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Riparian nitrogen dynamics in two geomorphologically distinct tropical rain forest watersheds: subsurface solute patterns

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Abstract. Nitrate, ammonium, dissolved organic N, and dissolved oxygen were measured in stream water and shallow groundwater in the riparian zones of two tropical watersheds with different soils and geomorphology. At both sites, concentrations of dissolved inorganic N (DIN; NH_4^+- and NO_3^--N) were low in stream water (< 110 ug/L). Markedly different patterns in DIN were observed in groundwater collected at the two sites. At the first site (Icacos watershed), DIN in upslope groundwater was dominated by NO_3^--N (550 ug/L) and oxygen concentrations were high (5.2 mg/L). As groundwater moved through the floodplain and to the stream, DIN shifted to dominance by NH_4^+-N (200—700 ug/L) and groundwater was often anoxic. At the second site (Bisley watershed), average concentrations of total dissolved nitrogen were considerably lower (300 ug/L) than at Icacos (600 ug/L), and the dominant form of nitrogen was DON rather than inorganic N. Concentrations of NH_4^+ and NO_3^- were similar throughout the riparian zone at Bisley, but concentrations of DON declined from upslope wells to stream water.

Differences in speciation and concentration of nitrogen in groundwater collected at the two sites appear to be controlled by differences in redox conditions and accessibility of dissolved N to plant roots, which are themselves the result of geomorphological differences between the two watersheds. At the Icacos site, a deep layer of coarse sand conducts subsurface water to the stream below the rooting zone of riparian vegetation and through zones of strong horizontal redox zonation. At the Bisley site, infiltration is impeded by dense clays and saturated flow passes through the variably oxidized rooting zone. At both sites, hydrologic export of nitrogen is controlled by intense biotic activity in the riparian zone. However, geomorphology appears to strongly modify the importance of specific biotic components.

Introduction

Work by Hynes (1983), Lowrance et al. (1984), Peterjohn & Correll (1984) and Grimm & Fisher (1984) demonstrates the potential importance of riparian and hyporheic zones in regulating terrestrial N fluxes to streams. More recently, several researchers have examined patterns of ammonium and nitrate in groundwater beneath and adjacent to streams and rivers (e.g. Stanford & Ward 1988; Triska et al. 1989; Ford & Naiman 1989; Cooper 1990; Duff & Triska 1990; Hill 1990; Triska et al. 1990; Valett et al. 1990; Hendricks & White 1991; Pringle & Triska 1991). Strong gradients in NO_3^--N concentration are often seen across the riparian zone, with nitrate loss as high as 95% for groundwater passing through organic mucks in an agricultural pasture (Cooper 1990). Similar losses are observed in other agricultural (Peterjohn & Correll 1984; Jacobs & Gilliam 1985) and forest soils (Davidson & Swank 1986; Hill 1990). Both denitrification by riparian microorganisms and plant uptake can reduce nitrate concentrations in the riparian zone (e.g. Lowrance et al. 1983). The magnitude of each process at a particular site has important implications for ecosystem nitrogen budgets, because denitrification represents a net loss of N from the terrestrial ecosystem to the atmosphere (in the form of N_2 or N_2O), while plant uptake conserves nitrogen.

Spatial patterns of ammonium and DON in the riparian zone are not as well documented as those of nitrate. Ammonium tends to show no strong spatial patterns across the riparian zone (Triska et al. 1989; Hill 1990), and concentrations in streamside groundwater generally do not exceed 100 ug/L. Very little is known about patterns of DON concentrations in riparian groundwater. In alder and old-growth redwood forests adjacent to Little Lost Man Creek, California, Triska et al. (1990) observed that concentrations of DON in groundwater were similar to those in adjacent stream water (50—100 ug/L), and showed no distinct spatial patterns.

Few studies have documented the effecs of geomorphology on nitrogen cycling in the riparian zone, although geomorphology is likely to be an important factor that regulates rates of production and loss of ammonium and nitrate in groundwater (Dahm et al. 1987). In this paper, we report patterns in NO_3^-, NH_4^+, dissolved organic nitrogen (DON), and dissolved oxygen (DO) in groundwater sampled across the riparian zone of two tropical rain forest catchments with different soils and geomorphology. We also examine the relationship of these patterns to differences in soil texture, hydrologic flow paths, and infiltration rates at the two sites.

Methods and materials

Site description

Luquillo Experimental Forest
Study sites were located in the Luquillo Experimental Forest, Puerto Rico (Fig. 1). Brown et al. (1983) provide a summary of research in the Luquillo Experimental Forest and describe the soils, vegetation, and climate of the area in detail. Scatena (1989) provides a detailed description of the Bisley watersheds of the Experimental Forest. Numerous ecological research projects have been conducted in the Forest, and an NSF-funded Long Term Ecological Research (LTER) site was established in the Luquillo Experimental Forest in 1988.

The Luquillo Experimental Forest is classified as subtropical moist, wet, lower montane wet, lower montane rain, and rain forest in the Holdridge Life Zone system (Ewel & Whitmore 1973). Elevation ranges from 200 to 1000 m. Plant communities vary with elevation; the tabonuco (*Dacroydes excelsa*) forest type dominates at elevations between 300 and 600 m and the colorado (*Cyrilla racemiflora*) forest type at elevations between 600 and 900 m (Wadsworth & Bonnet 1951). Palms (*Prestoea montana*) are common on steep slopes and in riparian zones. Vegetation

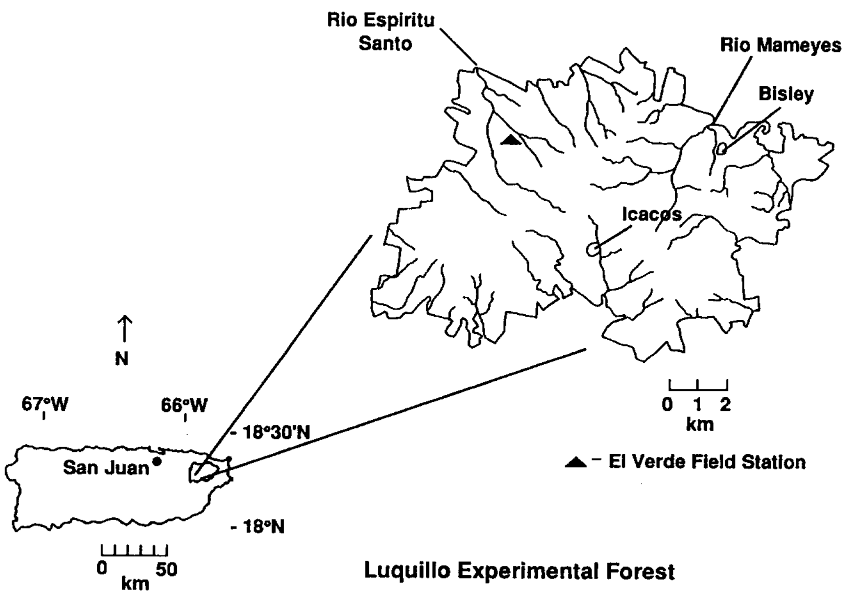


Fig. 1. Map of Puerto Rico showing locations of the study sites in the Luquillo Experimental Forest.

