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Groundwater nitrogen dynamics at the terrestrial-lotic interface of a small catchment in the Central Amazon Basin

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Abstract. Processes operating at the terrestrial-lotic interface may significantly alter dissolved nitrogen concentrations in groundwater as a result of shifting redox conditions and microbial communities. We monitored concentrations of total dissolved nitrogen, NO_3^-, NH_4^+, O_2 and Fe^{2+} for 10 months along two transects tracing groundwater flow from an upland (*terra firme*) forest, beneath the riparian forest, and into the stream channel of a small Central Amazonian catchment. Our aim was to examine the role of near-stream processes in regulating groundwater transfers of dissolved nitrogen from terrestrial to lotic ecosystems in the Central Amazon. We found pronounced compositional differences in inorganic nitrogen chemistry between upland, riparian, and stream hydrologic compartments. Nitrate dominated (average 89% of total inorganic nitrogen; TIN) the inorganic nitrogen chemistry of oxygenated upland groundwater but decreased markedly upon crossing the upland-riparian margin. Conversely, NH_4^+ dominated (average 93% of TIN) the inorganic chemistry of apparently anoxic riparian groundwater; NH_4^+ *and* TIN concentrations decreased markedly across the riparian-stream channel margin. In the oxygenated streamwater, NO_3^- again dominated (average 82% of TIN) inorganic nitrogen chemistry. Denitrification followed by continued ammonification is hypothesized to effect the shift in speciation observed at the upland-riparian margin, while a combination of several processes may control the shift in speciation and loss of TIN observed at the riparian-stream margin. Dissolved organic nitrogen concentrations did not vary significantly between upland and riparian groundwater, but decreased across the riparian-stream margin.
Our data suggest that extensive transformation reactions focused at the upland and stream margins of the riparian zone strongly regulate and diminish transfers of inorganic nitrogen from groundwater to streamwater in the catchment. This suggestion questions the veracity of attempts in the literature to link stream nitrogen chemistry with nutrient status in adjacent forests of similar catchments in the Central Amazon. It also complicates efforts to model nitrogen transfers across terrestrial-lotic interfaces in response to deforestation and changing climate.

Introduction

In recent years, increasing attention has focused on ecosystem processes operating at the terrestrial-lotic interface, due in part to its importance as a control point in energy and material fluxes (Naiman & Décamps 1990; Holland et al. 1991). Dissolved inorganic nitrogen species are particularly sensitive to the shifts in redox conditions and microbial communities which commonly occur at the upland and stream margins of riparian forests. Consequently, processes operating in these transition zones may be the principal regulators of groundwater transfers of inorganic nitrogen from terrestrial to lotic ecosystems. Major losses of groundwater NO_3^- reported at the upland-riparian margin have been attributed to denitrification in anaerobic, carbon-rich riparian soils (Pinay & Décamps 1988; Cooper 1990; Bowden et al. 1992; McDowell et al. 1992; Haycock & Burt 1993). Similarly, NH_4^+ losses reported across riparian-stream channel margins have been attributed to a somewhat more complicated and still poorly understood combination of processes in streambed sediments and the hyporheic zone (Ford & Naiman 1989; McDowell et al. 1992). The few studies which have examined dynamics of dissolved organic nitrogen report less severe concentration gradients across terrestrial-lotic interfaces (Triska et al. 1990; McDowell et al. 1992).

Existing data regarding nitrogen dynamics in aquatic ecosystems of the Amazon basin come primarily from the largest reaches of the river system (Richey & Victoria 1993) and adjoining floodplain lakes (Forsberg et al. 1988; Melack & Fisher 1988). A few studies have reported nitrogen exports from small Amazonian catchments (Ribeiro et al. 1978; Salati et al. 1982; Brinkmann 1983; Franken & Leopoldo 1984; Lesack 1993) and nitrogen concentrations in groundwater (dos Santos & Ribeiro 1975; Brinkmann 1985), but no study had yet addressed transformations in nitrogen chemistry across terrestrial-lotic interfaces of the basin. Increasing interest in nutrient cycles of Amazonian forests and the tendency to associate stream chemistry with forest nutrient status provide a considerable impetus to improve our understanding of nitrogen dynamics at Amazon terrestrial-lotic interfaces.

