

Dissolved nitrogen, phosphorus, and sulfur forms in the ecosystem fluxes of a montane forest in Ecuador

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Abstract. The N, P, and S cycles in pristine forests are assumed to differ from those of anthropogenically impacted areas, but there are only a few studies to support this. Our objective was therefore to assess the controls of N, P, and S release, immobilization, and transport in a remote tropical montane forest. The study forest is located on steep slopes of the northern Andes in Ecuador. We determined the concentrations of NO₃-N, NH₄-N, dissolved organic N (DON), PO₄-P, dissolved organic P (DOP), SO₄-S, dissolved organic S (DOS), and dissolved organic C (DOC) in rainfall, throughfall, stemflow, lateral flow (in the organic layer), litter leachate, mineral soil solution, and stream water of three 8–13 ha catchments (1900–2200 m a.s.l.). The organic forms of N, P, and S contributed, on average, 55, 66, and 63% to the total N, P, and S concentrations in all ecosystem fluxes, respectively. The organic layer was the largest source of all N, P, and S species except for inorganic P and S. Most PO₄ was released in the canopy by leaching and most SO₄ in the mineral soil by weathering. The mineral soil was a sink for all studied compounds except for SO₄. Consequently, concentrations of dissolved inorganic and organic N and P were as low in stream water (TDN: 0.34–0.39 mg N l⁻¹, P not detectable) as in rainfall (TDN: 0.39–0.48 mg N l⁻¹, P not detectable), whereas total S concentrations were elevated (stream water: 0.04–0.15, rainfall: 0.01–0.07 mg S l⁻¹). Dissolved N, P, and S forms were positively correlated with pH at the scale of soil pedo except inorganic S. Soil drying and rewetting promoted the release of dissolved inorganic N. High discharge levels following heavy rainstorms were associated with increased DOC, DON, NO₃-N and partly also NH₄-N concentrations in stream water. Nitrate-N concentrations in the stream water were positively correlated with stream discharge during the wetter period of the year. Our results demonstrate that the sources and sinks of N, P, and S were element-specific. More than half of the cycling N, P, and S was organic. Soil pH and moisture were important controls of N, P, and S solubility at the scale of individual soil pedo whereas the flow regime influenced the export with stream water.

Introduction

The major purpose of forest ecosystem research in the past decades was to assess the human impact on cycles of C, N, P, and S (Likens and Bormann 1995; Matson et al. 1999; Matzner 2004). To understand these cycles, element

sources and sinks and controls of their mobility have to be identified. The biogeochemical cycles of N, P, and S are complex because of the many different chemical species involved. Furthermore, they are influenced by fertilizer use and the deposition of NO_x and SO_2 released during combustion of fossil fuels. This impact changed the natural N, P, and S cycles in most forest ecosystems of the temperate zone (Likens and Bormann 1995; Stevenson and Cole 1999; Van Breemen 2002). In remote tropical montane forests, in contrast, the human impact is still likely to be small.

It has been hypothesized that in native ecosystems not affected by anthropogenic inputs organic N species contribute more to element cycles than in the forests of the industrialized world, where inorganic N dominates N fluxes (Perakis and Hedin 2002; Van Breemen 2002). However, the data basis to support this hypothesis is small. Furthermore, it is unknown whether P and S cycles are similarly affected.

The main 'reactor' compartments of forests are the canopy and the soil. The canopy of tropical forests can be a sink for plant nutrients because of their uptake by the leaves (Bentley 1987; Schrumpf 2004), but nutrients can also be leached from the canopy. This might be particularly true for organic species (Lilienfein and Wilcke 2004). Dissolved organic N, e.g., can account for about 50% of the total N concentrations in throughfall (Qualls et al. 1991). According to Parker (1983), who reviewed a large number of throughfall and stemflow studies in forests all around the world, canopy leaching has proved to be the major source of dissolved PO_4 contributing 70–90% to throughfall PO_4 . Furthermore, nutrients can be released because of the mineralization of dead organic matter accumulated in the canopy (Bentley and Carpenter 1980; Coxson 1990).

