



RESEARCH ARTICLE

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Key Points:

- Increasing $\delta^{15}\text{N}$ values in total dissolved nitrogen from throughfall to litter leachate correlated with an increasing organic contribution
- The retention of N-isotopically heavy dissolved organic nitrogen in the mineral topsoil decreased the $\delta^{15}\text{N}$ values in mineral soil solutions
- Increasing $\delta^{15}\text{N}$ values from the topsoil solution via the subsoil to the streamflow suggested gaseous N losses because of denitrification

Supporting Information:

Supporting Information may be found in the online version of this article.

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Sources and Sinks of N in Ecosystem Solutions Along the Water Path Through a Tropical Montane Forest in Ecuador Assessed With $\delta^{15}\text{N}$ Values of Total Dissolved Nitrogen

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Abstract The globally increasing reactive N richness affects even remote ecosystems such as the tropical montane forests in Ecuador. We tested whether the $\delta^{15}\text{N}$ values of total dissolved N (TDN), measured directly in solution with a TOC-IRMS, can be used to help elucidate N sources and sinks along the water path and thus might be suitable for ecosystem monitoring. From 2013 to 2016, the $\delta^{15}\text{N}$ values of TDN in bulk deposition showed the most pronounced temporal variation of all ecosystem solutions ($\delta^{15}\text{N}$ values: 1.9–5.9‰). In throughfall (TF), TDN was on average ^{15}N -depleted ($-1.8 \pm \text{s.d. } 0.4\%$) relative to rainfall ($3.4 \pm 0.9\%$), resulting from net retention of isotopically heavy N, mainly as NH_4^+ . Simultaneously, N-isotopically light NO_3^- -N and dissolved organic nitrogen (DON) with a $\delta^{15}\text{N}$ value between NO_3^- -N and NH_4^+ -N were leached from the canopy (leaves: $-3.5 \pm 0.5\%$). The increasing $\delta^{15}\text{N}$ values in the order, TF < stemflow (SF, $0.1 \pm 0.6\%$) < litter leachate (LL, $1.3 \pm 0.7\%$) concurred with an increasing DON contribution to TDN reflecting the $\delta^{15}\text{N}$ value of the organic layer ($1.9 \pm 0.9\%$). The lower $\delta^{15}\text{N}$ value of the mineral soil solution at the 0.15 m soil depth (SS15, $-1.5 \pm 0.3\%$) than in LL can be explained by the retention of DON and NH_4^+ and the addition of NO_3^- from mineralization and nitrification. The increasing $\delta^{15}\text{N}$ values in the order, SS15 < SS30 ($-0.6 \pm 0.2\%$) < streamflow (ST, $0.5 \pm 0.6\%$) suggested gaseous N losses because of increasing denitrification. There was no seasonality of the $\delta^{15}\text{N}$ values. Our results demonstrate that the $\delta^{15}\text{N}$ values of TDN in ecosystem solutions help identify N sources and sinks in forest ecosystems.

Plain Language Summary Many ecosystems experience increasing nitrogen availability because of nitrogen deposition from the atmosphere caused by human activities. The deposited nitrogen can produce a growth boost or be leached into groundwater and surface water. The stable isotope ratios of nitrogen ($\delta^{15}\text{N}$ values) provide a tool to investigate into the consequences of increasing nitrogen availability. Here, we applied a new direct measurement method of $\delta^{15}\text{N}$ values in total dissolved nitrogen of ecosystem solutions to follow sources and sinks of nitrogen in a tropical montane rain forest in Ecuador. We found that the isotopically heavy nitrogen input via rainfall is enriched by isotopically lighter nitrogen from plants and nitrogen turnover during the water passage through the canopy. Once, the solutions reach the mineral soil, dissolved organic nitrogen, which is comparatively rich in the heavy nitrogen isotope, is retained rendering the remaining nitrogen isotopically lighter. This process is reversed deeper in the soil by conversion of the nitrate to nitrogen gasses, which are depleted in the heavy nitrogen isotope and leave the ecosystem to the atmosphere. The direct measurement of $\delta^{15}\text{N}$ values provides a tool to monitor the changing nitrogen cycle in ecosystems.

1. Introduction

Tropical forests are generally described as nutrient-limited ecosystems. Lowland tropical forests are frequently considered P-limited (Aragão et al., 2009; Vitousek, 1984) and tropical montane forests N- or N+ P-co-limited (Fisher et al., 2013; Turner & Wright, 2014). As a consequence, tropical forests are susceptible to N and/or P deposition, which can increase their biomass production and threaten their frequently high biodiversity (Barthlott et al., 1996; Sala et al., 2000; Wassen et al., 2005).

Currently, N deposition increases the N availability in many global forest ecosystems (Galloway et al., 2004, 2008; Lamarque et al., 2013). At the same time, many forest ecosystems receive a low but constant input of P from

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the atmosphere (Bol et al., 2016; Sohrt et al., 2017; Tipping et al., 2014; Wilcke et al., 2019). In addition to the nutrient inputs, increasing dry phases in otherwise wet tropical montane forests enhance soil organic matter mineralization and result in an additional nutrient release (Peters et al., 2013; Wilcke et al., 2013). Thus, the availability of N and P is on the rise in many tropical forests. To assess the redistribution of increasingly available nutrients in forest ecosystems new methods that can be applied to monitoring efforts are helpful. For N, the recently developed direct measurement of the stable N isotope ratio ($\delta^{15}\text{N}$ values) of total dissolved N (TDN) in ecosystem solutions with a Total Organic Carbon Analyzer coupled to an Isotope Ratio Mass Spectrometer (TOC-IRMS), which allows for the measurement of stable C and N isotope ratios may provide such a method (Alvarez et al., 2023; Federherr et al., 2014; Kirkels et al., 2014).

Because transformations among different chemical species in the soil solution such as between NH_4^+ and NO_3^- do not change the $\delta^{15}\text{N}$ value of TDN in ecosystem solutions, observed changes of the $\delta^{15}\text{N}$ value of TDN can only be attributed to the addition or the loss of N with a $\delta^{15}\text{N}$ value deviating from the mean $\delta^{15}\text{N}$ value of the original TDN, that is, the TDN in the preceding ecosystem solution along the water path through the forest. Following the flow path of water through a forest ecosystem, the first source of N is the deposition from the atmosphere. It has been shown that the $\delta^{15}\text{N}$ values of NH_4^+ and NO_3^- in deposition from the atmosphere show a considerable temporal variation likely reflecting different sources of inorganic N (Felix et al., 2017; Garten, 1996; Schwarz et al., 2011). We are not aware of studies addressing the $\delta^{15}\text{N}$ values of total N in deposition. The deposited N comes first into contact with the forest canopy and thus could be influenced by the $\delta^{15}\text{N}$ values of leaves widely ranging from -7.8 to 8.7‰ (Craine et al., 2009, 2012). If N_2 fixation from the atmosphere is a major source of plant N, the $\delta^{15}\text{N}$ values of plant tissue are close to 0‰ , that is, similar to that of the atmospheric N_2 serving as international standard for $\delta^{15}\text{N}$ values and thus showing by definition a $\delta^{15}\text{N}$ value of 0‰ (Craine et al., 2015). As a consequence, throughfall and stemflow might be influenced by the $\delta^{15}\text{N}$ values of the leaves, because of N leaching, particularly in organic form (Goller et al., 2006; Schwarz et al., 2014; Wilcke et al., 2013). However, if ecosystems are N-limited, N is on balance retained in the canopy (Harrison et al., 2000; Lovett & Lindberg, 1993; Schwarz et al., 2014). Because the retention of inorganic N and leaching of organic N may fractionate N isotopes, the canopy interaction of the deposited N is likely to result in changed $\delta^{15}\text{N}$ values in throughfall and stemflow.

