

## **$^{15}\text{N}$ evidence for the origin and cycling of inorganic nitrogen in a small Amazonian catchment**

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**Abstract.** The  $\delta^{15}\text{N}$  composition of the dominant form of dissolved inorganic nitrogen (DIN) was determined in upland groundwater, riparian groundwater, and stream water of the Barro Branco catchment, Amazonas, Brazil. The  $\delta^{15}\text{N}$  composition of organic nitrogen in riparian and upland leaf litter was also determined. The data for these waters could be divided into three groups: upland groundwater DIN predominately composed of  $\text{NO}_3^-$  with  $\delta^{15}\text{N}$  values averaging  $6.25 \pm 0.9\text{‰}$ ; riparian groundwater DIN primarily composed of  $\text{NH}_4^+$  with  $\delta^{15}\text{N}$  values averaging  $9.17 \pm 1.0\text{‰}$ , and stream water DIN predominately composed of  $\text{NO}_3^-$  with  $\delta^{15}\text{N}$  values averaging  $4.52 \pm 0.8\text{‰}$ . Nitrate samples taken from the stream source and from the stream adjacent to the groundwater transects showed a downstream increase in  $\delta^{15}\text{N}$  from  $1.0\text{‰}$  to  $4.5\text{‰}$ . Leaf litter samples averaged  $3.5 \pm 1.2\text{‰}$ .

The observed patterns in isotopic composition, together with previously observed inorganic nitrogen species and concentration shifts between upland, riparian and stream waters, suggest that groundwater DIN is not the primary source of DIN to the stream. Instead, the isotopic data suggest that remineralization of organic nitrogen within the stream itself may be a major source of stream DIN, and that the majority of DIN entering the stream via groundwater flowpaths is removed at the riparian-stream interface.

## **Introduction**

Strong compositional and concentration gradients in dissolved inorganic nitrogen (DIN) at upland-riparian and riparian-channel boundaries of stream corridors have lead researchers to focus on riparian and hyporheic zones as control points of DIN fluxes (Haycock et al. 1993; Triska et al. 1993). In a recent study, McClain et al. (1994) reported dramatic shifts in DIN concentrations and compositions at these boundaries in a small Amazonian catchment. Nitrate dominated the DIN of upland groundwater but was replaced by  $\text{NH}_4^+$  as groundwater passed into the riparian zone. Upon crossing the riparian-stream margin, the dominant DIN species reverted to  $\text{NO}_3^-$ , and, in addition, DIN concentrations were reduced by 85%. Possible explanations for these shifts in composition and reductions in DIN concentrations included removal of DIN by plant uptake and streamside nitrification/denitrification, but available data

were insufficient to completely discriminate between competing hypotheses. Because denitrification and plant uptake alter the isotopic composition of the remaining DIN (Létolle 1980; Mariotti et al. 1982), we undertook measurements of nitrogen isotopes in groundwater and stream water DIN to provide more insight into the controlling mechanisms.

Most available isotopic studies of groundwater and stream/riverine DIN have concentrated upon the isotopic effects of anthropogenic nitrogen input to aquifers (i.e., Kreitler & Browning 1983; Wassenaar 1995). There have been few studies of undisturbed small scale groundwater-stream nitrogen dynamics using isotopic techniques (Kendall et al. 1995). In this paper we report results of our study of the isotopic composition of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in groundwater and stream water from a small tropical catchment. We discuss the results within the framework of existing hypotheses, while emphasizing the utility of isotopic techniques in elucidating groundwater-stream nitrogen dynamics.

### Site description and methods

The investigation was conducted in the Barro Branco catchment of the Instituto Nacional de Pesquisas da Amazônia's Reserva Ducke experimental forest. A complete site description can be found in McClain et al. (1994). Briefly, the site consists of a small (1.5 km<sup>2</sup>), largely undisturbed catchment drained by one perennial stream (Barro Branco) and several ephemeral streams. The stream is surrounded almost completely by a flat riparian zone up to 40 m wide.