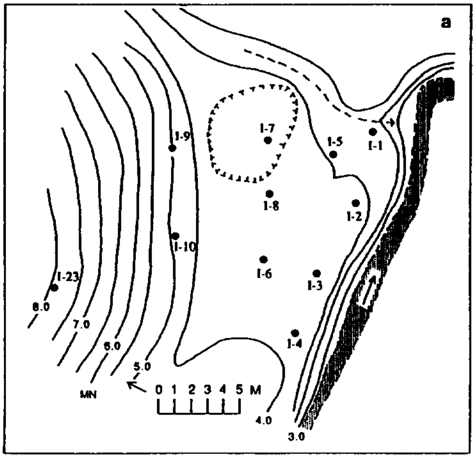
is shallow-rooted, and most roots (by number) are found within the uppermost 20 cm of the soil profile (Odum 1970; Frangi & Lugo 1985). Precipitation ranges from 250 to more than 450 cm/yr within the Experimental Forest and increases with elevation (Brown et al. 1983). Soils in the region are generally acidic clays (Ultisols) with low nutrient contents (Brown et al. 1983). Lower elevations in the tabonuco forest type were used for cultivation of coffee prior to the 1930's, but since that time, anthropogenic impacts on the Forest have been minimal.

Well fields

Study sites were established during August 1988 in the riparian zones of two watersheds in the Luquillo Experimental Forest: Icacos, and Bisley (site of the LTER project in Puerto Rico; Fig. 1). By riparian zone, we mean the ecotone between upslope forests and the open stream channel. We also refer to more specific geomorphological features (e.g. floodplain, stream bank) within each riparian zone as appropriate for the individual sites. The Icacos site is on a small floodplain of a tributary of the Rio Icacos (Fig. 2) at an elevation of 620 m above MSL; watershed area of the tributary adjacent to the well field is 12.4 ha. The Bisley site (elevation 240 m above MSL) is a variable source area (Fig. 2) draining a small catchment (< 0.5 ha) downstream of the primary LTER study watersheds; its likely origin is a small landslide (F. Scatena, personal communication). Watershed area of the stream draining the well field at the point of sampling is approximately 50 ha. Stream channel substrate is sand with occasional boulders at the Icacos site, and clay, cobbles and boulders at the Bisley site. Rainfall averages 480 cm at Icacos (Bogart et al. 1964; Curtis et al. 1986) and averages 350—500 cm at Bisley (F. Scatena, personal communication). Bedrock of quartz diorite underliees the Rio Icacos drainage basin; andesitic to basaltic volcanic sandstone, mudstone, and breccia underlie the Bisley site and the rest of the Luquillo Forest (Seiders 1971). These mid- to late-Cretaceous formations are common in the Caribbean and much of the neotropics.

Vegetation in each site was tagged and identified to species as part of the wellfield installation. At the Icacos site, palms (*Prestoea montana*) were dominant in the floodplain, and upslope vegetation was dominated by several large *Cyrilla racemiflora.* At the Bisley site, vegetation was dominated by *Prestoea montana, Swietinia macrophylla* and *Guarea guidonia* in the well field, with tabonuco (*Dacroydes excelsa*) common on ridges.

At the Icacos site, soils are classified as Utuado clays (Inceptisol), while at the Bisley site, soils are classified as Los Guineos clays (Ultisol; Boccheciamp 1977). Chemistry of the Los Guineos series and a soil



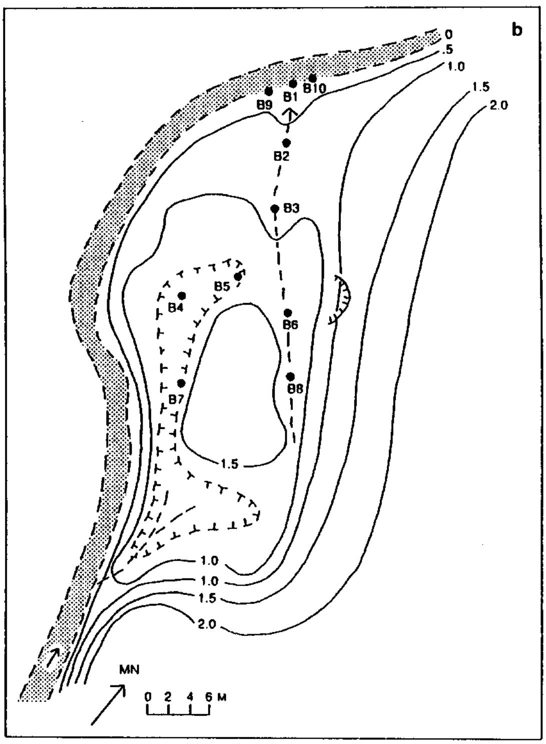


Fig. 2. Surface topography of the Icacos (a) and Bisley (b) well fields. Areas with frequent standing water are surrounded by hash marks. Dashed lines indicate intermittent drainage; shaded area is perennial stream channel. Elevations expressed relative to an arbitrarily chosen datum of approximately 620 m (Icacos) and 240 m (Bisley) above MSL.

similar to the Utuado clay (Picacho series) is described in detail by Fox (1982). Both C and N decrease rapidly with depth in both soils, and pH of soil-water slurries is 4.7—4.8.

Ten or eleven wells were installed at each site by hand augering with a 3.7 cm (1.5 in) bucket auger. At the Icacos site, wells were installed at the stream bank, in the floodplain, and up the adjacent ridge (Fig. 2a). At the Bisley site, wells were located at the stream bank and upslope into a variable source area (Fig. 2b). Depth of the wells was 180 and 210 cm in the Icacos watershed and 70 to 100 cm below the soil surface in the Bisley watershed. The well casings were 5.1 cm (2 in) diameter PVC with 61 cm (2 feet) of 0.25 mm (0.01 in) slotted screen and vented caps. Each screen was wrapped in a polyethylene geotextile fabric filter (Mirafi) to minimize clogging of the screens and turbidity in the samples. It was unnecessary to seal the wells due to the heavy clay texture of the surface soils at both sites. Deeper wells are impractical at the Bisley site because of numerous stones and dry, compact soil below about 40 cm.