When throughfall and stemflow reach the soil surface, they first come into contact with the soil organic layer on top of the mineral soil, where N can be retained or leached (Schwarz et al., 2016; Solinger et al., 2001; Wilcke et al., 2013). For a tropical montane forest in Ecuador, Goller et al. (2006) and Wilcke et al. (2013) have shown that the N concentration in the litter leachate is higher than in throughfall and stemflow pointing at a net enrichment of N because of organic matter mineralization. The NH_4^+ released by mineralization is N-isotopically lighter than the N in bulk organic matter (Högberg, 1997). If enough N is released into soil solution to activate nitrification, NH_4^+ becomes increasingly N-isotopically heavier while the produced NO_3^- is N-isotopically lighter than NH_4^+ (Craine et al., 2015; Högberg, 1997). Moreover, in a tropical montane forest, dissolved organic N (DON) was increasingly enriched from bulk deposition via throughfall and stemflow to litter leachate, indicating DON leaching from the vegetation and the organic layer (Goller et al., 2006; Wilcke et al., 2013). A preferential retention of NH_4^+ by cation-exchange sites or plant uptake and the leaching of DON and NO_3^- will likely be reflected by the $\delta^{15}\text{N}$ values of TDN in litter leachate. Temporally changing contributions of NO_3^- and DON leaching to the TDN in litter leachate can possibly be detected by determining $\delta^{15}\text{N}$ values in time series.

In the mineral soil, DON is adsorbed resulting in decreasing DON concentrations and fluxes (Goller et al., 2006; Michalzik et al., 2001; Wilcke et al., 2013). In the same tropical montane forest as in our study, the $\text{NO}_3^-/\text{NH}_4^+$ -N ratio increased strongly from litter leachate to mineral soil solution (Wilcke et al., 2013), suggesting the further production of NO_3^- by nitrification and/or a NH_4^+ retention in the mineral soil at cation-exchange sites or by fixation in clay minerals such as illites. The retention of DON and possibly also NH_4^+ will again likely change the $\delta^{15}\text{N}$ values of TDN in the soil solutions. Wilcke et al. (2020) and Alvarez et al. (2023) reported that root exudates and decomposing roots contribute to the dissolved organic matter concentrations in the mineral soil, which would also be a possible source of N for the mineral soil solutions. Because it has been reported that leaves show a lower $\delta^{15}\text{N}$ value than roots by 0.3 to $<1\text{‰}$ (Craine et al., 2005; Dijkstra et al., 2003), root-derived N might increase the $\delta^{15}\text{N}$ value of TDN in mineral soil solutions. Finally, denitrification favoring N-isotopically light NO_3^- will result in a higher $\delta^{15}\text{N}$ value of TDN in mineral soil solutions and stream water fed by mineral soil solutions. For the same tropical montane forest as studied here, Schwarz et al. (2011) observed an increasing $\delta^{15}\text{N}$ value of NO_3^- with increasing mineral soil depth and in the stream water relative to the soil solutions indicating

that denitrification indeed occurred in this ecosystem. In line with the assumption of a positive relationship between denitrification and soil depth, Castellano-Hinojosa et al. (2018), reported an increasing abundance of the denitrification genes with increasing soil depth which paralleled the decrease in dissolved oxygen concentrations. Dissolved organic C (DOC)-rich ecosystems such as the tropical montane forests with their thick organic layers (Wilcke et al., 2002) might favor denitrification, because Barrett et al. (2016) observed that DOC amendments to the soil resulted in larger denitrifier populations and N_2 emissions. Moreover, a high supply of NO_3^- to the subsoil as reported for the tropical montane forest in Ecuador (Wilcke et al., 2013) likely further enhances denitrification particularly under wet conditions (Arango & Tank, 2008). In summary, the multiple sources and sinks of TDN in ecosystem solutions along the water path from rainfall through the ecosystem to the stream water are expected to change the $\delta^{15}N$ values, which in turn could be used to identify the kind and size of these sinks and sources. Moreover, the direct measurement of $\delta^{15}N$ values could be used as a comparatively simple tool to monitor changes in the N cycle of ecosystems that can be applied to large sample numbers.

We studied the change in $\delta^{15}N$ values of TDN in ecosystem solutions along the water path from above-canopy rainfall through the forest ecosystem to streamflow during 4 years in quarterly resolution to test whether there are temporal changes in the N sources and sinks of ecosystem solutions. We hypothesized that the $\delta^{15}N$ values of TDN (a) in rainfall are temporally most variable of all ecosystem solutions reflecting changing N sources, (b) decrease from rainfall via throughfall and stemflow to litter leachate, because of increasing contributions of N-isotopically lighter N leached from the canopy, (c) decrease from litter leachate to the mineral soil, because of the retention of DON and NH_4^+ with higher $\delta^{15}N$ values than NO_3^- , and (d) increase from mineral topsoil solution via subsoil solution to stream water, because of increasing denitrification. Moreover, (e) we expected that the changes in the $\delta^{15}N$ values of TDN in ecosystem solutions showed a temporal variation reflecting temporally variable strengths of the various N sources and sinks.

2. Material and Methods

2.1. Study Site

We studied a 9.1-ha catchment at 1,850–2,150 m above sea level (a.s.l.) under evergreen lower tropical montane forest (Bruijnzeel & Hamilton, 2000) in the San Francisco Biological Reserve on the east-exposed slope of the Andean cordillera in south Ecuador (Beck et al., 2019). This catchment has been described in previous studies as Microcatchment (MC) 2 (Alvarez et al., 2023; Boy, Valarezo, & Wilcke, 2008; Wilcke et al., 2020).

The mean annual temperature during 1998–2013 was 14.9°C and the mean annual precipitation 2,320 mm. The study ecosystem is perhumid with always >100 mm of monthly precipitation (Figure S1 in Supporting Information S1). November and October have the lowest monthly precipitation and June has the highest. Particularly, in the period October–November, there can be extended dry spells of up to several weeks, called “veranillo.” From 1998 to 2010, it has been reported that throughfall, relative humidity, and the soil moisture content decreased, while interception loss from the forest canopy increased (Wilcke et al., 2013). Soils are mainly shallow, loamy Folic Dystric Cambisols (IUSS Working Group WRB, 2014) developed from phyllite with some interlayering of metasandstone. The soils are covered by partly thick organic layers (Wilcke et al., 2002). The clay mineralogy of the mineral soil is dominated by illite, vermiculite, and kaolinite (Schrumpf et al., 2001). The mean pH value of the mineral topsoil is 4.4, the mean effective cation-exchange capacity $63 \pm$ standard deviation $26 \text{ mmol}_c \text{ kg}^{-1}$, the mean organic C concentration $32 \pm 19 \text{ g kg}^{-1}$, and the mean C/N ratio 11 ± 2.8 (Wilcke et al., 2017). The vegetation growth was reported to be N+P co-limited (Homeier et al., 2012; Velescu et al., 2016).

2.2. Field Sampling

Leaves of 10 common tree species of the study forest were sampled from October to December 2016 (see species names in Table S1 and Figure S2 of Supporting Information S1). Additionally, leaves of two common tree species were sampled during the period 2005–2015 to determine the temporal variation (Figure S3 in Supporting Information S1). Species-specific fine roots segments (diameter $\leq 2 \text{ mm}$, length $> 10 \text{ cm}$) were sampled from individuals of the same 10 common tree species from which leaves were sampled from October to December 2016. Further details of root sampling and processing are described in Pierick et al. (2021). Samples of the Oi, Oe, Oa, A, and B horizons of 20 soil profiles were collected during two campaigns in 2006 and 2016. Leaf, root, Oi, Oe, and Oa samples were subsequently ground with a knife mill (Grindomix GM 200, Retsch, Haan, Germany)

and a planetary ball mill (PM 200, Retsch, Haan, Germany). Mineral soil samples were sieved <2 mm and ground with the planetary ball mill.

The Long-term Ecosystem study was set up in April 1998 and since then continuously run with the same field sampling methods. Here, we considered ecosystem solution samples from the period 2013–2016 that were collected weekly. Rainfall was collected at two gaging stations, each consisting of five Hellmann-type collectors, placed on clear-cut areas. Those collectors were permanently open and sampled bulk deposition, that is, wet deposition and the soluble part of coarse particulate dry deposition that sediments into the collectors (Wilcke et al., 2013, 2017, 2020). Throughfall was collected with 20 fixed-position hand-made funnel collectors which were placed randomly along three 20-m long transects at the lower to middle slope at each of approximately 1,900, 1,950, and 2000 m a.s.l. Stemflow was collected with polyurethane collars at five trees in the lower part of the catchment. Litter leachate was collected with three zero-tension lysimeters per transect installed laterally below the organic layer. Mineral soil solutions were sampled with three suction cups (mullite, $1 \pm 0.1 \mu\text{m}$ pore size) installed at the 0.15 and 0.3 m mineral soil depths, respectively (Wilcke et al., 2020). Streamflow was sampled weekly from the middle of the undisturbed flowing stream above a weir (Fleischbein et al., 2006).