We monitored concentrations of total dissolved nitrogen, NO_3^-, NH_4^+, O_2 and Fe^{2+} for 10 months along two transects tracing groundwater flow from an upland (*terra firme*) forest, beneath the riparian forest, and into the stream channel of a small Central Amazonian catchment. We addressed the question, 'Is groundwater nitrogen chemistry modified upon crossing the terrestrial-lotic interface, and if so, how?'

Site description

The investigation was conducted in the Barro Branco catchment of the Instituto Nacional de Pesquisas da Amazônia's Reserva Ducke experimental forest (2°56′ S, 60°58′ W). The catchment lies within the Central Amazon Trough, a physiographic region characterized by low-relief terrain composed of multiple generations of abandoned alluvial terraces and massive active floodplains (Klammer 1984). The largely undisturbed catchment covers an area of approximately 1.5 km^2 and is drained by one perennial stream (Barro Branco) and several ephemeral streams. Annual rainfall is approximately 200 cm and is concentrated during a rainy season extending from December through May. The geomorphology of the basin is remarkably consistent. A flat riparian zone up to 40 m in width forms a nearly complete border between the stream channel and surrounding hillslopes. Hillslopes rise abruptly from the back of the riparian zone at slopes of 10° to 20°, reaching elevations of 10 m to 20 m above the stream channel; hillslope widths range from 50 m to more than 100 m. At the section studied in detail, the riparian zone is 12 m wide, giving way to a hillslope rising at an approximate slope of 15° to an elevation of 11 m above the stream channel. The width of the hillslope is 50 m.

There have been no comprehensive and detailed descriptions of soils in the catchment. Nortcliff & Thornes (1981) suggest that the hillslope soils are probably plinthic haplorthox in the nomenclature of Soil Taxonomy, but, more generally, they are yellow- and red-stained, well-drained oxisols characteristic of vast areas of the Amazon basin (Sombroek 1984). Hillslope soils are capped by a thick (~6 cm) root mat and are densely rooted to a depth of approximately 10 cm. Soils of the riparian zone are more difficult to classify. They have been previously labeled as both sandy oxisols (Brinkmann & dos Santos 1973) and spodosols (Livingston et al. 1988), but our observations correspond better with the sandy oxisol classification. They are uniformly gray, with a thinner root mat (~3 cm) than hillslope soils and a greater penetration (to ~20 cm) of densely packed roots. Riparian vegetation is compositionally and structurally distinct from that of the hillslope, consisting of a shorter canopy (30 m maximum) and a greater abundance of palms. Only 13 tree species are known to be common to both forest types (Guillaument 1987).

The Barro Branco stream follows a meandering course through the flat-bottomed valley. It averages roughly 1 m in width, is generally less than 50 cm deep, is sandy-bottomed, and is completely covered by the canopy of the riparian forest. The surficial hydrology and water budget of the Barro Branco catchment was investigated by Franken & Leopoldo (1984) and Leopoldo et al. (1984). Over the period of their study (1976–77 and 1981–82), mean monthly discharges ranged from 5 to 20 L/s. Discharge fell as low as 0.1 L/s during dry periods and reached upper extremes of 500 L/s during large storms (Leopoldo et al. 1984). Nortcliff & Thornes (1978, 1981, 1984) and Nortcliff et al. (1979) examined subsurface hydrologic flowpaths linking the hillslope, riparian zone, and stream channel. Their findings indicate that flow within the unsaturated zone of the hillslope is dominantly vertical, with little lateral flow even during storms. Thus, the principal linkage between hillslope and riparian zone is groundwater flow along the potentiometric gradient. Under baseflow conditions, groundwater flow continues across the low gradient of the riparian zone to produce runoff in the stream channel. No information