Samples were collected on four occasions (June 1993, January 1994, May 1994 and June 1995) from both stream and groundwater sites along Barro Branco (Figure 1). Groundwater samples were collected from seven piezometers positioned along two transects normal to the stream and approximately 1000 m from the stream's source. All piezometers were installed within the upper 2 m of the saturated zone (Figure 2b) and were allowed to equilibrate with the surrounding groundwater for three weeks prior to sampling. Three piezometers sampled upland groundwater (S1-S3) and four sampled riparian groundwater (R1-R4). Stream samples were collected concurrently from the middle of the channel, just below the water surface. Additional stream samples were collected in May 1994 and 1995 from the stream source and in May 1994 from approximately 500 m downstream of the source (Figure 1a). In addition, samples of forest floor leaf litter from both upland and riparian zones were collected. After collection, stream and groundwater samples were transported to the laboratories of the Instituto Nacional de Pesquisas da Amazônia, where they were filtered through precombusted Gelman type A/E glass fiber filters

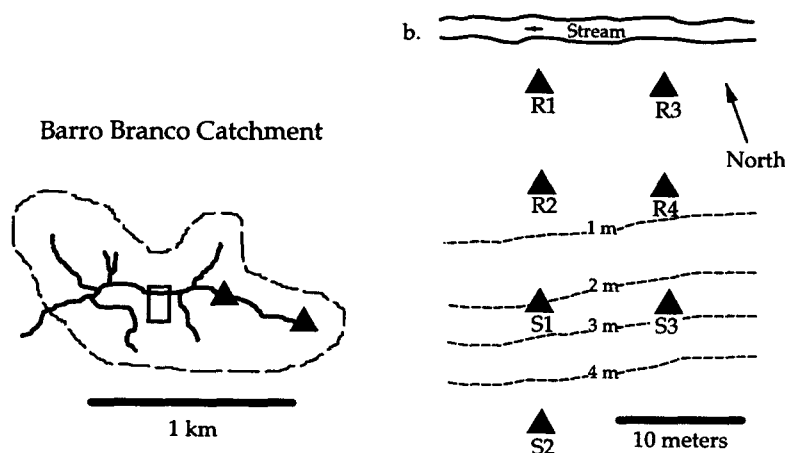


Figure 1. (a) Diagram of study site. Dotted line encloses approximate limits of drainage basin. Groundwater samples were collected from piezometers installed within area bounded by rectangle in the middle of the basin. Stream samples were collected from source (right triangle), midway between source and groundwater piezometer installation (left triangle) and next to piezometer installation (within rectangle). (b) shows enlarged view of area bounded by rectangle in Figure 1a. Triangles represent piezometer locations where samples were collected for this study. Dotted lines represent approximate ground elevation contours in meters above mean stream surface, while arrow indicates direction of stream flow.

and analyzed colorimetrically for dissolved nitrate and ammonium concentrations according to the methods of Strickland & Parsons (1972) and Koroleff (1969), respectively. Subsamples were poisoned with  $\text{HgCl}_2$  and shipped to the University of Washington where isotopic analyses were performed. A more detailed description of sample collection and handling techniques can be found in McClain et al. (1994).

Isotopic measurements were performed individually on the dominant DIN species in each hydrologic compartment ( $\text{NO}_3^-$  in upland groundwaters and streamwaters,  $\text{NH}_4^+$  in riparian groundwaters) and on particulate organic nitrogen in leaf litter. In most samples >80% of the DIN was in either the  $\text{NH}_4^+$  or  $\text{NO}_3^-$  form, and in these cases, the secondary species of DIN was not analyzed due to mass spectrometer sample size restrictions. In a few cases where DIN concentrations of both  $\text{NO}_3^-$  and  $\text{NH}_4^+$  exceeded  $2 \mu\text{M}$  (1 upland and 1 stream sample) both species were analyzed individually. Ammonium samples were prepared for analysis according to the method proposed by Velinsky et al. (1989). For  $\text{NO}_3^-$  analyses the sample pH was increased to >13 using NaOH and the sample distilled to 1/3 of its initial volume under  $\text{N}_2$  to remove  $\text{NH}_4^+$ . Afterwards distilled deionized water was added to the sample and the remaining  $\text{NO}_3^-$  was converted to ammonium and distilled into a separate collection flask under  $\text{N}_2$  using the methods of Cline & Kaplan