Rainfall, throughfall, and stemflow water volumes were measured in the field and converted to water fluxes based on the collection surface of the samplers (RF, TF) or extrapolated according to the number of trees ha^{-1} (SF) (Wilcke et al., 2017). Water fluxes of litter leachate and soil solutions were estimated with the Soil Water Balance Model (DVWK, 1996) using data from 1999 to 2003 and then calculated for our study period by regression equations described in Wilcke et al. (2020) and Schwarz et al. (2011), respectively. We combined the weekly samples into volume-weighted quarterly samples, except for litter leachate and mineral soil solutions from which we composited the same volume of each weekly sample, because the samplers do not collect the solutions in a way that is representative for the fluxes. All ecosystem solutions were filtered in the field laboratory with ashless folded filters of 4–7 μm pore size, Type 392 (Sartorius-Stedim, Göttingen, Germany), except the mineral soil solutions. Alvarez et al. (2023) tested whether the TOC concentrations in our samples differed from DOC, which is conventionally filtered to <0.45 μm and did not detect a difference.

2.3. Chemical Analyses

The pH of the organic and mineral horizons was determined in a suspension of 10 and 40 g of soil in 100 mL of deionized water for organic and mineral horizons, respectively, using a pH glass electrode (Orion U402-S7, Thermo Scientific, Waltham, USA) after equilibration overnight. In the ecosystem solutions, the pH was measured directly with the same electrode type in an aliquot that was afterward discarded.

The $\delta^{15}\text{N}$ values and N concentrations of leaf, root, and soil samples were measured with an elemental analyzer (Thermo Scientific, Flash 2000 HT Plus, Bremen, Germany) coupled to an IRMS (Thermo Scientific, Delta V Advantage, Bremen, Germany) through a ConFlo IV interface. We used acetanilide as calibration standard for N concentrations, an organic-rich sediment (OAS, IVA Analysentechnik, Meerbusch, Germany) as IRMS working standard, and an aromatic polyimide (EMA-P2, Elemental Microanalysis, Okehampton, UK) for drift correction. IAEA-N-1 ($\delta^{15}\text{N}$: +0.40‰), IAEA-N-2 ($\delta^{15}\text{N}$: +20.30‰) and USGS-61 ($\delta^{15}\text{N}$: -2.87‰) were used to reference the results to the N_2 in air scale by linear regression. The precision of the $\delta^{15}\text{N}$ values determined by routinely performed, repeated measurements of the working standard was 0.20‰.

Total dissolved nitrogen (TDN) and dissolved inorganic nitrogen ($\text{DIN} = \text{NH}_4\text{-N} + \text{NO}_3\text{-N}$) were measured using high resolution colorimetry and photometric detection with a continuous flow analyzer (CFA San+++, Skalar, Breda, The Netherlands). Dissolved organic nitrogen (DON) was calculated as the difference between TDN and DIN. Cl^- concentrations were also measured by CFA using an ion-selective electrode (Orion Ionplus, Thermo Scientific, Beverly, USA).

The $\delta^{15}\text{N}$ values of TDN were determined with an elemental analyzer for liquid samples optimized for stable isotope measurements (isoTOC cube, Elementar Analysensysteme, Langenselbold, Germany), which was coupled via a low concentration module for peak focusing (LCM) to an IRMS (Vision, Isoprime, Stockport, UK). A volume of 1–2.5 mL of sample was injected via a four-way valve into the combustion tube. The combustion occurred at 850°C in a He flow on a Pt catalyst, while O_2 was introduced as reaction gas by a mass-flow controller. Excess O_2 was removed and NO_x compounds were reduced to N_2 by elemental Cu in a reduction tube at 500°C. Water was removed by a condenser, a trap filled with phosphorus pentoxide and a membrane dryer. Volatile

halogen compounds were bound on silver wool. The background caused by dissolved atmospheric N₂ was reduced during sample uptake by a membrane degasser. N₂ was focused by an adsorption column at −38°C in the LCM and then rapidly desorbed at 100°C and transported by the carrier gas to the open split of the IRMS.

We applied a linear calibration function to reference the measured δ¹⁵N values to the N₂ in air scale using the reference materials USGS-25 (δ¹⁵N: −30.4‰), IAEA-N-1, USGS-64 (δ¹⁵N: +1.76‰), IAEA-600 (δ¹⁵N: +1.0‰) and USGS-62 (δ¹⁵N: +20.17). We used repeated measurements of caffeine (USGS-61, δ¹⁵N: −2.87‰) for drift correction. Linearity corrections followed the procedure suggested by Federherr et al. (2014) for δ¹³C measurements. The precision of the measurement was determined by triplicate measurements of the reference materials at the beginning and at the end of each sequence. The standard uncertainty of the δ¹⁵N values according to Federherr et al. (2016) in the TDN concentration range of 1.4–6 mg L^{−1} was ~0.4‰. It was not possible to measure δ¹⁵N values in all the quarterly composited samples of RF and ST because of TDN concentrations <1.4 mg L^{−1}. In such cases, we based the quarterly values on selected weekly samples that contained a TDN concentration of at least 1.4 mg L^{−1}.

2.4. Calculations and Statistical Evaluation

We calculated the canopy budget CB_N for total nitrogen to determine if N is leached or retained in the canopy (Equation 1) according to Ulrich (1984). A negative CB_N indicates retention and a positive one leaching. Because gaseous N deposition is unknown, the CB_N might be overestimated.

$$CB_N = (TF_N + SF_N) - TD_N \quad (1)$$

where TF_N is the N flux with throughfall, SF_N is the N flux with stemflow and TD_N is total deposition. TD_N was calculated with Equation 2.

$$TD_N = BD_N + DD_N \quad (2)$$

where BD_N is the TN flux with rainfall and DD_N is the particulate dry deposition estimated with Equation 3 assuming that Cl[−] is an inert tracer in the forest canopy and thus only reflects the dry deposition but no leaching from the canopy.

$$DD_N = \left(\frac{TF_{Cl} + SF_{Cl}}{BD_{Cl}} \times BD_N \right) - BD_N \quad (3)$$

where TF_{Cl} and SF_{Cl} are the Cl[−] fluxes with TF and SF ; BD_{Cl} is the Cl[−] flux with rainfall; $\frac{TF_{Cl} + SF_{Cl}}{BD_{Cl}}$ is the deposition ratio of Cl[−]. Because of time delays between dry deposition to the canopy and wash down into the throughfall and stemflow collectors, the deposition ratio of Cl[−] is only stable and meaningful if it integrates longer time periods. We therefore calculated the annual dry deposition of N. Our estimate of dry deposition includes particulate but not gaseous N deposition.

To compare mean properties among the solid samples and among the solution samples, we used ANOVA followed by Tukey's Honest Significant Difference post-hoc test. Homoscedasticity was assessed with the Levene's test. Normality of residuals was checked by visual inspection. To compare differences between leaves and roots, we conducted a paired *t*-test for connected data sets, in which the normal distribution of the differences between each pair of values was checked using the Shapiro-Wilk test. The level of significance in both cases was set at $p < 0.05$. We used R, version 4.1.1 for data handling, analysis, and graphs (R Core Team, 2021).

3. Results

The pH of the soil horizons was acidic, except for the uppermost organic soil horizon (Oi) which mainly consists of the little decomposed litterfall (Table 1). The total carbon (TC) and total nitrogen (TN) concentrations and the TC/TN concentration ratios decreased markedly with increasing soil depth from the organic to the mineral horizons. The highest TC/TN ratios occurred in leaves followed by roots.