Sampling regime

Wells were bailed 1 day (Icacos) or 2—3 days (Bisley) before sample collections. The longer recovery period was needed in Bisley to obtain sufficient water to sample. Prior to bailing, well elevations and dissolved oxygen concentrations were measured. Dissolved oxygen (DO) was measured in each well using a YSI Model 58 meter and a YSI probe and stirrer; readings were taken at the bottom of the well casing to minimize contamination due to atmospheric diffusion. At the Icacos site, tests showed differences in DO concentrations (average of 0.38 mg/L for initial values less than 1 mg/L; 0.95 mg/L for concentrations > 1 mg/L) between lower and upper depths in the wells, indicating either atmospheric contamination or vertical stratification of DO within the water table. Therefore, DO concentrations were probably maximum estimates, and may have been lower in situ. Wells in the Bisley watershed had too little standing water in the casing for similar comparisons. Due to the shallow water column, they were more likely to have been influenced by atmospheric oxygen.

Following the recovery period (1 day for Icacos or 3 days for Bisley) water samples were obtained from the bottom of each well using a portable peristaltic pump or Teflon bailer. Samples were pressure filtered for NH_4^+, because initial tests showed that during vacuum filtration there was a potential for loss of volatile NH_3 from some samples with high NH_4^+ concentration and pH 6—7. Vacuum filtration generally was used for all other analyses. An aliquot was acidified for NH_4^+ analysis; NO_3^- and total dissolved nitrogen were measured on an untreated aliquot. Data are reported for August 1988—1 September 1989, except for the Icacos wellfield. Hurricane Hugo passed over the Luquillo Experimental Forest on September 18—19, 1989, with major effects on vegetation and ecosystem-level processes (summarized by Lodge & McDowell 1991). Both the Bisley and Icacos watersheds suffered significant damage. The Icacos wellfield, however, was undamaged and data from August 1988 to June 1991 are reported here.

Hydrology

Saturated hydraulic conductivity in the vicinity of each well was determined by the Hvorslev method, in both bail and slug modes. Water levels in the Bisley wells were often below the top of the well screen, which introduces an error in the Hvorslev calculation for data from bail tests. In these cases an auger hole method was used to provide a second estimate of k_{sat} (Boersma 1965). We found that results from the Hvorslev method agreed well with the auger hole method when the Hvorslev calculation was corrected for the effective screen height when the water table fell below the top of the screen.

Infiltration rates of surface soils were determined using double-ring infiltrometers (12 cm diameter inner ring; 10 cm diameter outside ring). Infiltration rate was determined after allowing an initial 1 cm drop in water level in the inner ring (Bouwer 1986).

Analytical methods

Nitrate and ammonium were analyzed using automated Cd-Cu reduction (EPA 1983 method 353.2) and phenol-hypochlorite (EPA 1983 method 350.1), respectively. Dissolved organic N was estimated as the difference between dissolved inorganic N and total dissolved N measured by persulfate digestion of samples in sealed glass ampoules (Solorzano & Sharp 1980) followed by hydrazine reduction (EPA 1983 method 353.1) to measure NO_3^- in the digestate. Beginning in September 1989, single column ion chromatography with UV detection (214 nm) was used to measure nitrate and nitrite (EPA A-1000) using a mobile phase of buffered borate-gluconate (1.2 ml/min) and a Waters IC Pak A anion column. Extensive intercalibration showed excellent agreement between the two methods; detection levels improved by an order of magnitude with the ion chromatographic method. Duplicate analyses, internal standards, and blind analysis of EPA quality assurance samples were used to insure quality control.

Soil C and N content were analyzed on oven-dried (65 °C) samples using a Perkin Elmer 240B elemental analyzer with acetanilide as a standard. Soil pH was measured electrometrically in a 1:10 soil:water slurry in 0.01 N $CaCl_2$. Soil particle size distribution (pipet method; Day 1965) was determined on air-dried samples which were sonicated in Calgon (sodium metaphosphate) solution to disperse aggregates.

Results

Soils and hydrology in the well fields

At the Icacos site, soils showed strong vertical zonation in texture and redox status in the floodplain (Table 1). Oxidized clays at the surface graded to reduced clays and very reduced sands and gravel at depths of 1.8—2.1 m below the surface (Fig. 3a). In upslope sites, surface soils were oxidized (red and yellow) clays, grading to red sand and saprolite at depths greater than 2.5 m (Fig. 3a). In both floodplain and upslope soils, earthworm tubes were commonly observed to depths of 30 cm or more.

At the Bisley site, soils consisted of a mosaic of oxidized and reduced clays, with similar textures in surface and deeper soils (Table 1). An intermittent stratum with high gravel content was observed at 40—50 cm depth (Fig. 3b) at many locations.

Infiltration at the soil surface in non-ponded areas (Fig. 2) was more rapid at the Icacos (2—9 cm/min) than the Bisley site (0.07—1.5 cm/min). Although infiltration rates at the Icacos site were typically greater than at the Bisley site, infiltration rates at both sites exceed typical rainfall intensities (0.8 cm/hr or 0.013 cm/min, Brown et al. 1983). Soil C and N contents at the Icacos site were almost double those at the Bisley site, and declined sharply with depth at both sites (Table 1).

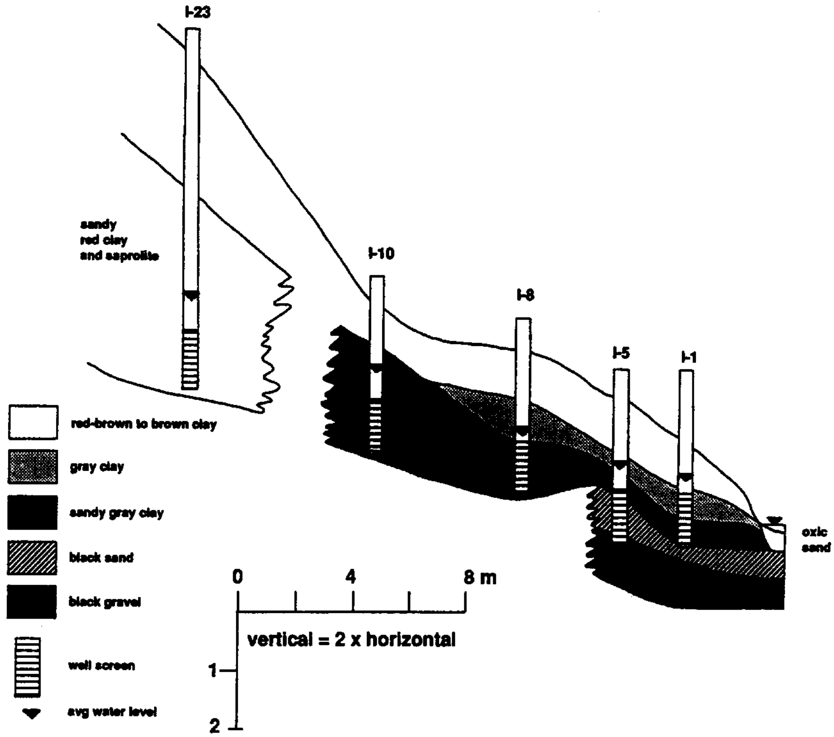
Results from bail tests indicated that saturated hydraulic conductivities near the wells were similar at both sites (about 1×10^{-5} to 1×10^{-4} cm/sec; Fig. 4). The conductivity of stream-side wells also tended to be higher at both sites than the conductivity of upslope wells. Results from slug tests were similar to those obtained with the bail tests at the Icacos site, but were higher by 10 to 100 times for wells at the Bisley site. In a homogeneous and saturated medium, there is no reason to expect that results from the two modes of measurement (bail and slug) should differ.