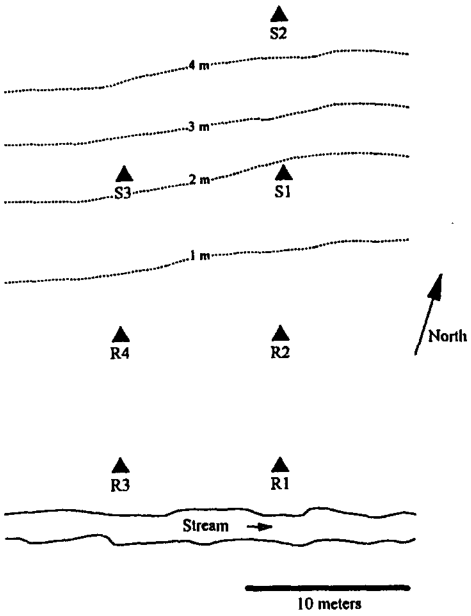

Fig. 1. Site map showing stream, sampling network, and approximate elevation contours.

is currently available regarding the dimensions or hydrodynamics of the stream's hyporheic zone.

Methods

Two parallel transects spaced 10 m apart and oriented perpendicular to the stream channel were instrumented (Fig. 1). A total of seven piezometers were installed to varying depths below the water table; three piezometers sampled upland groundwater and four sampled riparian groundwater (Table 1). Each consisted of a 5 cm I.D. PVC tube sealed at the bottom and slotted over the lower 50 cm. Piezometers were developed by removing 10 casing volumes of water and were then allowed to equilibrate for 3 weeks with the surrounding groundwater. The relative elevation of each piezometer was measured using a hand-held level and staff. Over the 10 months of the study, water samples were collected at 1 to 2 week intervals using a PVC bailer after evacuating three casing volumes of water or after bailing the piezometer dry. The water level in each piezometer was measured prior to bailing using a metal tape measure. Baseflow stream samples were collected as grab samples from the center of the stream just below the water surface.

Table 1. Characteristics of sampling network. Piezometer I.D.'s correspond to those in Fig. 1.

Piezometer I.D.	Zone	Depth (cm)	Distance from stream (m)	Mean[1] water table depth (cm)	Mean[1] water table elev. (cm)	Ground elevation (cm)
R1	riparian	149	2	35	−35*	0*
R2	riparian	149	10	38	−13*	25*
R3	riparian	198	2	28	−28†	0†
R4	riparian	200	10	53	−12†	41†
S1	upland	496	20	201	−15*	186*
S2	upland	594	30	405	+41*	446*
S3	upland	450	20	223	0†	223†

[1] mean of all 18 sampling times
* elevation relative to R1 ground surface
† elevation relative to R3 ground surface

Upon collection, groundwater and stream samples were transported to laboratories of the Instituto Nacional de Pesquisas da Amazônia, where they were filtered (within 2 hrs) through precombusted Gelman A/E glass fiber filters and analyzed colorimetrically (within 6 hrs) for NO_3^-, NH_4^+, and Fe^{2+} according to the methods of Strickland & Parsons (1972), Koroleff (1969), and Stookey (1970), respectively. Separate aliquots of samples collected between May and August, 1993, were sent to the University of Washington for total dissolved nitrogen (TDN) analyses according to the method of Valderrama (1981). Dissolved organic nitrogen (DON) was calculated as the difference between TDN and the sum of NO_3^- and NH_4^+. On several occasions, dissolved oxygen was measured, following purging, in the base of each piezometer using a YSI oxygen meter. This technique allowed for some aeration of the groundwater and thus provides a maximum value of dissolved oxygen. Statistical comparisons of datasets were made using a two sample *t*-test assuming unequal variances.