Table 1

Mean pH, Total Carbon (TC), Total Nitrogen (TN), and TC/TN Concentration Ratios of Leaves ($n = 10$), Roots ($n = 10$), and Soil Horizons ($n = 20$); and Quarterly Mean TOC Concentrations and TOC/DON and Nitrate/Ammonium Concentration Ratios (\pm Standard Deviations) in Ecosystem Solutions During the Period 2013–2016 ($n = 16$)

Solid samples	pH	TC mg g ⁻¹	TN mg g ⁻¹	TC/TN	Ecosystem solutions	pH	TOC mg L ⁻¹	TOC/DON	NO ₃ ⁻ -N/ NH ₄ ⁺ -N
Leaves		481 (\pm 16.7) e	12.4 (\pm 3.5) b	41.4 (\pm 8.6) e	Rainfall (RF)	4.8 (\pm 0.2) ab	2.5 (\pm 1.1) a	10.2 (\pm 2.0) a	1.4 (\pm 1.2) a
Roots		493 (\pm 8.6) e	12.5 (\pm 5.3) b	44.2 (\pm 16.7) e	Throughfall (TF)	6.2 (\pm 0.3) c	13.3 (\pm 5.6) c	15.9 (\pm 2.5) bc	1.6 (\pm 0.7) a
Oi	6.1 (\pm 0.7) b	436 (\pm 29.5) d	17.0 (\pm 4.2) b	24.1 (\pm 3.7) c	Stemflow (SF)	6.7 (\pm 0.3) d	26.8 (\pm 11.5) d	19.1 (\pm 2.8) d	1.3 (\pm 1.2) a
Oe	4.8 (\pm 0.3) a	373 (\pm 67.6) c	22.2 (\pm 3.6) c	17.3 (\pm 4.6) b	Litter leachate (LL)	4.9 (\pm 0.2) b	49.6 (\pm 14.7) e	22.2 (\pm 3.8) e	2.7 (\pm 1.6) a
Oa	4.0 (\pm 0.2) a	295 (\pm 124) b	33.9 (\pm 34) d	13.7 (\pm 3.8) a	Soil solution at the 0.15 m depth (SS15)	4.7 (\pm 0.1) a	7.6 (\pm 1.2) b	18.3 (\pm 2.1) cd	33 (\pm 9.1) c
A	4.3 (\pm 0.4) a	32.8 (\pm 13.3) a	2.6 (\pm 0.9) a	12.7 (\pm 2.0) a	Soil solution at the 0.30 m depth (SS30)	4.7 (\pm 0.1) a	5.9 (\pm 0.9) ab	18.8 (\pm 3.8) d	24 (\pm 7.0) b
B	4.7 (\pm 0.2) a	12.7 (\pm 8.8) a	1.2 (\pm 0.6) a	10.3 (\pm 2.7) a	Streamflow (ST)	7.0 (\pm 0.3) e	2.8 (\pm 2.5) a	15.1 (\pm 4.1) b	0.40 (\pm 0.20) a

Note. Different lowercase letters indicate significant differences among the plant and soil samples or the ecosystem solutions according to Tukey's HSD post-hoc test.

The pH increased from RF via TF to SF, decreased in the soil solutions (LL, SS15, SS30), and increased from SS30 to ST (Table 1). The TOC concentrations and TOC/DON ratios increased from RF via TF and SF to LL and then decreased from LL via SS15 and SS30 to ST. The NO₃⁻-N/NH₄⁺-N concentration ratios slightly increased from RF to LL, markedly in SS15 and SS30, and finally decreased markedly between SS30 and ST (Table 1).

The mean $\delta^{15}\text{N}$ values of the 10 considered tree species varied from -6.0 to -1.9‰ in leaves and from -3.6 to 1.6‰ in roots (Figure S2 in Supporting Information S1). The roots were N-isotopically heavier than the leaves by 2.2‰ and the difference was statistically significant according to a paired *t*-test. *Prunus opaca* Walp showed the lowest $\delta^{15}\text{N}$ value for leaves (-6.0‰) and *Matayba inelegans* Radlk. the highest value for roots (1.6‰). The $\delta^{15}\text{N}$ values in leaves of *Graffenrieda emarginata* Triana increased significantly from 2005 to 2015, while those of *Myrcia myrtiformis* Naudin. did not change (Figure S3 in Supporting Information S1).

Quarterly mean TDN, NH₄⁺-N, and DON concentrations increased in the order, RF < TF < SF < LL and then decreased in the order, SS15 > SS30 > ST (Figure 1). The highest mean quarterly NO₃⁻-N concentration was found in LL, which decreased slightly with increasing soil depth and strongly in ST. Aboveground, TF had the highest mean quarterly NO₃⁻-N concentration followed by stemflow and rainfall (Figure 1). The contribution of DON to TDN increased from 35% to 52% in the order TF < SF < LL and was lower in RF, SS15, SS30, and ST with a range of 21%–24%. The NH₄⁺-N contribution decreased from RF to LL (39%–17%), with the highest contribution in ST (59%) and the lowest in the mineral soil solutions (4%). The highest NO₃⁻-N contribution to TDN was found in soil solutions with 76% and the lowest in streamflow with 17% (Figure S4 in Supporting Information S1).

The bulk deposition, that is, the mass flux with RF, of N in Figure 2 was higher than the 5.2–11 kg ha⁻¹ at other tropical forest sites compiled by Boy et al. (2008a). The estimated mean fine particulate dry deposition of N without gaseous exchange, based on the mean annual Cl⁻ deposition ratio, was 1.7 times the bulk deposition. The high dry deposition may in part be related with the fact that in spite of the high precipitation at the study sites, there are frequent dry spells, which can even extend over several weeks during the veranillo in October/November (Peters et al., 2013; Wilcke et al., 2013). The N fluxes with TF had a similar size as the bulk N deposition, while the N fluxes with SF were negligibly small (Figure 2). The canopy budget of N was negative in all four study years indicating N retention by the canopy organisms (Figure 2).

The temporal variation in the $\delta^{15}\text{N}$ values of TDN were not related with the variation in monthly rainfall (Figure 3, Figure S3 in Supporting Information S1). The $\delta^{15}\text{N}$ values of TDN in RF, which were determined in selected weeks with sufficiently high N concentrations for isotopic analysis, showed the highest variation from 1.9 to 5.9‰ pointing at different N sources. The $\delta^{15}\text{N}$ value of TDN in TF varied from -2.6 to -1.0‰ reflecting the high variability in the $\delta^{15}\text{N}$ values of TDN in rainfall and in the leaves (Figure S2 in Supporting Information S1).

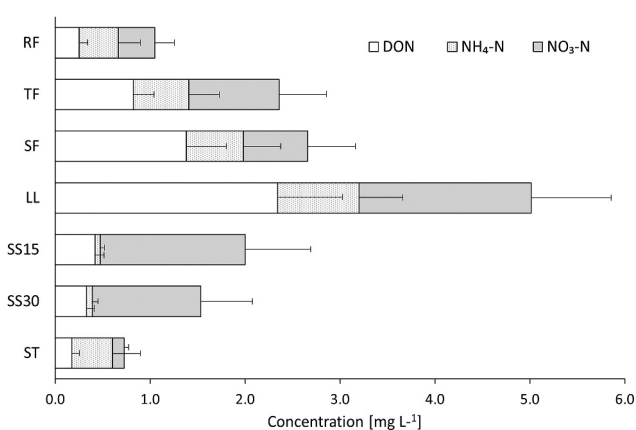


Figure 1. Mean quarterly concentrations of DON, NH₄⁺-N, and NO₃⁻-N from 2013 to 2016 in a tropical montane forest in south Ecuador. Error bars represent standard deviations. RF is rainfall, TF throughfall, SF stemflow, LL litter leachate, SS15 and SS30 mineral soil solutions at the 0.15 and 0.30 m depths, respectively, and ST streamflow.

4. Discussion

4.1. Temporal Variation in the δ¹⁵N Values of Total Dissolved Nitrogen in Rainfall

The δ¹⁵N values of TDN in RF showed the highest temporal variation of all ecosystem solutions in line with our first hypothesis that TDN in RF reflects temporally changing N sources (Figure 3). Similarly, Knapp et al. (2010) and (Rolff et al., 2008) reported that the δ¹⁵N values of TDN in rainfall in Bermuda and the Baltic Sea region varied strongly from −8.0 to +12.3‰. The δ¹⁵N values of NO₃⁻-N and NH₄⁺-N in RF, which are more frequently reported than those of TDN, showed a minimum of −7.7‰ for NH₄⁺-N and a maximum of +5.3‰ for NO₃⁻-N at a south Chinese subtropical forest site Koba et al. (2012). A wide variation in δ¹⁵N values (from −4.9‰ for NH₄⁺-N to 0.5‰ for NO₃⁻-N) in RF was also reported by Lee et al. (2012) in a Korean agricultural area. At our study site in Ecuador, Schwarz et al. (2011) found a variation from −2.64 to 2.76‰ for the δ¹⁵N values of NO₃⁻ in RF during differently wet quarters of one study year further confirming different sources of the

The δ¹⁵N values of SF varied from −1.2 to +1.0‰ with a mean value near 0‰, typical of N₂ fixation. Throughfall, SF, and LL showed a similar temporal pattern. The solutions at the 0.15 and 0.30 m mineral soil depths exhibited the lowest temporal variation. The δ¹⁵N values of ST, again determined in selected weeks with sufficiently high N concentrations, varied from −0.1 to 1.5‰ which was higher than in the soil solutions but lower than in RF (Figure 3).