This difference may be related to differences in the structure of the Bisley soil compared to the Icacos soil. At the Icacos site, the well screens were always below the watertable and were embedded in a relatively homogeneous, conductive soil matrix. At the Bisley site, the watertable

Table 1. Characteristics of soils in the riparian zone in the Icacos and Bisley watersheds of the Luquillo Experimental Forest, Puerto Rico.

	Texture (% sand/silt/clay)		Carbon (%)		Nitrogen (%)		pH		Sulfide	
	Icacos	Bisley	Icacos	Bisley	Icacos	Bisley	Icacos	Bisley	Icacos	Bisley
Surface soils (0—10 cm)	20/43/37 (10/9/3)	11/37/51 (1/4/5)	8.1 (2.0)	4.1 (2.2)	0.36 (0.19)	0.27 (0.06)	4.5 (0.1)	4.6 (0.1)	−	−
Mid-level soils (45—55 cm)	22/30/49 (3/3/4)	8/38/54 (4/7/4)	6.1 (1.7)	0.90 (0.15)	0.24 (0.06)	0.08 (0.03)	4.2 (0.1)	4.4 (0.1)	+/−	−
Mid-level soils (90—100 cm)	36/27/37 (7/1/9)	10/39/51 (1/5/5)	3.2 (2.4)	0.53 (0.26)	0.12 (0.05)	0.04 (0.03)	4.3 (0.1)	4.4 (0.1)	+	−
Deep soils (1.8—2.2 m)	64/21/15 (25/13/13)	NS	2.1 (0.3)	NS	0.09 (0.02)	NS	4.9 (0.1)	NS	++	NS

NS indicates not sampled. C and N expressed as % dry weight; pH is measured in $CaCl_2$. Sulfide characterized as absent (−), present (+) and very strong (++) based on smelling the soil after smearing between two fingers. Mean (standard deviation) shown for three soil cores taken approximately 5 m from the stream channel in both watersheds.



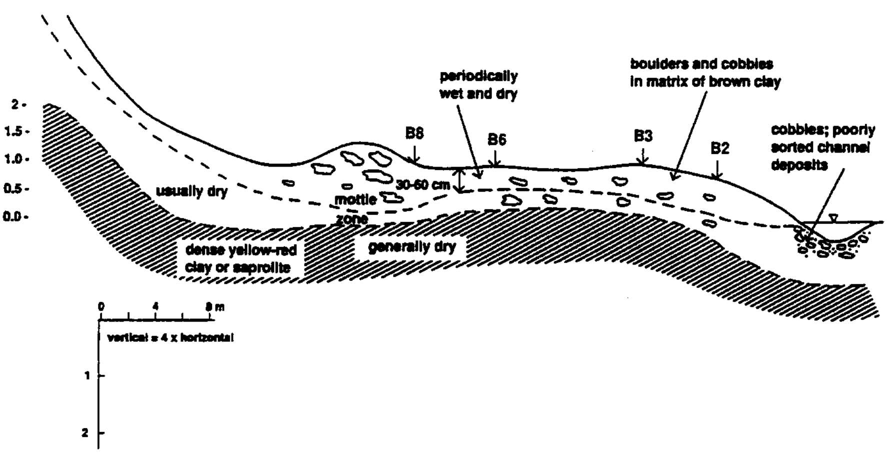
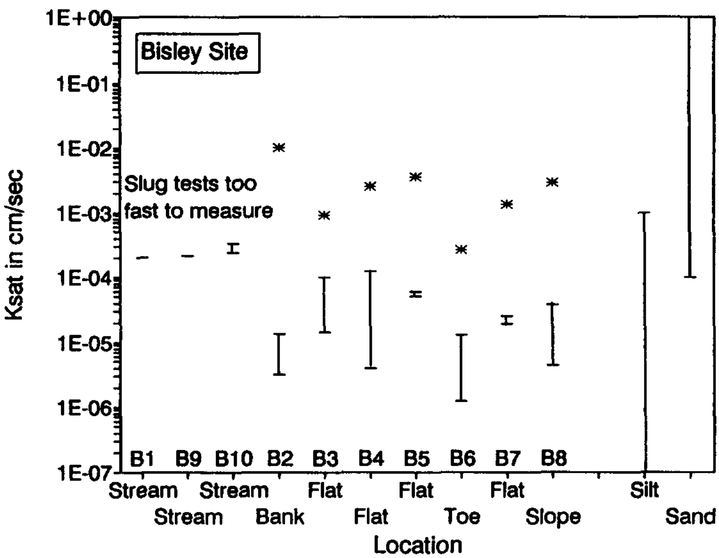


Fig. 3. Soil profiles in a transect across the Icacos (upper panel) and Bisley (lower panel) well fields, showing well locations and depths. For Icacos, average elevation of the water table is also included. Note differences in vertical exaggeration.