Results

Water table levels varied greatly over the study period in response to seasonal patterns of precipitation. Figure 2 presents water table elevations versus distance from the stream for the combined transects during selected sampling events; also presented are average water table elevations versus distance for

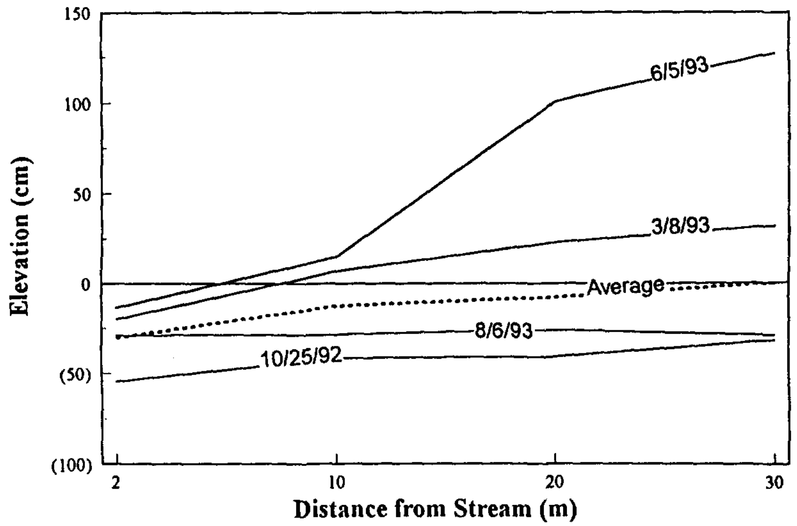

Fig. 2. Water table elevations versus distance from the stream for two dry-season sampling events (10/25/92 & 8/6/93) and two rainy-season sampling events (3/8/93 & 6/5/93). The average water table elevations over the study period are also shown. Elevations are relative to the ground levels at piezometer R1. Data from the two transects are combined. The stream level ranged from 30 to 60 cm beneath the 0 datum.

the study period. In the riparian piezometers, the water table was generally within 30 to 50 cm of the ground surface, while in the hillslope piezometers water table depths ranged from 2 to 4 m, depending on the piezometer's distance upslope (Table 1). Water table elevations varied by as much as 2 m in upland piezometer S3, but varied by no more than 0.5 m in the riparian piezometers. Overall during the study period, the water table sloped toward the stream at a gradient of approximately 0.001.

Pronounced compositional differences in inorganic nitrogen exist between upland, riparian, and stream hydrologic compartments (Fig. 3). Nitrate dominated the inorganic nitrogen pool of upland groundwater, while NH_4^+ dominated in riparian groundwater. This change in speciation is even clearer in Fig. 4, where concentrations of NO_3^- are plotted versus NH_4^+ for all samples. The greatest departure from this trend was seen in upland piezometer S3, which contained comparable concentrations of both NO_3^- and NH_4^+ during the first two months of sampling. Overall, NO_3^- accounted for an average of 89% of the upland inorganic nitrogen pool and NH_4^+ accounted for an average of 93% of the riparian inorganic nitrogen pool. In the stream, concentrations of total inorganic nitrogen were consistently low, with NO_3^- dominant (Fig. 3). DON was an important component of the TDN pools of all three hydrologic compartments, accounting for approximately 41% of TDN

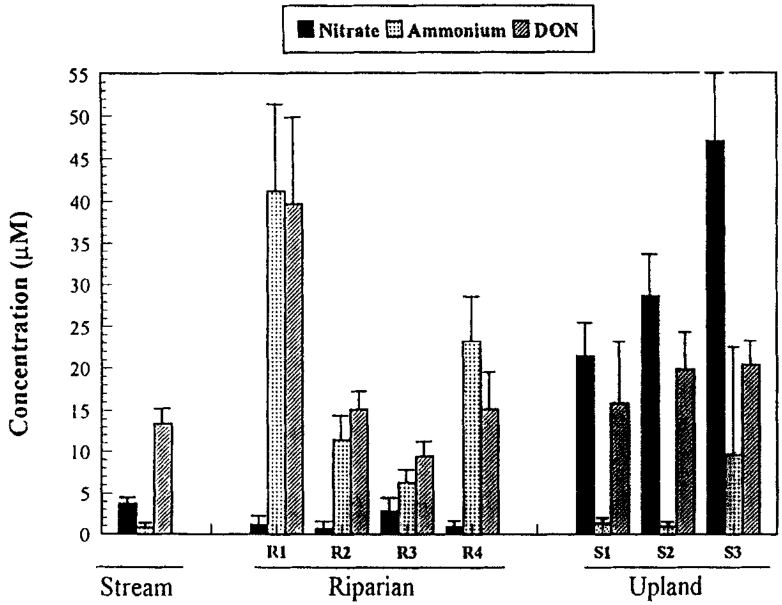

Fig. 3. Nitrogen data grouped by zone. Piezometer locations shown in Fig. 1. Bars denote standard deviations.