The mean δ¹⁵N value of TDN in RF was the highest of all ecosystem solutions (Figure 4). The TDN in TF was N-isotopically lighter than in RF but heavier than in the leaves. The mean δ¹⁵N values of TDN increased in the order, TF < SF < LL. The mean δ¹⁵N value of TDN in LL was similar to the thickness-weighted mean δ¹⁵N value of the whole organic layer. The δ¹⁵N value of the organic horizons increased with increasing depth (i.e., Oi < Oe < Oa). Fine roots, a large part of which occurred in the organic layer, were N-isotopically lighter than the organic horizons but heavier than the leaves. The TDN in SS15 was N-isotopically lighter than in LL. Below-ground, the δ¹⁵N values of TDN increased in the order, SS15 < SS30 < ST. The δ¹⁵N values of the mineral A and B horizons were similar and N-isotopically heavier than the soil solutions (Figure 4).

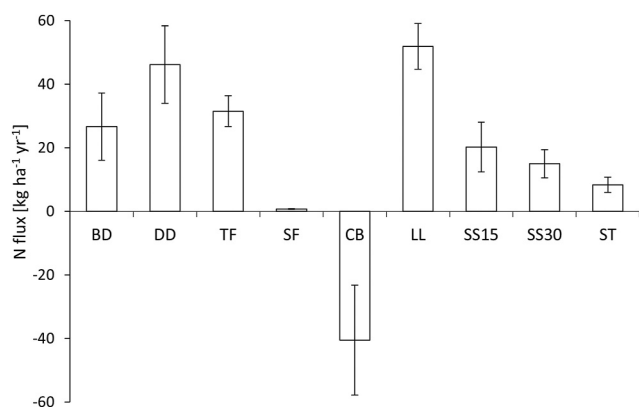


Figure 2. Mean annual N flux with bulk deposition (BD), dry deposition (DD, Equation 3), throughfall (TF), stemflow (SF), the resulting canopy budget (CB, Equation 1), litter leachate (LL), mineral soil solution at the 0.15 m (SS15) and 0.30 m depths (SS30), and streamflow (ST) from 2013 to 2016. The DD is based on the deposition ratio of Cl⁻ assuming negligible Cl⁻ leaching from the canopy and does not include the gaseous N exchange between the canopy and the atmosphere. The error bars represent standard deviations to illustrate temporal variation among the four study years.

N deposition to the study forest. Boy et al. (2008a) have shown that the forest fires of the Amazon basin were a major source of N deposition at our study site. These authors used a satellite-based fire pixel count to define “fire” and “no fire” periods in the Amazon basin and demonstrated that during the “fire” periods, both bulk and dry deposition of NO₃⁻-N, DON and total N were significantly higher than during “no fire” periods, because the emitted N is transported to the study area by the northeasterly trade winds that dominate during most of the year. The fact that the dry deposition of TOC was also significantly higher during “fire” than “no fire” periods in the Amazon basin points at a strong contribution of organic aerosols to dry deposition (Boy, Rollenbeck, et al., 2008). However, during a short period at the end of the year, westerly winds dominated and might have carried some N from anthropogenic emissions in the densely settled inter-Andean depression to our study site, although both bulk and dry deposition of N were lower than during the Amazonian “fire” periods (Boy, Rollenbeck, et al., 2008; Wilcke et al., 2013). Moreover, Alvarez et al. (2023) observed indications that occasional pasture fires in the near surroundings of the study site can also contribute to the N input at our study site, with likely a strong dry deposition component. Moreover, there might be some N emissions from the connection road between the provincial capitals of Loja and Zamora-Chinchipec, which passes nearby the study area and from local animal grazing. We suggest that the different sources of N (Amazonian and local vegetation fires, local and

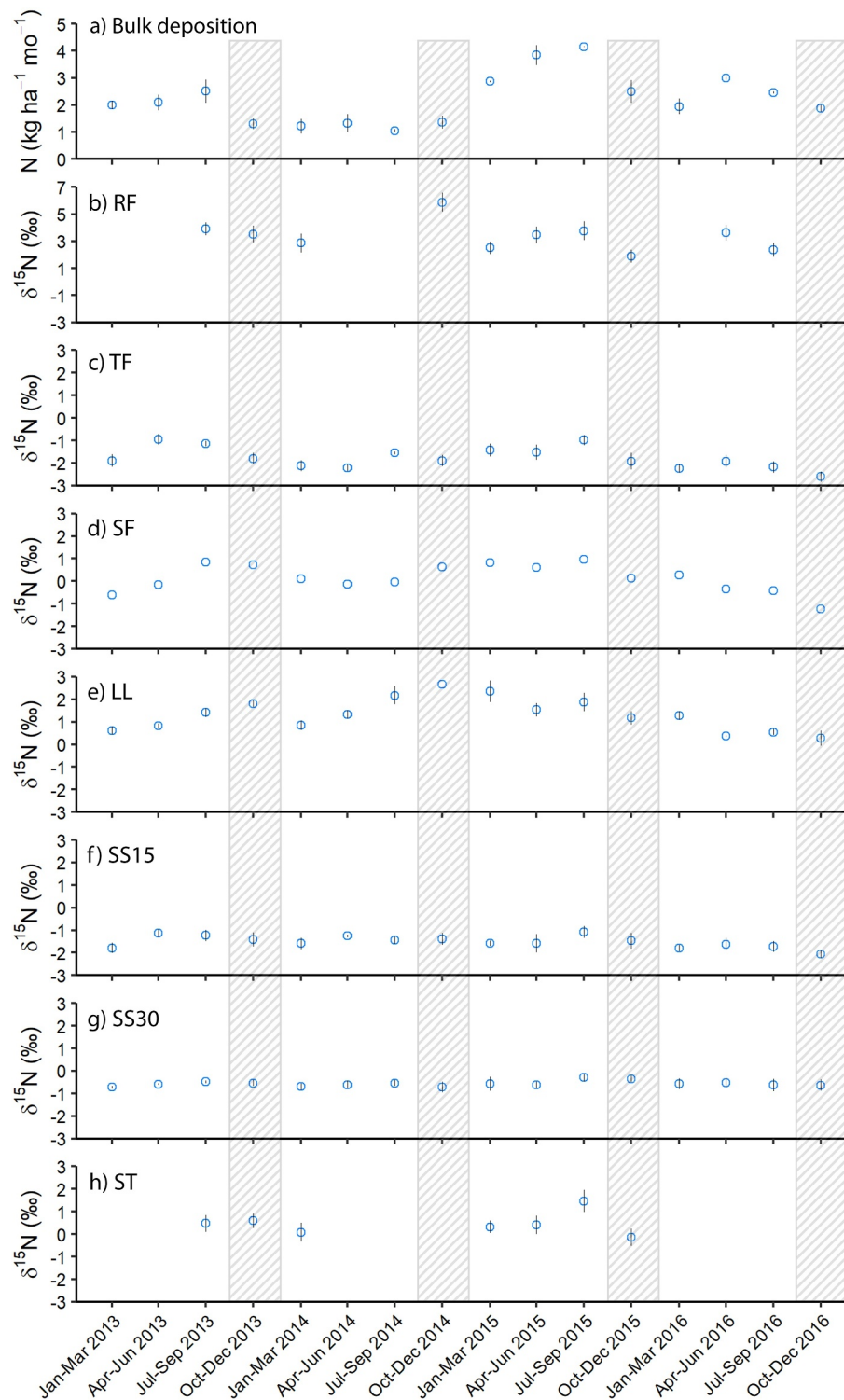


Figure 3. Bulk deposition of N (a) and course of the quarterly $\delta^{15}\text{N}$ values in ecosystem solutions along the water path through the forest ecosystem from January 2013 to December 2016 (b–g). Error bars represent the standard deviation of three study transects at approximately 1,900, 1,950, and 2,000 m a.s.l. RF is rainfall, TF throughfall, SF stemflow, LL litter leachate, SS15 and SS30 mineral soil solutions at the 0.15 and 0.30 m depths respectively, and ST streamflow. The $\delta^{15}\text{N}$ values in rainfall and streamflow could only be measured in individual weeks when the TDN concentrations were sufficiently high. Oblique hatching indicates the periods with the lowest rainfall and extended dry spells (the “veranillo”) (Figure S4 in Supporting Information S1). Mind the different Y axis scaling in (b) than in all other subfigures showing $\delta^{15}\text{N}$ values.