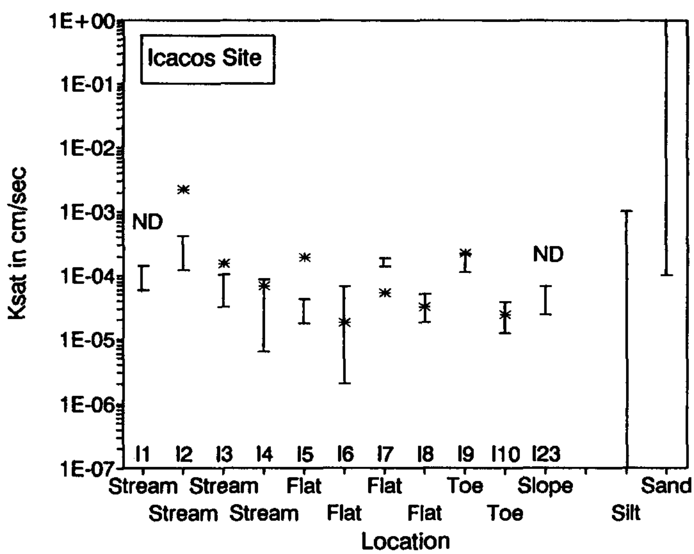


Fig. 4. Saturated hydraulic conductivity (k_{sat}) in the vicinity of individual wells in the two study sites. For reference, commonly reported values for silt and sand are also included (Boersma 1965). Vertical bars are +/− one standard error of the mean determined using bail tests. Asterisks represent values obtained from slug tests.

was often below the top of the well screen at the start of the bail-mode tests. This fact was taken into account in the Hvorslev calculation. However, we believe that the recovery of these wells following bailing was dependent on transport of water by relatively slow matrix flow through the structureless sub-soil near the bottom of the well screen. In contrast, soil nearer the surface (in the vicinity of the upper portion of the well screens) has a subangular, blocky structure that allows relatively rapid water flow through preferential flow paths around the soil blocks. Thus, in the slug mode, water inside the wells rapidly drained via this shallow, preferential flow network. We believe that this shallow flow network is responsible for the high infiltration rates at the Bisley site and promotes rapid, shallow interflow after storm events. Well levels in both watersheds responded very quickly to periods of intense rainfall (e.g. Fig. 5). Although some overland flow was observed in the well fields during such intense events, most incoming precipitation quickly entered subsurface flow paths, with shallower water movement through the Bisley site and deeper water movement at the Icacos site.

Groundwater surfaces sloped sharply toward the stream in the Icacos watershed (Fig. 6a). At the Icacos site, groundwater elevations indicated movement of water diagonally across the wellfield, with an average head differential of 2.1 m over 22 m. At the Bisley site, subsurface water movement likely followed the topographic surface, following the swale from upslope to downslope wells (Fig. 2b), with an average difference in groundwater elevation of 1.7 m over 24 m.

It appears that the sampling sites in both watersheds are in close hydrologic contact with the adjacent streams. Large gradients in water table elevation (Fig. 6) and moderate to high saturated hydraulic conductivities (Fig. 4) result in relatively rapid specific discharges (8.2×10^{-4} to 1.5×10^{-1} m/day at the observed hydraulic gradient). This conclusion is further supported by the rapid response of the well elevations to rainfall (Fig. 5).

Spatial and temporal variability in well chemistry

Large differences were observed in nitrate and ammonium concentrations of groundwater collected at the two sites. At all points in the riparian transect, concentrations of dissolved inorganic N were approximately five-fold greater at the Icacos site than at Bisley (Fig. 7), despite the fact that stream water concentrations at the two sites were similar. At Bisley, most dissolved nitrogen in groundwater was found as DON, while at Icacos, most was found as ammonium. Concentrations of dissolved organic N were comparable in both watersheds (100—300 ug/L; Fig. 7).

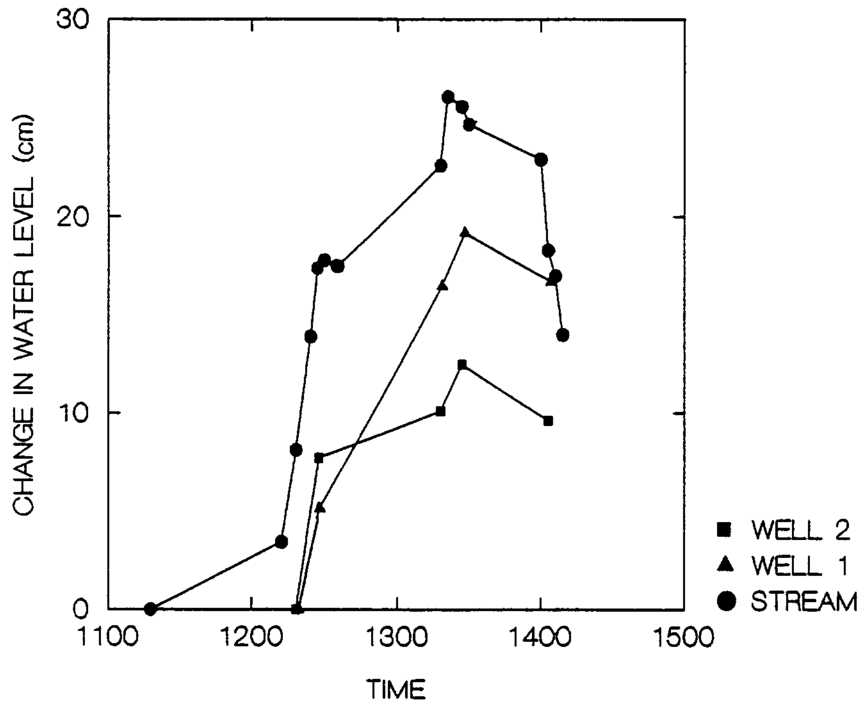


Fig. 5. Changes in elevation of stream and groundwater surface in the Icacos well field in response to a rainstorm on June 2, 1989.

Strong spatial patterns were observed across the riparian zone at the Icacos site for all constituents sampled. In upslope wells, 90—95% of total inorganic N was found as nitrate, and DO concentrations were high (averaging 5 mg/L in well 23). However, within the floodplain, NO_3^- and DO fell to concentrations of 9 ug/L and 1.4 mg/L, respectively. In contrast, NH_4^+ levels in upslope wells were typically very low (less than 30 ug/L) but concentrations increased significantly within the floodplain, to levels which often exceeded 500 ug/L. In the adjacent stream, nitrate concentrations were never as high as those observed in upslope wells, nor were ammonium concentrations ever as high as those observed in floodplain wells, even those 1—2 m from the stream bank (wells 1—4). There was a very consistent inverse relationship between nitrate and ammonium concentrations in samples from the Icacos wells, with very few samples containing both in appreciable quantities (Fig. 8a).