(1975). The distilled  $\text{NH}_4^+$  from either analysis method was extracted onto an ion sieve (Velinsky et al. 1989), collected onto a quartz fiber (Whatman QM-A) filter, sealed into an evacuated quartz ampoule and combusted to  $\text{N}_2$  at  $900^\circ\text{C}$ . The contents of the combusted tubes were extracted onto a molecular sieve at  $-90^\circ\text{C}$  and transferred to a Finnegan Mat 251 isotope ratio mass spectrometer, in which the  $^{15}\text{N}/^{14}\text{N}$  ratio of the samples was measured versus an atmospheric  $\text{N}_2$  standard. Results are reported as  $\delta^{15}\text{N}$  in per mil (‰) units. Typical reproducibility (samples and standards) of both nitrate and ammonium samples was  $\pm 0.25\text{‰}$  with an overall accuracy of  $0.2\text{‰}$ . Leaf litter samples were homogenized and ground into coarse ( $<0.5\text{ mm}$ ) pieces. Subsamples were then transferred to quartz combustion tubes,  $\text{Cu}/\text{CuO}$  added, evacuated, sealed and combusted at  $900^\circ\text{C}$  to convert the organic nitrogen to  $\text{N}_2$  gas for isotopic analysis.

## Results

Dissolved inorganic nitrogen concentration and isotopic results combined for both transects are shown in Figure 2a. The average composition of upland water DIN was  $>90\%$   $\text{NO}_3^-$  with a  $\delta^{15}\text{N}$  of  $6.3 \pm 0.9\text{‰}$  ( $n = 17$ ), while riparian zone DIN averaged  $>90\%$   $\text{NH}_4^+$  with a  $\delta^{15}\text{N}$  of  $9.2 \pm 1.0\text{‰}$  ( $n = 17$ ) and streamwaters averaged  $>80\%$   $\text{NO}_3^-$  with a  $\delta^{15}\text{N}$  of  $4.5 \pm 0.8\text{‰}$  ( $n = 10$ ). Both the average composition and isotopic values of the primary form of DIN varied significantly ( $>99\%$  CI, 2-tailed t-test) between the three zones (upland, riparian and stream) sampled. In one upland sample (from piezometer S3, Figure 1b) and one stream sample there was enough of both DIN species to measure isotopically, and in each case there was no significant difference between the isotopic values of  $\text{NO}_3^-$  and  $\text{NH}_4^+$ . However, in most cases the minority constituent of DIN was too low in concentration to measure accurately for isotopic content.

Samples collected at the stream head were isotopically lighter ( $\delta^{15}\text{N} = 1.0 \pm 0.7$ ,  $n = 2$ ) and lower in DIN concentration ( $[\text{NO}_3^-] = 2.5 \pm 0.5\text{ }\mu\text{M}$ ) than stream waters collected at either the piezometer transect site or midway between the transect site and the stream head (both  $\delta^{15}\text{N} = 4.5 \pm 0.8$ ,  $[\text{NO}_3^-] = 5.3 \pm 1.0\text{ }\mu\text{M}$ ,  $n = 12$ ). Samples from the stream adjacent to the piezometer site collected during May/June were significantly different than those collected during December ( $\delta^{15}\text{N} = 4.1 \pm 0.2$ ,  $n = 7$  vs.  $\delta^{15}\text{N} = 5.7 \pm 0.1$ ,  $n = 2$ ), although there was no significant difference in DIN concentrations during the two seasons. Finally,  $\delta^{15}\text{N}$  of leaf litter from both uplands and riparian zones ( $\delta^{15}\text{N} = 3.5 \pm 1$ ,  $n = 20$ ) was lighter than the DIN in groundwaters within each zone.