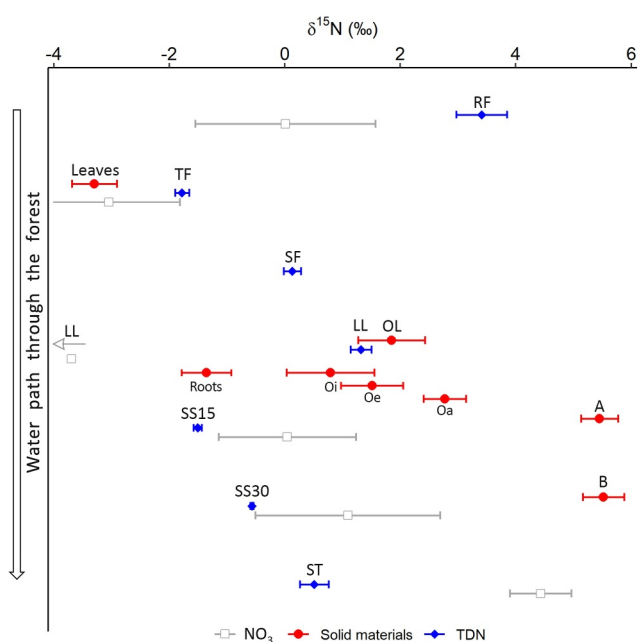


Figure 4. Mean $\delta^{15}\text{N}$ values of TDN (rhombi) and dissolved NO_3^- (squares) taken from Schwarz et al. (2011) in ecosystem solutions along the water path through the forest and in solid materials (circles) that could serve as source or sink of N. RF is rainfall, TF throughfall, SF stemflow, LL litter leachate, SS15 and SS30 mineral soil solutions at the 0.15 and 0.30 m depths, respectively, and ST stream flow. Leaves are live canopy leaves, OL is the organic layer, Oi, Oe, Oa are the three differently decomposed organic horizons, A and B are the mineral top- and subsoil horizons. Error bars represent standard errors referring to the means of quarterly samples of the ecosystem solutions (averaged for the three transects, $n = 16$ for TDN and $n = 4$ for NO_3^-), 20 Oi, Oe, Oa, A, and B horizons from the whole catchment, 20 horizon thickness-weighted organic layer means (OL), and 10 samples of each of fresh leaves and roots from 10 different tree species. The mean $\delta^{15}\text{N}$ value of NO_3^- in litter leachate was -7.43 ± 1.98 and is not shown to scale. To avoid the overlap of error bars, data points that should appear on the same level were slightly offset on the Y axis.

inner-Andean agriculture) explain the high variation in the $\delta^{15}\text{N}$ values of TDN in rainfall.

4.2. Change in the $\delta^{15}\text{N}$ Values of Total Dissolved Nitrogen From Rainfall to Litter Leachate

The finding that the $\delta^{15}\text{N}$ value of TDN decreased substantially from RF to TF partly supported our second hypothesis that expected decreasing $\delta^{15}\text{N}$ values from rainfall via throughfall and stemflow to litter leachate, because of increasing contributions of N-isotopically lighter N leached from the vegetation. However, against this hypothesis, the $\delta^{15}\text{N}$ values of TDN increased again in the order $\text{TF} < \text{SF} < \text{LL}$. The N-isotopically lighter TF than RF (Figure 4) concurred with a net N retention in the leaves as indicated by the negative canopy budget (Figure 2). The net retention of N in the canopy is in line with the reported N+P colimitation of the vegetation growth at our study site (Homeier et al., 2012; Velescu et al., 2016). Similarly, Boy et al. (2008a) observed net N retention in the forest canopy during the Amazonian “fire” period. Wullaert et al. (2010) and Velescu et al. (2016) reported that N was still retained in the canopy after the amendment of N as urea to the soil of the study forest in an accompanying fertilizer experiment next to our study site indicating that the study ecosystem has not yet reached N saturation. Still prevailing N limitation in spite of the on-going high N deposition is further suggested by a ratio of bulk deposition to N export with the stream of 3.2 during the study period (2013–2016; mean bulk deposition of $26.7 \text{ kg ha}^{-1} \text{ yr}^{-1}$ divided by the dissolved N export with ST of $8.4 \text{ kg ha}^{-1} \text{ yr}^{-1}$, Figure 2), particularly because Martinson et al. (2013) reported that even after the addition of 100 kg ha^{-1} of N as urea in the accompanying fertilization experiment, gaseous N_2O emission were still small ($0.1\text{--}0.2 \text{ kg ha}^{-1} \text{ yr}^{-1} \text{ N}_2\text{O-N}$ in the unfertilized controls and up to 1.4 kg ha^{-1} in the N+ P-fertilized treatments) so that gaseous N losses little influenced the catchment budget. If the estimated dry deposition of $46.2 \text{ kg ha}^{-1} \text{ yr}^{-1}$ was considered the input/output ratio would even increase to 8.7.

The N-isotopically lighter TF than RF can be explained by the preferred retention of isotopically heavy N in the deposition. Alternatively, N-isotopically light dry deposition could be dissolved in TF. Unfortunately,

we don't know the $\delta^{15}\text{N}$ value of the dry deposition so that we cannot explore this possibility further. It is well known that mineral N deposited from the atmosphere can be taken up by the plants via leaf surfaces and by canopy-dwelling organisms (Bourgeois et al., 2019; Dail et al., 2009; Guerrieri et al., 2015; Houle et al., 2015). In a mesocosm experiment, 40% of ^{15}N -labeled NH_4^+ sprayed on seedlings of *Populus euramericana* Neva was taken up by the leaves (Wang et al., 2021). However, a net N retention in the canopy does not mean that all N species are retained to the same degree so that a differential retention of different N species with different $\delta^{15}\text{N}$ values could help explain the change in the $\delta^{15}\text{N}$ values of TDN between RF and TF. Garten and Hanson (1990) reported that from the applied ^{15}N -labeled NH_4^+ and NO_3^- to the leaves of white oak and red maple via artificial rainfall, NH_4^+ was strongly retained (84% and 58%) while most of the NO_3^- was leached (73% and 87%, respectively). The apparent preferential retention of NH_4^+ might also be related with nitrification in the canopy as has been inferred by Schwarz et al. (2011) for our study region based on the N-isotopically lighter NO_3^- in TF than in RF (Figure 4).

Another possible reason for lower $\delta^{15}\text{N}$ values of TDN in TF than in RF would be the leaching of N-isotopically light N as DON. Although the $\delta^{15}\text{N}$ values in leaves of 10 common tree species varied considerably (-5.9 to -1.9‰ , Figure S2 in Supporting Information S1), which can in part be attributed to the species-specific uptake of different N species (Wittich et al., 2015), they were consistently N-isotopically lighter than the TDN (Figure 4). However, the fact that with increasing DON concentrations, the $\delta^{15}\text{N}$ values of TDN increased from TF via SF to LL rather pointed at a comparatively heavy N isotope ratio in the increasingly leached DON (Figure 1). Thus, the decreasing $\delta^{15}\text{N}$ values of TDN in TF relative to RF can probably be explained by the preferential retention of N-

isotopically heavy N in the canopy, presumably mainly as NH_4^+ , and the leaching of N-isotopically light NO_3^- , partly produced by nitrification in the canopy.