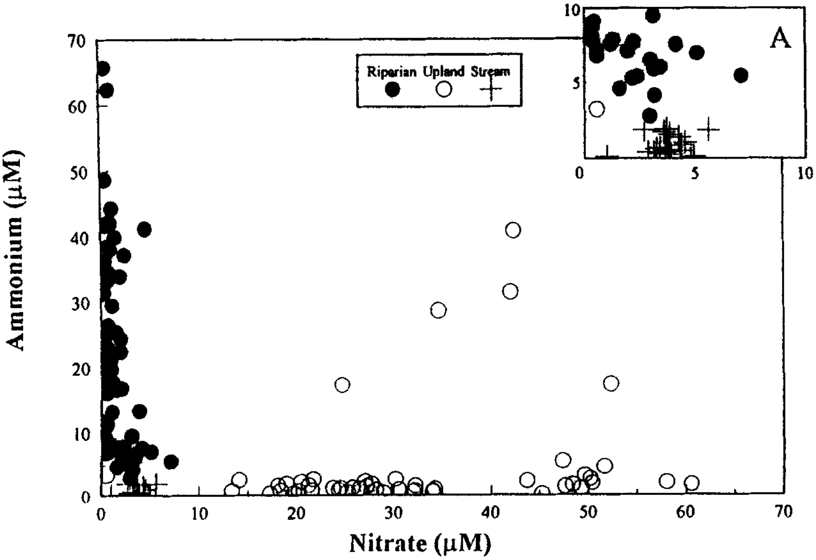

Fig. 4. Plot of ammonium vs. nitrate for all samples. Points toward the center of the plot are from the first two months of sampling in S3. Values for this piezometer subsequently fell to the nitrate axis. The inset (A) is an expanded view of the 0–10 μM range of the axis.

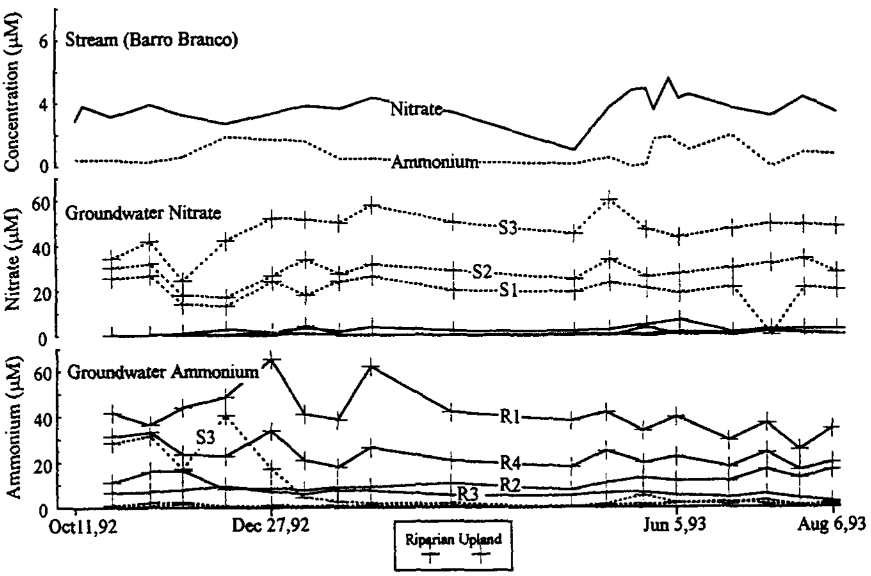

Fig. 5. Time-series plot of ammonium and nitrate in the stream and groundwater. No significant seasonal trends are depicted in the data.

in groundwater and 75% of TDN in the stream. Mean DON concentrations were not significantly ($P = 0.05$) different between hillslope (mean 18.81 μM, SD = 5.19) and riparian (mean 20.02 μM, SD = 13.31) piezometers, but mean DON concentrations in both hillslope and riparian piezometers were significantly ($P = 0.05$) higher than that in streamwater (mean 13.38 μM, SD = 1.79) (Fig. 3).