At the Bisley site, the relationship between NH_4^+ and NO_3^- was weak, with frequent co-occurrence of the two ions and generally low concentrations (Fig. 8b) compared to Icacos. At Bisley, there was a consistent decline in TDN and DON across the riprian catena, but no consistent

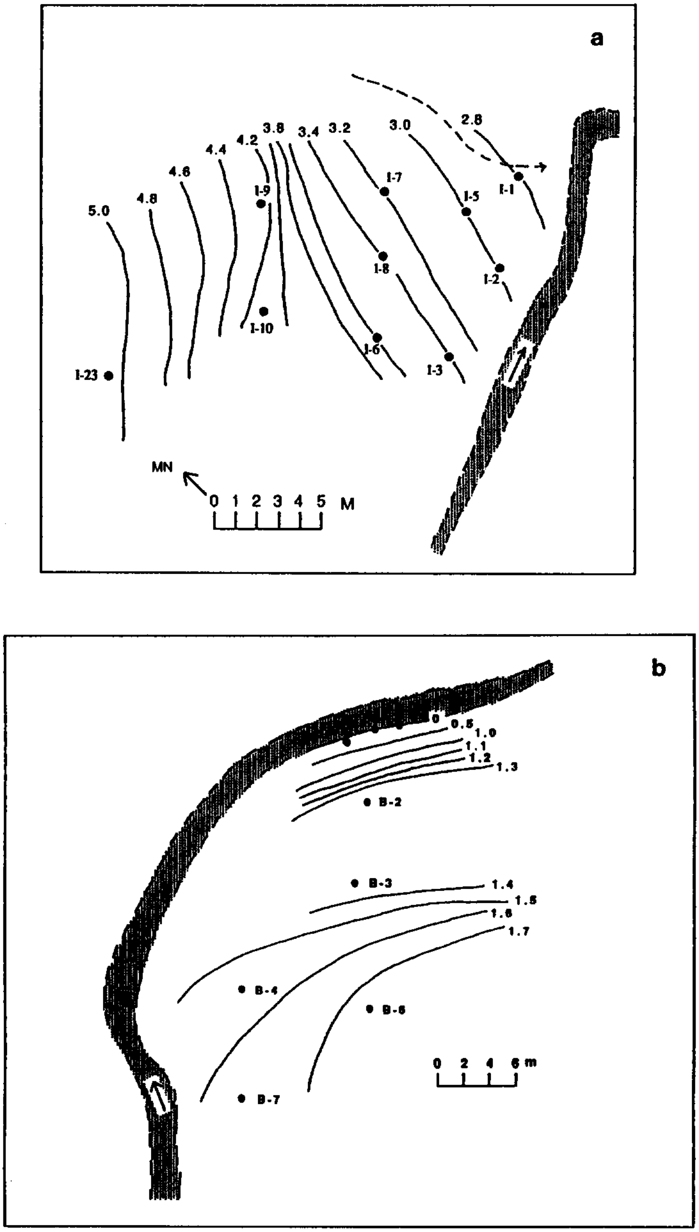


Fig. 6. Topography of the water table in the Icacos (a) and Bisley (b) well fields. Elevations are relative to the same datum used in Fig. 2. For Icacos, well 4 is anomalous (mean elevation 623.0 m) and is not shown. For Bisley, all wells which contained water on 75% or more of the sampling dates are shown.

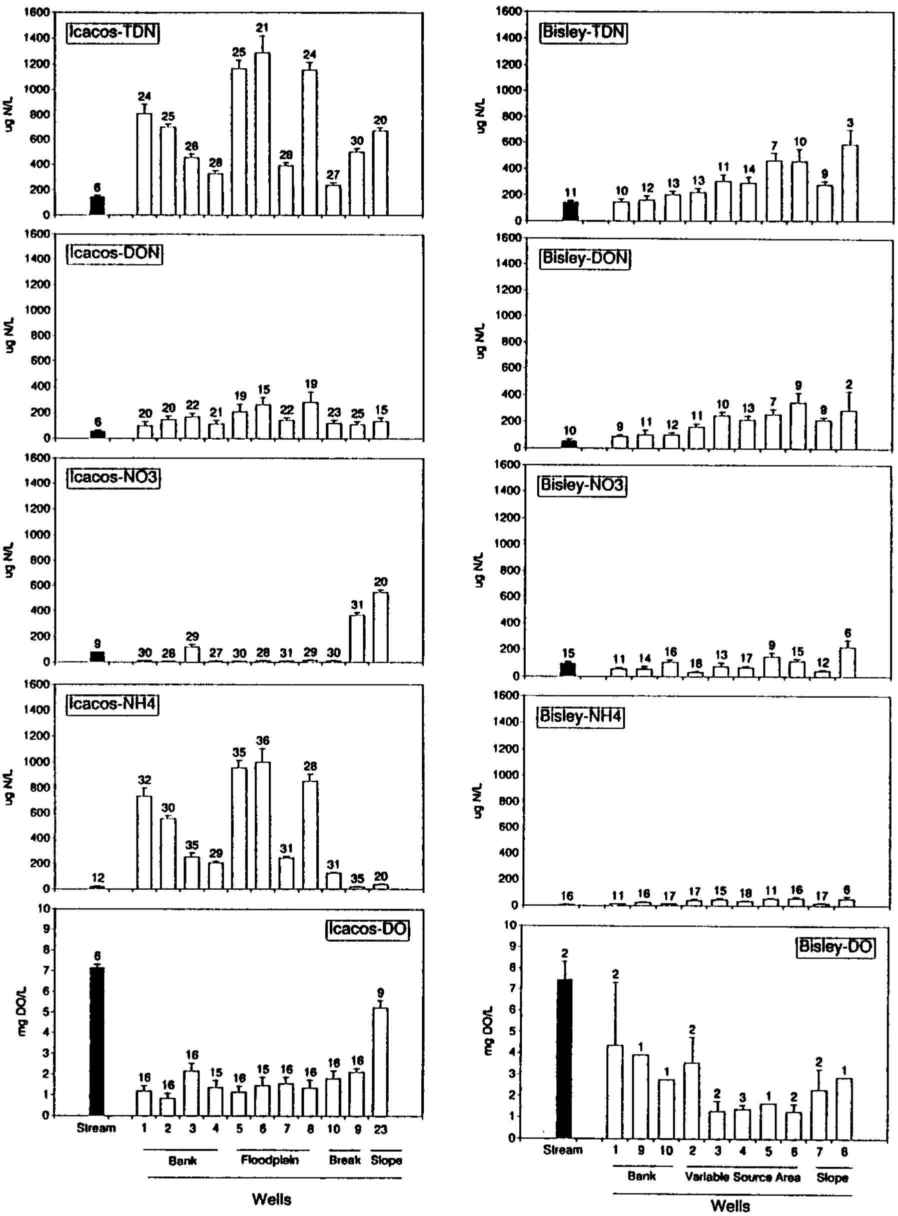


Fig. 7. Spatial variability in groundwater chemistry at the Icacos and Bisley sites. Well locations are shown in Fig. 2. Means are shown; error bars represent one standard error of the mean, and the number of observations is placed above each bar.