A representative leaching of N from the bark or bark-associated lichens might not explain the higher $\delta^{15}\text{N}$ values of TDN in SF than in TF (Figure 4), because Feng et al. (2008) reported that the outer bole bark of old Norway spruce trees (*Picea abies* (L.) Karst) with a $\delta^{15}\text{N}$ value of -4.8‰ was even N-isotopically lighter than other tree tissues. Moreover, lichens growing on the bark of a Norway spruce forest were N-isotopically lighter than the bark itself (-8.7 to -3.5‰ ; Potapov et al. (2018)). In a study of 665 samples of lichen, moss, and bark samples, the $\delta^{15}\text{N}$ values ranged from -15.2 to -1.5‰ (Boltersdorf et al., 2014). Most of the $\delta^{15}\text{N}$ values in bark and bark-associated lichens or mosses in the literature have been reported from the temperate zone and it is unclear if these findings can be transferred to the tropics. In the only study of a tropical forest, we found, the $\delta^{15}\text{N}$ values of bark were around 0‰ and thus had a similar $\delta^{15}\text{N}$ value than the TDN in our SF (Wang et al., 2018). Moreover, leaching of N originating from N_2 -fixing organisms like cyanobacteria living on the bark which should show a $\delta^{15}\text{N}$ value close to 0‰ could contribute to explain the $\delta^{15}\text{N}$ values of TDN in our SF. In a forest in south Chile dominated by *Nothofagus* and *Araucaria* trees, the cyanolichen *Pseudocyphellaria berberina* (G. Forster) D. Galloway & P. James and *Pseudocyphellaria coriifolia* (Müll. Arg.) Malmé sampled from the tree barks (both including *Nostoc* sp.) had a $\delta^{15}\text{N}$ value of -3.1 and -2.8‰ (Pérez et al., 2017) and were enriched in ^{15}N relative to the bark, but showed lower $\delta^{15}\text{N}$ values than the TDN in our SF. Additionally, SF might also contain more unchanged rainfall-N than TF, because of a faster flow of RF water along the trunks of the trees than during the partly cascading passage through the canopy and thus include more of the N-isotopically heavier RF-N than TF. Therefore, leaching of isotopically heavy compounds from the bark and/or a higher contribution of unchanged RF could explain the $\delta^{15}\text{N}$ values in SF in contrast to our second hypothesis.

Again in contrast to our second hypothesis, the $\delta^{15}\text{N}$ values of TDN in the LL were higher than in TF and SF (Figure 4). The similar $\delta^{15}\text{N}$ values of TDN in the LL and total N in the organic layer and the highest N concentration of all ecosystem solutions suggested a strong role of DON leaching from the organic layer (Figures 1 and 4). This assumption is corroborated by the highest DON contribution to total N in LL of all ecosystem solutions (Figure S4 in Supporting Information S1). Because the dissolved organic matter (DOM) in litter leachate was dated at approximately 10 years (Wilcke et al., 2002), which corresponds to the mean residence time of the organic layer at our study site (Wilcke et al., 2020), it can be concluded that the increase in DON concentrations originated mainly from the leaching of the Oa horizon and that the resulting $\delta^{15}\text{N}$ value of TDN represents a mixture of DON leached from the Oa horizon and N from TF and SF. The many roots in the organic layer (Soethe et al., 2007) showed a much lower $\delta^{15}\text{N}$ value than TDN in LL and are therefore unlikely to contribute to the TDN in the LL (Figure 4). Similarly, the nitrification that had been observed by Schwarz et al. (2011) in the organic layer and subsequent stronger leaching of N-isotopically light NO_3^- supported by the strong increase in the $\text{NO}_3^-/\text{N}/\text{NH}_4^+/\text{N}$ ratio between TF/SF and LL (Wilcke et al., 2013) (Table 1) cannot have markedly contributed to the $\delta^{15}\text{N}$ value of TDN in LL, because it would have shifted the $\delta^{15}\text{N}$ to lower values.

4.3. Change of the $\delta^{15}\text{N}$ Values of Total Dissolved Nitrogen From Litter Leachate to Topsoil Solution

The abrupt decrease in the $\delta^{15}\text{N}$ values of TDN from LL to SS15 indicated strong sorption of N-isotopically heavy DON in the upper mineral soil (Figure 4). The assumed DON sorption is in line with the strongly decreasing DON contribution to total N in the mineral soil solutions (Figure 1 and Figure S4 in Supporting Information S1). These results support our third hypothesis which expected decreasing $\delta^{15}\text{N}$ values from litter leachate to the mineral soil because of the strong retention of N-isotopically heavy DON and NH_4^+ with respect to the role of DON. In line with our interpretation, Michalzik et al. (2001) explained the decreasing DON concentrations with increasing depth by either strong selective sorption on mineral surfaces or decomposition. Sorption has been shown in the field and in laboratory experiments to be more important than decomposition in mineral soil horizons (Qualls & Haines, 1991, 1992; Vandenbruwane et al., 2007). Another explanation for lower $\delta^{15}\text{N}$ values of TDN in SS15 than in LL could be an addition of N-isotopically light inorganic N from mineralization and nitrification. However, Schwarz et al. (2011) had shown that NO_3^- in SS15 was N-isotopically heavier than in LL (Figure 4), so that this NO_3^- would increase the $\delta^{15}\text{N}$ values of TDN in SS15, while we observed the opposite. Dissolution of N from the A horizon or contributions of N-isotopically heavy microbial N compounds can be largely ruled out because of their much higher $\delta^{15}\text{N}$ values than in the TDN of SS15 (Dijkstra et al., 2006). On the contrary, some contributions of N from the N-isotopically similar roots to SS15 seem possible and can also contribute to explain the shift between LL and SS15. The latter would be similar to the likely contribution of roots to the DOM in mineral soil

solutions suggested by Wilcke et al. (2020) and Alvarez et al. (2023). The decrease in NH_4^+ concentrations from LL to SS15 (Figure 1) suggests that the sorption of isotopically heavy NH_4^+ to clay minerals such as the illites that occur in the study soils (Schrumpf et al., 2001) contributed to the shift in $\delta^{15}\text{N}$ values of TDN from LL to SS15, which would support our third hypothesis also with respect to NH_4^+ . Finally, the similar $\delta^{15}\text{N}$ values of TF and SS15 suggest that some direct leaching of throughfall into the mineral soil without changing the $\delta^{15}\text{N}$ values of TDN could also have contributed to the $\delta^{15}\text{N}$ value of TDN in SS15. The latter had already been suggested by Wilcke et al. (2020) based on the young age of DOM in SS15 of only approximately 1 year.