Nitrate and NH_4^+ concentrations for baseflow streamwater and groundwater did not vary seasonally (Fig. 5). The initially high values of NH_4^+ in piezometer S3 occurred in the sampled dry season (Oct. and Nov.) and early rainy season (Dec.) of 1992, but high NH_4^+ concentrations did not return during the subsequent dry season.

Ferrous iron concentrations reflected NH_4^+ concentrations, although they were more variable (Fig. 6a). Mean Fe^{2+} concentrations in the riparian piezometers (mean 51.4 μM, SD = 40.6) were significantly ($P = 0.01$) higher than those in the upland piezometers (mean 3.8 μM, SD = 7.3) and the stream (mean 2.1 μM, SD = 2.5).

Mean O_2 concentrations in the riparian piezometers (mean 1.88 mg/l, SD = 0.74) were significantly ($P = 0.01$) below those in the upland piezometers (mean 4.10 mg/l, SD = 0.84) and stream (mean 6.09 mg/l, SD = 0.63) but remained above zero (Fig. 6b). However, the presence of reduced species

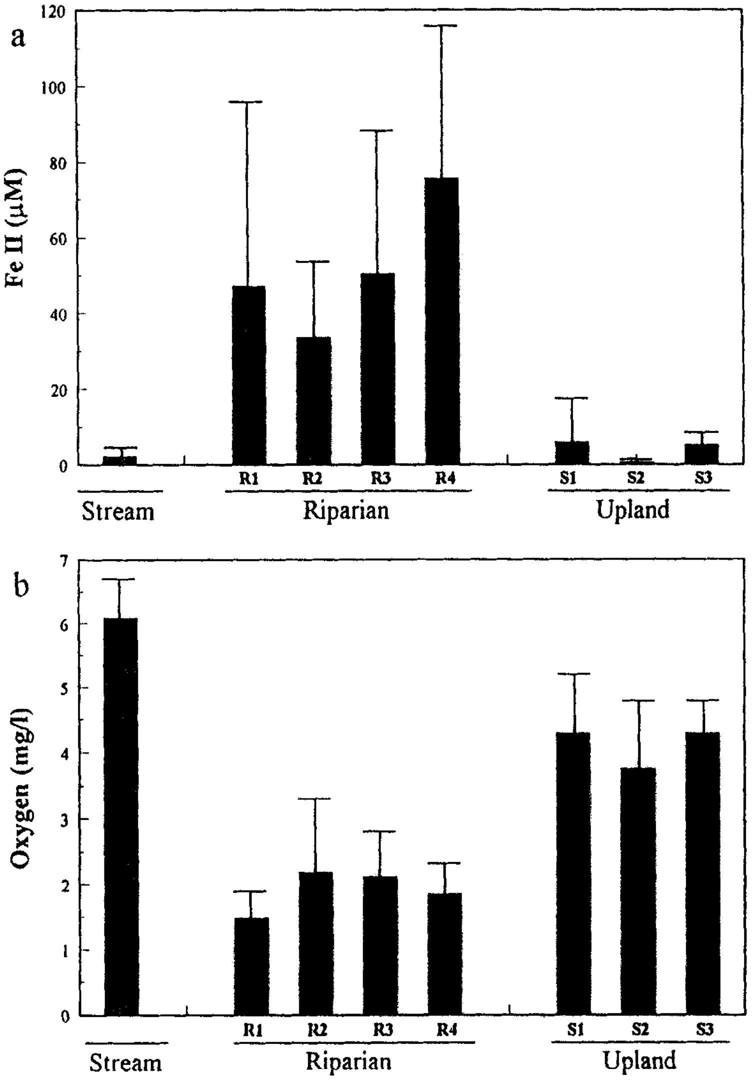

Fig. 6. Iron II(a) and oxygen (b) data grouped by zone. Bars denote standard deviations.