## Discussion

McClain et al. (1994) reported that, although groundwater levels at Barro Branco fluctuated greatly throughout the year, on average the water table sloped towards the stream with a gradient of 0.001 (Figure 2b). Nortcliff & Thornes (1988) observed a similar water table configuration at the site, and, using a hydraulic conductivity of  $4 \times 10^{-4} \text{ cm s}^{-1}$ , went so far as to calculate a groundwater flux of  $1.85 \times 10^{-4} \text{ cm m}^{-2} \text{ s}^{-1}$ . Thus, subsurface flowpaths in the Barro Branco catchment appear to conduct groundwater, presumably along with its associated DIN, from the upland across the riparian zone and into the stream channel. If there were no alteration of this DIN, concentrations and speciation would be expected to be similar within all three areas. However, our results indicate that significant compositional and isotopic differences in DIN do exist along this flowpath, and thus significant alteration of DIN is occurring. The strongest concentration and isotopic shifts occur between the riparian zone and stream channel, where waters containing dramatically different DIN are found within several meters of each other. Significant differences in isotopic content and DIN composition were also observed between upland and riparian groundwaters. Assuming that groundwaters are transported between these regions along a flowpath from upland through riparian to stream waters, in the following sections we discuss the isotopic evidence for mechanisms controlling these observed shifts in DIN composition.

### *Upland-riparian margin*

The general shift in DIN speciation across the upland-riparian boundary from a  $\text{NO}_3^-$ -dominated to  $\text{NH}_4^+$ -dominated system (McClain et al. 1994) is accompanied by an increase in the  $\delta^{15}\text{N}$  of the DIN pool (Figure 2a,c). Overall, the  $\delta^{15}\text{N}$  values of riparian DIN were consistently the highest measured in this study. Denitrification at the upland-riparian zone boundary followed by release of  $\text{NH}_4^+$  by organic matter remineralization within the riparian zone was hypothesized to account for this speciation shift (McClain et al. 1994). An alternate explanation for this shift is the direct conversion of  $\text{NO}_3^-$  entering the riparian zone to  $\text{NH}_4^+$  via direct dissimilatory reduction; however this process does not appear to be favored in soils that are not highly anaerobic (Tiedje et al. 1981; Correa & Germon 1991). The study soils tend to be relatively low in organic carbon content ( $\sim 1\%$ ) below the upper 10 cm and thus are unlikely to be able to support extremely anoxic conditions needed for this process. As little information on the isotopic effects of direct dissimilatory reduction exists, the isotopic data cannot be used to distinguish between these competing hypotheses. However, although  $\text{NH}_4^+$  concentrations varied widely between