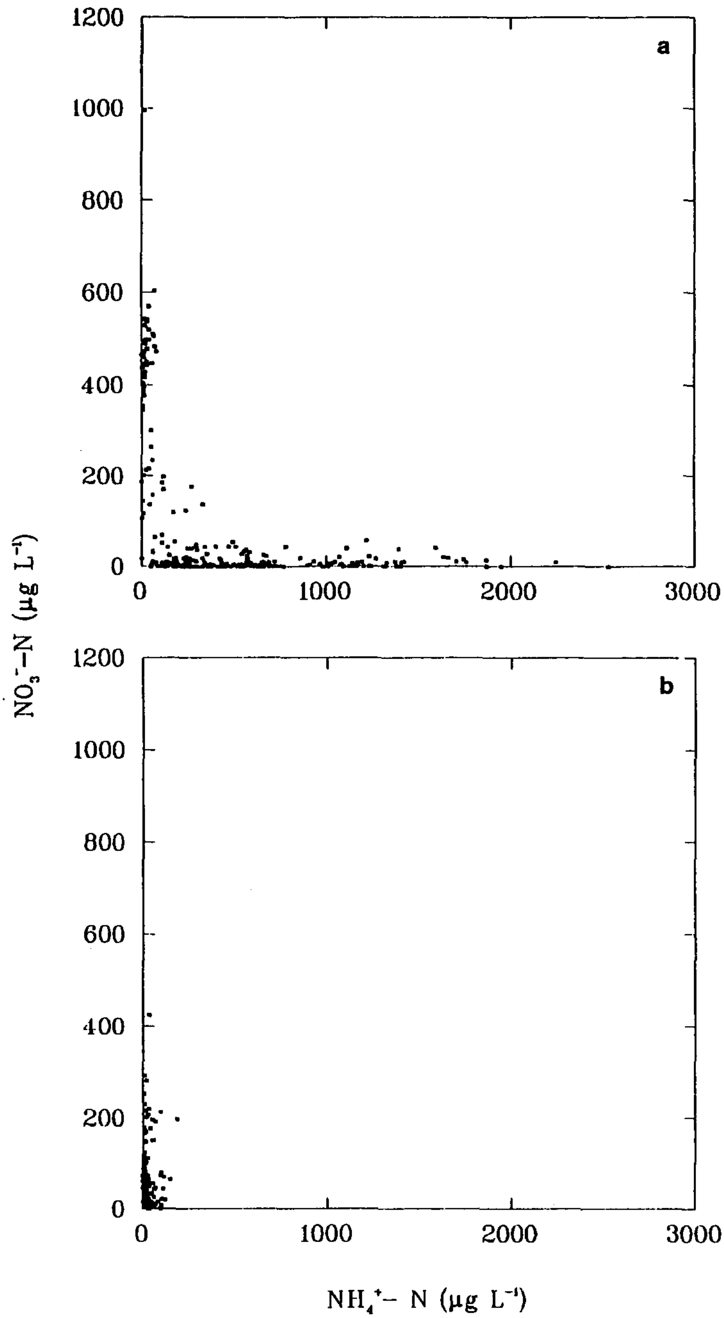


Fig. 8. Relationship between NO_3^- and NH_4^+ concentrations in groundwater collected in the Icacos (a) and Bisley (b) watersheds.

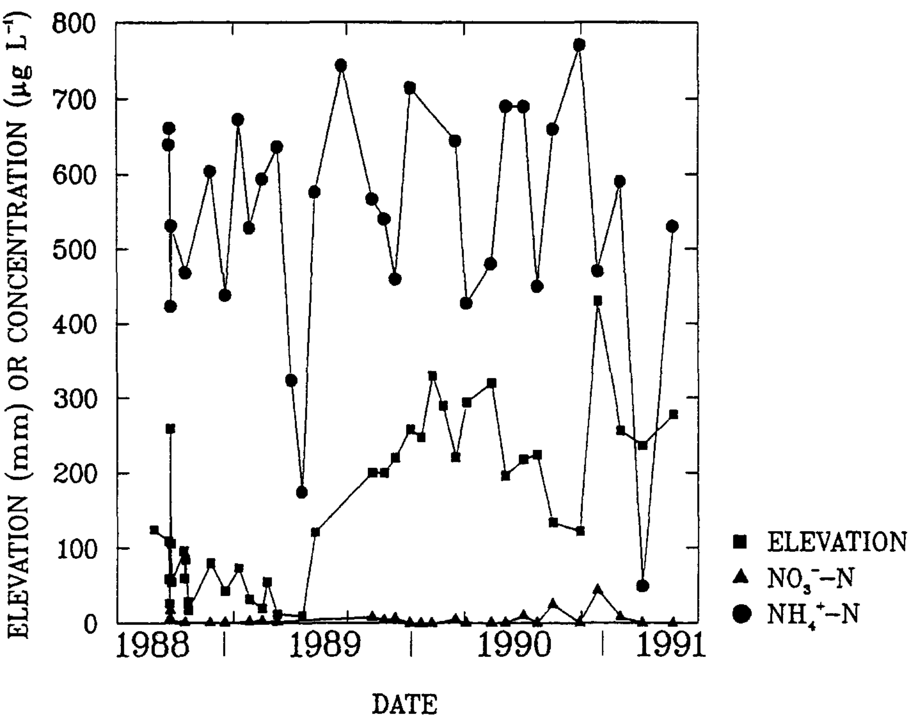


Fig. 9. Variation in elevation (mm above minimum recorded value) and inorganic nitrogen chemistry in well 2 of the Icacos site during the three-year study period.

trends were observed for NH_4^+ or NO_3^- concentrations (Fig. 7b). There was a strong gradient in dissolved oxygen from low levels in the variable source area to higher levels in the stream itself (Fig. 7b), as also observed at the Icacos site (Fig. 7a). However, unlike the Icacos site, there was no gradient in nitrogen species across this interface (Fig. 7b).

Concentrations of dissolved inorganic N showed no consistent seasonal variation or variation with water table elevation at either site (e.g. Fig. 9). Although several individual wells did show statistically significant variation in ammonium and nitrate concentrations as a function of piezometic head at the Icacos site, no consistent pattern emerged. Increases in DON concentrations were observed in several of the Icacos wells in early 1991, but similar patterns were not observed for NO_3^- or NH_4^+.

Discussion

Spatial patterns of N within the riparian zone

The riparian zone links terrestrial and aquatic ecosystems, and thus can alter hydrologic export from a basin (Gregory et al. 1991). Because hydrologic loss of nutrients from terrestrial ecosystems is widely used to measure the impact of disturbance or otherwise characterize nutrient losses, nitrogen transformation within the riparian zone may strongly affect perceptions of watershed-level nutrient dynamics.