4.4. Change in the $\delta^{15}\text{N}$ Values of Total Dissolved Nitrogen From Topsoil Solution to Streamflow

The $\delta^{15}\text{N}$ values of TDN increased in the order, SS15 < SS30 < ST (Figure 4), supporting our fourth hypothesis that the $\delta^{15}\text{N}$ values of TDN increase from mineral topsoil via subsoil solution to stream water because of increasing denitrification. In line with similar findings for the $\delta^{15}\text{N}$ values of NO_3^- of Schwarz et al. (2011) (Figure 4), N-isotopically light gaseous N losses by increasing denitrification with increasing depth seem to be the most likely explanation. Denitrification in the subsoil is further supported by the fact that the NO_3^- concentrations decreased strongly from the soil solutions to the streamflow suggesting that a large part of NO_3^- was consumed by denitrification (Figure 1). The total loss of NO_3^- -N between SS15 and ST amounted to $13.8 \text{ kg ha}^{-1} \text{ yr}^{-1}$, of which $9.8 \text{ kg ha}^{-1} \text{ yr}^{-1}$ were lost between SS30 and ST. While in the topsoil there is likely still considerable uptake of NO_3^- by soil organisms and plants, in the deeper soil most of this loss is more likely attributable to denitrification which thus results in a total gaseous N loss in the range of a few kg. This is higher than reported by Martinson et al. (2013), who, however, only measured N_2O -N losses but not N losses as other N gases like NO and N_2 . Moreover, the measurements of Martinson et al. (2013) date back to the years 2008–2009, while until our observation period (2013–2016) the N deposition has further increased. Interestingly, there must have been a source of NH_4^+ to the stream because the NH_4^+ concentrations increased strongly in streamflow relative to the mineral soil solutions. This NH_4^+ might have been flushed from the organic layers directly into the stream as was observed during strong rain events by Boy et al. (2008b), because of a fast responsiveness of the shallow catchment to rainfall events at the scale of hours to days (Goller et al., 2005). Alternatively, the NH_4^+ in ST might originate from mineralization of subsoil organic matter. Both the organic layer and the subsoil organic matter showed markedly higher $\delta^{15}\text{N}$ values than the mineral soil solutions so that the NH_4^+ released by mineralization possibly also showed a high $\delta^{15}\text{N}$ value (Figure 4). The NH_4^+ in streamflow could also have been released from sequestered NH_4^+ in clay minerals or the phyllite by weathering. In line with this assumption, Steffens and Sparks (1997) reported the release of nonexchangeable NH_4^+ from clay minerals and Smith et al. (1994) showed that this release only occurred at low NH_4^+ concentrations in soil solutions, which was indeed the case for the mineral soil solutions at our study site (Figure 1). To explain why NH_4^+ only seems to be released by weathering in the deeper soil and the riparian zone, we speculate that at the 0.3 m soil depth the conditions were still sufficiently aerobic so that any potentially released NH_4^+ was quickly immobilized or nitrified, while the riparian zone was sufficiently anaerobic to reduce organismic uptake and prevent nitrification so that the weathered NH_4^+ could be released into the stream water. Unfortunately, we don't know the $\delta^{15}\text{N}$ value of the NH_4^+ sequestered in soil clay minerals or parent rock. Moreover, some N-isotopically heavy NH_4^+ might have been released from dying microorganisms which are usually enriched in ^{15}N relative to extractable and total N in soil (Coyle et al., 2009; Dijkstra et al., 2006, 2008). Our finding of elevated NH_4^+ concentrations in ST relative to the soil solutions is in line with reports that the soil solution in riparian zones and groundwater are frequently rich in ammonium (Hill, 1990; Young & Briggs, 2005).

4.5. Temporal Variation in the $\delta^{15}\text{N}$ Values of Ecosystem Solutions

The $\delta^{15}\text{N}$ values of TDN in all ecosystem solutions showed a considerable temporal variation, which roughly paralleled that of the $\delta^{15}\text{N}$ values of TDN in RF and TF and was increasingly delayed and dampened along the water path through the ecosystem, particularly in the mineral soil (Figure 3). Thus, the input signal of deposited N, as reflected by TF which includes bulk and dry deposition, was passed through the ecosystem. In addition to the input signal, there are processes that further modify the $\delta^{15}\text{N}$ values of TDN in ecosystem solutions. In several studies, leaf $\delta^{15}\text{N}$ values were negatively correlated with mean annual rainfall and water availability, that is, during moist conditions leaves were N-isotopically lighter than during dry conditions (Handley et al., 1999; Roa-Fuentes et al., 2015). This pattern was also confirmed by a modeling approach that showed that water availability was the main driver of leaf $\delta^{15}\text{N}$ values (Vitousek et al., 2021). As a consequence, the TDN leached from leaves,

bark, and the Oi horizon (containing newly fallen leaves) should show lower $\delta^{15}\text{N}$ values during wet than during dry phases. In our study area, TF, SF, and LL showed the lowest $\delta^{15}\text{N}$ values of TDN from April to December 2016 (Figure 3), which is in line with the increasing precipitation from 2013 to 2016 (from 2,075 to 2,586 mm, Figure S5 in Supporting Information S1). The highest $\delta^{15}\text{N}$ values of TDN were observed during October–December 2013 and 2014. This is in line with the fact that during the observation period from 2013 to 2016 the last quarter of the year showed the lowest mean precipitation (412 ± 13 mm) of all quarters (Quarters 1–3: 565–795 mm) in the San Francisco Biological Reserve (Figure S5 in Supporting Information S1).

In the soil solution at the 0.15 cm depth (SS15), the $\delta^{15}\text{N}$ values were slightly higher in July–September 2015 (Figure 3), which is consistent with a low precipitation period (Figure S5 in Supporting Information S1). Lower $\delta^{15}\text{N}$ values of TDN were observed from January to December 2016, a period with high precipitation (Figure S5 in Supporting Information S1). Soil water content and temperature together have been reported as main drivers of mineralization (Curtin et al., 2012; Glass et al., 2023). Under aerobic conditions, mineralization rates increase with increasing temperature and soil moisture (Jin et al., 2013). Therefore, higher mineralization rates in the least moist periods could have released more N-isotopically heavy N from the solid phase organic matter than during wetter periods in this perhumid forest, where water logging occurs frequently. During wet phases, denitrification should be enhanced because of the lower redox potential, which would drive the $\delta^{15}\text{N}$ of TDN to higher values as a consequence of the enhanced release of N-isotopically light N gases. However, in SS30, we did not observe such a change and in ST we lack $\delta^{15}\text{N}$ values of TDN for the wettest period, that is, the second and third quarters of the year 2016 (Figure 3). In summary, our fifth hypothesis that expected that the changes in the $\delta^{15}\text{N}$ values of TDN in ecosystem solutions showed a temporal variation reflecting temporally variable strengths of the various N sources and sinks is largely not supported, because ecosystem processes apparently contributed little to the observed temporal variation of the $\delta^{15}\text{N}$ values of TDN in ecosystem solutions, which were mainly inherited from RF.

5. Conclusions

Our results confirmed the first hypothesis that the highest variation in the $\delta^{15}\text{N}$ values of TDN of all studied solution types occurred in RF. We attribute this to varying contributions of N from different sources. The $\delta^{15}\text{N}$ value of TDN decreased strongly in TF relative to RF. The reasons included a net N retention, particularly of the likely N-isotopically heavy NH_4^+ , and leaching of N-isotopically light NO_3^- . This partly confirmed our second hypothesis. However, against our second hypothesis, the $\delta^{15}\text{N}$ values in TDN increased in the order $\text{TF} < \text{SF} < \text{LL}$, along with increasing contributions of likely N-isotopically comparatively heavy DON to the TDN. The abrupt decrease in the $\delta^{15}\text{N}$ value of TDN between LL and SS15 can be attributed to the sorption of DON in the first centimeters of the mineral soil. Moreover, N-isotopically light NO_3^- from nitrification and N from TF, that was flushed unchanged through the organic layer might have contributed to the TDN in SS15. Together, this supported our third hypothesis. The increasing $\delta^{15}\text{N}$ values in the order $\text{SS15} < \text{SS30} < \text{ST}$ can mainly be explained by gaseous N losses because of increasing denitrification with increasing soil depth which is in line with our fourth hypothesis. However, we had to largely reject our fifth hypothesis, because most of the variation in the $\delta^{15}\text{N}$ value of TDN in all ecosystem solutions was inherited from RF, while in situ processes in the ecosystem were still detectable but seemed to play a smaller role than the variation in the $\delta^{15}\text{N}$ values of TDN in the atmospheric input. Our results demonstrate that the $\delta^{15}\text{N}$ values of TDN in ecosystem solutions indeed provide information about N sources and sinks in forest ecosystems and thus offer a novel straight-forward approach to explore the fate of N in forest ecosystems. This approach is particularly suitable for long-term observations in high temporal resolution.

Global Research Collaboration

The first draft of this manuscript was written by an Ecuadorian Ph.D. student from the Universidad Nacional de Loja, Ecuador who is the first author and who has conducted most of the analytical work at the Karlsruhe Institute of Technology in Germany, where he is enrolled as a doctoral student. The study was realized in the frame of a long-term German-Ecuadorian cooperation since 1997, resulting in a multitude of international scientific publications with shared German-Ecuadorian authorships, extensive capacity building of Ecuadorian scientists at the level of university certificates and doctoral studies, several information booklets in Spanish language on the research results, a long-standing cooperation with the nongovernmental organization Nature and Culture International who provided the study area, and regular public scientific symposia hosted by the Ecuadorian partner

universities in Ecuador. All work was realized in compliance with the national laws of Ecuador under a repeatedly renewed research permit.

Data Availability Statement

We have uploaded the original data to the data repository Pangaea (<https://www.pangaea.de>). From there it can be retrieved openly under <https://doi.org/10.1594/PANGAEA.968791> (Alvarez et al., 2024a) and <https://doi.org/10.1594/PANGAEA.968797> (Alvarez et al., 2024b).

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