increases both the gaseous and hydrologic export rates of N, but to similar levels (3—6 and 2—20 kg N ha^{-1} yr^{-1}, respectively). In agricultural systems, where surface and subsurface runoff may contain high concentrations of nitrate from manure and fertilizers, both hydrologic and gaseous exports of N may also be high. Lowrance et al. (1984b), for example, reported 13 kg N ha^{-1} yr^{-1} exported in stream water draining an agricultural area in the Georgia piedmont area, versus 31.5 kg N ha^{-1} yr^{-1} lost by denitrification. Using a mass balance approach, Peterjohn and Correll (1984) suggested that as much as 63 kg N ha^{-1} yr^{-1} may be denitrified in riparian forests next to agricultural fields in the Chesapeake Bay area, while only 9.3 kg N ha^{-1} yr^{-1} may be lost in stream discharge.

Our data suggest that gaseous losses of N from riparian zones in this tropical rain forest are as important as hydrologic losses of ionic N. Furthermore, if denitrification is the dominant mechanism for N_2O loss and the molar ratio of N_2O production by denitrification is low, then total gaseous N loss (by N_2) may be greater than we have estimated. Although riparian areas represent only a small fraction of the total area within these watersheds, our data show that their impacts on hydrologic export can be large. Furthermore, the sites we chose to study are characteristic of 98%

of the Luquillo Experimental Forest. Consequently, the impacts of riparian processing are likely to be large on a regional scale as well. Additional information about the fine-scale, spatial extent of the geomorphological characteristics that control N_2O production at these sites will be necessary to refine regional-scale estimates further.

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