(NH_4^+ and Fe^{2+}) and uniformly gray color of riparian soils suggest that anoxic conditions predominate in riparian groundwater.

Discussion

Differences in organic nitrogen speciation between upland groundwater, riparian groundwater, and streamwater may be attributed to existing redox conditions, which are in turn linked to hydrologic conditions and levels of soil organic matter. In the riparian zone, a shallow water table maintains groundwater in contact with relatively large amounts of soil organic matter and anaerobic conditions probably prevail (McClain unpubl. data). Whereas, upland groundwater occurs well below organic-rich surface horizons and remains oxygenated. What is more interesting is the abruptness of the shifts in speciation documented at Barro Branco and the potential importance of processes at the riparian margins in regulating the transfer of nitrogen between the forest hydrologic system and the stream.

Transformations across the upland-riparian margin

The shift from NO_3^- to NH_4^+ dominance in groundwater is completed between hillslope piezometers S1 and S3 and riparian piezometers R2 and R4. We hypothesize that denitrification reactions focused near the upland margin of riparian groundwater account for the NO_3^- losses, as they have been shown to in several other systems (Pinay & Décamps 1988; Cooper 1990; Bowden et al. 1992; McDowell et al. 1992; Haycock & Burt 1993). Livingston et al. (1988) and Keller et al. (1988) each found net denitrification rates in the surface soils of the catchment to be largely NO_3^- limited. A similar NO_3^- limitation of denitrification reactions in the riparian groundwater would tend to focus these reactions at the riparian boundary, where NO_3^- is supplied by inflowing upland groundwater. Under this conceptual model, the lateral extent of the zone in which denitrification reactions are focused will vary as a function of reaction rates and incoming flux of NO_3^-, but micro-scale measurements at the oxic-anoxic interface of stream and lake sediments suggest that the zone of enhanced denitrification may be centimeters or less in thickness (Christensen et al. 1989; Sweerts & de Beer 1988). Ammonium concentrations in anaerobic riparian groundwater may be explained by continued ammonification in the absence of oxygen-dependent nitrification reactions. Alternatively, the observed shift in inorganic species dominance from NO_3^- to NH_4^+ may be explained by direct dissimilatory reduction of NO_3^- to NH_4^+, but this reaction pathway does not appear to be favored in soils (Tiedje et al. 1981). The lack of significant trends in DON concentrations is not unexpected given that DON chemistry is not inherently sensitive to shifts in redox conditions.

Transformation across the riparian-stream channel margin

The riparian-stream channel margin is marked by both a shift in speciation and a sharp decrease in total inorganic nitrogen concentrations (Fig. 3). The speciation shift may again be attributed to changing redox conditions, however, the observed concentration losses are not easily explained. The possibility of dilution by low-nitrogen water from sources upstream cannot as yet be discounted, but the uniformity of catchment geomorphology and low order of the stream suggest that there are unlikely to be volumetrically important sources dissimilar to the riparian groundwater we sampled. Three potential scenarios remain. Observed inorganic nitrogen losses may occur 1) along groundwater flowpaths initially entering the hyporheic zone, 2) in the stream channel, or 3) along exchange flowpaths re-entering the hyporheic zone.

The most likely fate of riparian-derived NH_4^+ entering an aerobic hyporheic zone is oxidation to NO_3^- by microbes (Blackburn 1983), but stream NO_3^- concentrations are too low to account for this reaction pathway alone. Alternatively, NH_4^+ decreases with no commensurate NO_3^- increase could be attributed to nitrogen uptake by plants at the stream edge. This mechanism is difficult to quantify but as there is no noticeable increase in vegetation along the stream edge and no good explanation of why uptake should be concentrated here, again this process alone does not appear to account for measured inorganic nitrogen losses. A third possibility as groundwater crosses the anoxic-oxic interface is coupled nitrification-denitrification reactions which oxidize NH_4^+ directly to N_2O or N_2 (Seitzinger 1988). Recently, Triska et al. (1994) presented convincing evidence for coupled nitrification-denitrification in the hyporheic zone of the Shingobee River in Minnesota. As for the possibility that NO_3^- derived from NH_4^+ oxidation is consumed within the stream channel, several studies have reported inorganic nitrogen removal through inchannel biotic uptake (Cooper & Cooke 1984; Richey et al. 1985; Valett 1993). Finally, NO_3^- may be lost via denitrification occurring along exchange flowpaths re-entering the hyporheic zone (Grimm & Fisher 1984; Triska et al. 1989; Duff & Triska 1990).