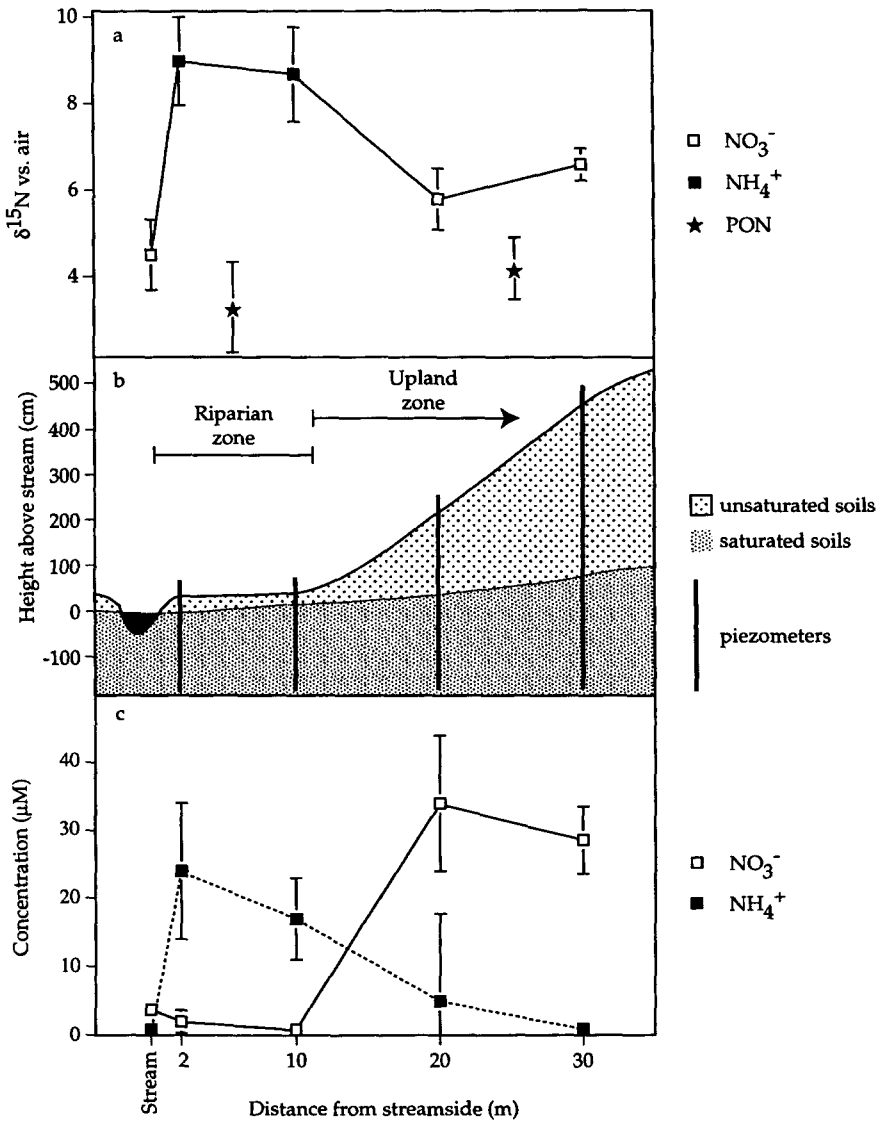


Figure 2. (a, b and c). Composition and isotopic values of DIN in groundwater and stream water, leaf litter PON isotopic values and illustration of piezometer location and water-table depth for primary sampling site. Nitrate values are represented by open symbols, Ammonium values by closed symbols and leaf litter PON samples by stars. (a) shows average isotopic composition (both transects combined,  $\pm 1$  S.E.) of the dominant species of DIN within groundwaters at each distance from streamside, as well as the average stream value and average values of leaf litter PON taken from upland and riparian zones. (b) illustrates approximate relationship between ground elevation and the saturated soil horizon, as well as indicating the approximate locations and depths for piezometers. (c) shows average concentrations of nitrate and ammonium (both transects combined) at each distance from streamside (data from McClain et al. 1994).

riparian wells (McClain et al. 1994) the  $\delta^{15}\text{N}$  of samples taken from these wells was very similar (Figure 2a), implying a localized enriched source of DIN within the riparian zone.

However, if the source of groundwater DIN is local organic matter, riparian DIN is enriched isotopically compared to both leaf litter (Figure 2a) and bulk soil organic matter (McClain et al., unpublished data). Three mechanisms could explain the increase in isotopic composition: 1) partial nitrification, followed by nearly complete denitrification of the resulting  $\text{NO}_3^-$ , at the upper oxic boundary of the riparian zone (Mariotti et al. 1981); 2) preferential removal of DIN by plant uptake (Nadelhoffer & Fry 1994); or 3) direct  $\text{NH}_3$  losses as gas (Hübner 1986). All of these processes remove  $^{14}\text{N}$  preferentially and could enrich the remaining  $\text{NH}_4^+$ , although direct  $\text{NH}_3$  losses at this site are not likely as the groundwaters are acidic ( $\text{pH} < 6.0$ ).

### *Riparian-stream channel margin*

McClain et al. (1994) posed four main hypotheses to explain the strong reduction in DIN concentrations and change in speciation across the riparian-stream channel margin at Barro Branco (Figure 2c). The same hypotheses were posed by McDowell et al. (1992) at Icacos, Puerto Rico, where similar concentration gradients were reported. Briefly, the hypotheses are 1) plant uptake, 2) open channel consumption, 3) coupled nitrification-denitrification, and 4) unrepresentative samples. Both studies assumed that stream DIN derived largely from infiltrating riparian groundwater, albeit in reduced concentrations. However, neither study included sufficient data to completely discriminate between these competing hypotheses. The isotopic data collected at Barro Branco, which indicate a decrease in  $\delta^{15}\text{N}$  across this margin, together with published work on isotopic effects of different input and loss terms, enable a test of these hypotheses.