We hypothesize that differences in geomorphology and solute flow paths strongly influence N flux and transformation in the riparian zones of the Icacos and Bisley watersheds. At the Icacos site, water quickly infiltrates through the rooting zone and into shallow groundwater, where it moves rapidly to the stream through highly conductive subsurface soils. At the Bisley site, surface infiltration is also rapid, but dense clays appear to retard infiltration to deeper soils. Subsurface flow at the Icacos site follows a deep trajectory past the rooting zone and through a highly reduced, conducting layer, while water at the Bisley site appears to follow a shallow trajectory through the rooting zone.

This difference in geomorphology appears to control both the form and concentration of N in shallow groundwater at the two sites, and suggests the following conceptual model. At the Icacos site, after infiltrating through oxic surface soils, subsurface runoff must flow through distinct oxic (upslope) and reduced (floodplain) zones with spatial scales of centimeters to meters. This subsurface flow occurs below most plant roots. Under these conditions mineralization, nitrification, plant uptake, and denitrification are segregated in space, so that ammonium and nitrate accumulate in distinct zones. In contrast, at the Bisley site, subsurface runoff remains near the surface in a variably oxidized zone in which redox conditions apparently vary over a scale of only fractions of a centimeter. Under these conditions, mineralization, nitrification, plant uptake, and denitrification might coexist so that ammonium and nitrate concentrations are persistently low and variable. This conceptual model is consistent with our hydrologic and geochemical data from the wells, but remains to be rigorously tested.

Spatial patterns of N at the stream-riparian interface

One of the most striking patterns observed in this study was the large decrease in concentrations of dissolved nitrogen between groundwater in the floodplain and adjacent stream water at the Icacos well field (Fig. 7a).

Declines in NH_4^+ concentrations were especially large. Several alternative hypotheses could explain these observations, including 1) our site is unrepresentative of the basin; 2) uptake by riparian vegetation removes NH_4^+, the dominant form of N in the floodplain; 3) in-stream processes remove NH_4^+; or 4) coupled nitrification and denitrification in the near-stream zone result in gaseous losses of N.

The first hypothesis that might explain the rapid loss of NH_4^+ at the Icacos site is that groundwater sampled at our study site was not representative of groundwater entering throughout the catchment. If this were the case, then the low DO, high-NH_4^+ groundwater we sampled would simply have been diluted by a much greater flow of high-DO, low-NH_4^+ stream water. We have observed, however, that large amounts of orange, flocculated iron accumulate throughout the length of the stream channel during low flow conditions. This indicates the presence throughout the stream basin of anoxic groundwater, which is likely to contain elevated NH_4^+ levels such as those observed in the floodplain.

The second hypothesis that might explain NH_4^+ loss at the Icacos site is vegetative uptake by palms and palm seedlings in the narrow strip between streamside wells and the stream channel. A simple mass balance calculation, however, suggests that N accumulation in riparian biomass cannot explain the entire NH_4^+ loss. Net annual biomass increment of palms in floodplain forest is about 2000 g/m^2 (Frangi & Lugo 1985), and riparian palms contain 0.7% N (Scatena et al. in press), for a total N accumulation of 14 g/m^2 in the riparian zone. Average annual runoff from the Icacos basin (Curtis et al. 1986) is 413 cm, or 5.1×10^8 L/yr from the 12.4 ha basin upstream of the well field. At an average change in NH_4^+-N concentration of 400 ug/L (difference between wells 1—4 and stream concentrations), a total loss of 204 kg NH_4^+-N must be accounted for. The area in which the observed N loss occurs is a 1.5-m wide strip at our study site (Fig. 2a). If similar losses of NH_4^+ occur along the entire stream channel above our site (600 m, or about 1800 m^2 of riparian stream bank), the rate of NH_4^+-N loss is equivalent to 113 g/m^2 in the riparian zone. Although these are only crude estimates, the difference between estimated plant uptake (14 g/m^2) and apparent NH_4^+ loss (113 g/m^2) is so large that mechanisms other than plant uptake must be responsible for losses of N from solution in the riparian zone.

The third hypothesis that might explain the large difference in NH_4^+ concentrations in streamside groundwater and open channel flow is that N removal (through microbial immobilization, nitrification-denitrification, or algal uptake) occurs within the open stream channel. Whole-stream enrichments (McDowell et al. in prep.), however, suggest that both NH_4^+ and NO_3^- loss in the open channel are small.

The fourth hypothesis that could explain the large apparent loss of NH_4^+ at the Icacos site is coupled nitrification and denitrification in the stream bank or beneath the channel in the hyporheic zone. This hypothesis requires the coexistence of both oxic and anoxic conditions in microzones (on the scale of millimeters), and implies that sharp gradients in NH_4^+ and NO_3^-, as well as large gaseous efflux of N (as N_2 or N_2O), occur in the stream bank and hyporheic zone. Ongoing work on groundwater chemistry suggests that the stream bank as well as the hyporheic zone may be sites of unusually active nitrogen transformation. The flux of N_2O measured by Bowden et al. (*this issue*) is equivalent to an annual flux of only 32 g/m^2 at the stream bank, far less than the 113 g/m of N which appears to be lost there annually (as calculated above). However, if the molar ratio for N_2O production is low (high proportion of N_2 production), denitrification might quantitatively account for this loss of inorganic nitrogen. We do not yet know what the molar ratio might be and so can not assess the importance of N_2 production. Thus, without further experimentation, none of the four alternate hypotheses outlined above can fully explain the losses of inorganic N we observed in shallow goundwater.

Conclusions

Patterns in nitrogen concentration and speciation in the Bisley watershed are similar to those observed at other forested sites, with moderate declines in some fractions and modest gradients in dissolved oxygen across the riparian zone (e.g. Triska et al. 1989; Hill 1990). In the Icacos basin, in contrast, gradients in dissolved oxygen and N species across the riparian zone are among the largest reported in the literature for undisturbed forested catchments (Triska et al. 1989; Hill 1990; Triska et al. 1990; Pringle & Triska 1991). Even in agricultural catchments, with large anthropogenic inputs of N, changes in NH_4^+ across the riparian zone are not as large as those observed at the Icacos site (Lowrance et al. 1983; Peterjohn & Correll 1984; Schnabel 1986), and NO_3^--N in groundwater is rarely lowered to levels observed in the Icacos floodplain (often less than 1 ug/L).

The different spatial patterns of N we measured in shallow riparian groundwater in the Luquillo Forest coincide with different dominant subsurface flow paths. It is likely that different flow paths dominate due to geomorphological differences within this heterogeneous, tropical landscape.

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