McDowell et al. (1992) observed similar inorganic nitrogen losses between groundwater and streamwater in the Icacos basin of Puerto Rico. Upon evaluation of four hypotheses, including unrepresentative samples, plant uptake, open channel consumption, and coupled nitrification-denitrification, they concluded that, without further experiments, none of the four could completely account for the observed inorganic nitrogen losses. Although they believed coupled nitrification-denitrification to be the most reasonable explanation, they were unable to state this unequivocally without further experiments (McDowell et al. 1992). Similarly, at Barro Branco our present data do not allow for a quantifiable explanation of inorganic nitrogen losses across the riparian-stream channel margin. It is likely that a combination of the processes mentioned accounts for the observed TIN losses. The investigation and quantification of these processes is the focus of our continuing efforts at the site.

DON concentrations also decrease between riparian groundwater and streamwater, suggesting that organic matter is also consumed at the stream edge. This corresponds to the findings of Ford & Naiman (1989) and Wallis et al. (1981) who reported organic matter losses from groundwater upon passing through streambed sediments.

Implications in the Central Amazon and similar regions

The foregoing results and discussion suggest that transfers of inorganic nitrogen from forest groundwater to streamwater are strongly mitigated by reactions focused at the upland and stream margins of the riparian zone, and only a small proportion of inorganic nitrogen carried by groundwater actually becomes part of the stream inorganic nitrogen pool. The importance of groundwater contributions of inorganic nitrogen to the stream is further reduced when one considers that the stream receives on the order of 0.6 $kg/m^2/yr$ of direct litterfall, 67% of which is leaves (Franken et al. 1979). Leaves are quickly decomposed in Amazonian lotic environments, thereby releasing nitrogen directly into streamwater (Stark & Holley 1975; Henderson & Walker 1986).

Salati et al. (1982), Brinkmann (1983), Franken & Leopoldo (1984), and Lesack (1993) each calculated nitrogen exports in streamwater from Central Amazonian catchments and sought to relate these exports to the nutrient status of adjacent forests. Our findings question the veracity of this relationship in the Central Amazon or anywhere else where near-stream processes significantly alter nitrogen chemistries. In such areas, measurements of inorganic nitrogen losses from upland forests via leaching must be made upgradient of the riparian-forest boundary. Bruijnzeel (1991) voiced a similar concern while reviewing existing literature on nutrient input-output budgets in tropical catchments, citing the complexities brought by gaseous forms of nitrogen. He concluded that available data are inadequate to close catchment nitrogen budgets.

The suggestion from our data that near-stream processes strongly mitigate transfers of inorganic nitrogen from groundwater to streamwater also impacts modeling efforts to link terrestrial and aquatic ecosystems. Neal et al. (1992) applied the MAGIC model to Barro Branco in order to evaluate the potential effects of climate change and deforestation on streamwater quality. In their simulation, cutting the upland forest led to a release of NO_3^- into soilwater. The model then routed this excess NO_3^- directly to the stream with no consideration of riparian processes. At Barro Branco, modeled losses of NO_3^- produced commensurate losses of base cations. In the absence of sufficient levels of base cations, the model mobilized H^+ ions, which may then mobilize aluminum and perhaps produce toxic conditions in the stream. These two possible model scenarios are driven by NO_3^- transfers from upland forests to the Barro Branco stream, transfers which our findings suggest are strongly diminished by processes operating at the margins of the riparian zone. In such instances where inorganic nitrogen plays a deciding role in whole-system biogeochemical dynamics, the complexities of nitrogen dynamics at the terrestrial-lotic interface must be considered more thoroughly. Consideration should also be given to how near-stream processes might be impacted by forest cutting and increased nitrate loading.

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