Considering the hypotheses in turn, streamside uptake of DIN was deemed unlikely by McDowell et al. (1992), who calculated that only a small percentage of the estimated input of DIN from the riparian zone could be removed by plants, given apparent growth rates. McClain et al. (1994) reached a similar conclusion. The isotopic data from this study also directly discount this hypothesis, as the apparent input term of DIN into the stream is near 4‰. Removal of DIN by plant uptake preferentially removes  $^{14}\text{N}$  (Mariotti et al. 1982), thereby enriching the remaining DIN. Therefore one would expect stream DIN to contain  $\delta^{15}\text{N}$  values  $> 9\text{‰}$ . Similarly, if most of the DIN is consumed by algal or other plant uptake in the stream itself, one would likewise expect a higher stream DIN  $\delta^{15}\text{N}$  value than is observed. This conclusion holds whether we consider riparian or upland DIN as a potential source.

The hypothesis of coupled nitrification-denitrification in the hyporheic zone is difficult to evaluate due to the complicated nature of the effects of this process on the  $\delta^{15}\text{N}$  signal of DIN. Isotopic studies of coupled nitrification-denitrification are rare. Brandes et al. (1994) investigated coupled nitrification-denitrification in coastal sediments of Puget Sound and found that DIN became slightly heavier over the course of the experiment; however, that system had no advective component and is thus difficult to compare to the current study. Incomplete oxidation of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  creates isotopically light  $\text{NO}_3^-$  at the expense of enriching the remaining  $\text{NH}_4^+$  (Mariotti et al. 1981). Conversely, denitrification preferentially converts light  $\text{NO}_3^-$  to  $\text{N}_2$ , leaving enriched  $\text{NO}_3^-$  (Létolle 1980; Hübner 1986). Both processes have similar isotopic fractionation factors. The isotopic signal of coupled nitrification-denitrification is therefore difficult to predict and will depend upon the degree of completeness of each step in the removal mechanism for DIN. If  $\text{NH}_4^+$  is first completely oxidized to  $\text{NO}_3^-$  under low oxygen conditions and the resulting  $\text{NO}_3^-$  partially removed via denitrification, the remaining  $\text{NO}_3^-$  advected into the stream would be heavier (higher  $\delta^{15}\text{N}$ ) than the riparian  $\text{NH}_4^+$  source. Ammonium may also be only partially oxidized to  $\text{NO}_3^-$ , which is then removed via denitrification. In this case, the remaining  $\text{NH}_4^+$  could be advected into the stream and oxidized to  $\text{NO}_3^-$  there. This, however, would also result in DIN that is heavier than its riparian source. The only mechanism that would allow an input of isotopically "light" (compared to source) DIN from riparian groundwaters to the stream would be partial oxidation of riparian  $\text{NH}_4^+$  to  $\text{NO}_3^-$  followed by complete removal of the remaining  $\text{NH}_4^+$  by uptake (without appreciably affecting the  $\text{NO}_3^-$ ). This mechanism seems unlikely, especially given that the  $\text{NH}_4^+$  present in the stream on the one occasion that it could be measured was similar isotopically to stream  $\text{NO}_3^-$  and not heavier as required by this scenario. The existing evidence would therefore imply that partial DIN loss due to coupled nitrification-denitrification at the riparian-stream boundary is unlikely to account for the apparently light source ( $\sim 4.5\text{‰}$ ) of DIN to the stream. Clearly denitrification can occur at the riparian-stream boundary (Bowden et al. 1992), however, these processes may be so efficient that almost no DIN escapes into the stream. In this case riparian zone groundwater DIN would make little or no contribution to stream DIN and thus would not affect the  $\delta^{15}\text{N}$  of stream DIN. We note that stream  $\text{NO}_3^-$  isotopic values were significantly lower at the end of the wet season (May-June), when groundwater gradients and expected baseflows are greatest (McClain et al. 1994), than end of the dry season (December) values ( $4.1 \pm 0.2\text{‰}$  vs.  $5.7 \pm 1.1\text{‰}$ ). Therefore, even during periods when groundwater contribution to the stream should be at a maximum, stream DIN is significantly different than DIN within adjacent groundwaters.



The question of unrepresentative samples cannot be assessed in this preliminary study. Our transects exhibit patterns that are internally consistent both compositionally and isotopically, and sample terrain that is typical of that surrounding the stream; however, the transects lie within 10 m of each other, while the stream source lies 1 km upstream. Since stream DIN is from an integrated mixture of sources within this basin, we cannot be certain that all groundwaters that feed the stream are the same as those described here. Indeed, there is some indication that the groundwaters around the source region may differ isotopically from those further down the watershed. Also, the possibility exists that water may be entering the stream channel via alternative pathways with differing isotopic and concentration signals that are not assessed here. It is also the case that our groundwater samples were taken from the upper 1 m of the water table, and groundwaters collected from deeper in the aquifer may have different  $\delta^{15}\text{N}$  signatures. However, as the stream is less than 1 meter deep and the hydrologic gradient in this area is shallow, it is reasonable to assume that the stream is fed by near surface groundwaters and not waters from several meters below the streambed. Also stream DIN appears to reach a relatively constant  $\delta^{15}\text{N}$  value within 500 m of the stream source, implying that our hypothesis of relatively "light" (relative to groundwater) isotopic value DIN sources to the stream is correct. This issue cannot be resolved until a more extensive hydrologic survey of the area is undertaken to establish the exact nature of baseflow sources.

The isotopic data, therefore, indicate that at least two of the hypotheses (streamside uptake and in-channel uptake) used to explain the reduced DIN concentrations across the riparian-stream channel margin are very unlikely, and that a third hypothesis, combined nitrification-denitrification, is also somewhat unlikely because it would require a very specific set of conditions that are not easily met. All of the hypotheses assume that streamwater DIN derives largely from groundwater inputs. It is likely, given the observed isotopic patterns, that almost all of the riparian DIN is removed at the riparian-stream boundary by a combination of the previously mentioned processes. In this case, if our samples are representative, an additional hypothesis to account for the source of DIN to the streamwaters must be brought forth.

#### *Stream channel patterns and sources of stream DIN*

Some evidence suggests that stream DIN may be derived predominantly from an internal source such as leaf litter decomposition. McClain et al. (1994) pointed to the potential importance of this internal source as Barro Branco receives on the order of  $600 \text{ g m}^{-2}\text{yr}^{-1}$  of direct litterfall (Franken et al. 1979). This leaf litter is quickly decomposed in Amazonian stream environments (Henderson & Walker 1986; Stark & Holley 1975), and although

initially nitrogen is immobilized in microbial biomass during the decomposition process (Triska & Buckley 1978), eventually DIN may be released during the final stages of leaf decomposition. Our preliminary measurements of leaf litter  $\delta^{15}\text{N}$  indicate that it falls at or below stream  $\delta^{15}\text{N}$  values (Figure 2a), thus providing a source for stream DIN that is consistent with the observed  $\delta^{15}\text{N}$  of the DIN. This explanation is consistent with our measurement of stream  $\text{NH}_4^+$  (4‰), which should more closely reflect the isotopic value of source organic matter if our hypothesis is correct. Finally, an internal source of isotopically light DIN from leaf decomposition could also allow some input of isotopically heavy riparian zone DIN to the stream, although this input will be difficult to quantify.

In conclusion, the isotopic data presented here provide a means for testing existing hypotheses about the sources and fates of groundwater and streamwater DIN. Although tentative, the patterns in isotopic composition strongly suggest that none of the previously posed hypotheses can adequately explain differences between groundwater and streamwater DIN at this location. Instead, the isotopic data suggest that remineralization of organic nitrogen within the stream may be the predominant source of stream DIN and that stream DIN may therefore be substantially decoupled from adjacent groundwater DIN. The presence of three isotopically distinct nitrogen pools within a distance of less than 20 m provides further evidence that rapid alteration and cycling of groundwater DIN is taking place in this area.

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