In temperate forests, the soil organic layer is usually the main source of dissolved organic matter (DOM) including associated N, P, and S (Kaiser et al. 2000; Kalbitz et al. 2000; Michalzik et al. 2001). It is frequently a sink of inorganic N, P, and S in temperate and tropical forests because of microbial immobilization (Yavitt and Fahey 1986; Qualls et al. 1991; Alewell et al. 1999) and conservation by roots and mycorrhizae (Stark and Jordan 1978; Cuevas and Medina 1986). In some tropical forests, however, inorganic N concentrations in litter leachate are higher than in throughfall. This indicates that inorganic N is leached from the organic layer material because N release rates by mineralization are higher than the requirement of the vegetation and soil microorganisms (Hafkenschied 2000; Wilcke et al. 2001; Schrumpf 2004). Dissolved P in forests on acid soils cycles mainly between the canopy and the organic layer because of P fixation in the mineral soils (Sanchez 1976; Sollins et al. 1988; Stevenson and Cole 1999). In litter leachates from Germany, DOP was the dominant P form (79–81%, Kaiser et al. 2000). In the O horizon of a boreal forest in Canada, in contrast, DOP only contributed 25% to total dissolved P (Huang and Schoenau 1998). The microbial release of SO_4 during mineralization is a major source of soluble S in many soils (Stevenson and Cole 1999). Organic S contributed up to 54% to total S in ecosystem fluxes of eight catchments under temperate forest in the USA (Homann et al. 1990).

Important controls of element cycles on the pedon and catchment scale are soil pH and the water flow regime. Although an increasing pH promotes the release of DOM (Kalbitz et al. 2000), results from laboratory and field experiments are inconsistent (Michalzik et al. 2001). Contrasting results have also been reported concerning the effect of pH on microbial activity and the associated nitrification rate. While some authors conclude that low pH reduces nitrification because of reduced activities of autotroph nitrifiers (Kilham 1990), others did not detect a significant relationship between pH and nitrification rates (Robertson 1982).

The water flux in soils is a major control of the dynamics of inorganic N (Mitchell 2001), DOC and DON (Hagedorn et al. 2000), total P (Frangi and Lugo 1985), DOP and DOS (Kaiser et al. 2000) in forested water catchments, especially after rainstorms. Therefore, it can be hypothesized that the influence of the water flux on element dynamics in tropical regions, which are typically characterized by frequent rainstorms associated with high rainfall volumes and intensity, should be prominent (Schellekens 2000). Furthermore, small water catchments on steep hillslopes show a rapid response of catchment discharge to strongly increasing rainfall volumes (Mulholland et al. 1990; Schellekens 2000). The increase in DOC concentrations in catchment runoff during peakflow has been documented in numerous studies (e.g., Jardine et al. 1990; Brown et al. 1999; Casper 2002). Similar observations were reported for NO₃ by Mitchell (2001) and for dissolved P by Frangi and Lugo (1985). Earlier results from our study forest in Ecuador showed that during rainstorms a large portion of the rain water drains quickly in lateral direction through the near-surface soil to the stream (Goller et al. 2005). This resulted in elevated DOC concentrations in stream water (Wilcke et al. 2001).

The above compilation of literature results shows that we are far from being able to draw generalized conclusions concerning sources and sinks of N, P, and S in forest ecosystems and the controls of their transfer processes. Therefore, our objectives were to (i) quantify the contribution of organic forms to the cycling of N, P, and S, (ii) identify sources and sinks of N, P, and S and (iii) to assess the controls of their release and immobilization in a remote tropical montane forest located on steep slopes of the northern Andes in Ecuador. We hypothesized that (i) organic forms contributed substantially to the element cycles, (ii) the thick organic layer with its large stock of nutrients is the major source of N, P, and S and (iii) transfer processes of these elements are mainly controlled by the hydrological processes in catchments.

Materials and methods

Study area

The study area is located on the eastern slope of the 'Cordillera Real', the eastern Andean cordillera in south Ecuador facing the Amazon basin

between the cities of Loja and Zamora at $4^{\circ}00' S$ and $79^{\circ}05' W$. We selected three $30\text{--}50^{\circ}$ steep and $8\text{--}13$ ha large microcatchments (MC1–3) under montane forest at an altitude of $1900\text{--}2200$ m above sea level (a.s.l.) for our study (Figure 1). We installed our equipment in each MC on transects, about 20 m long with an altitude range of 10 m, on the lower part of the slope at $1900\text{--}1910$ m a.s.l. (transects MC1, MC2.1, and MC3). Moreover, we installed extra instrumentation at $1950\text{--}1960$ (MC2.2) and $2000\text{--}2010$ m a.s.l. (MC2.3). All transects were located below forest canopy and aligned downhill. Three unforested sites near these microcatchments were used for rainfall gauging. Gauging site 2 existed since April 1998, gauging sites 1 and 3 were built in May 2000. All catchments drain via small tributaries into the Rio San Francisco which flows into the Amazon basin.

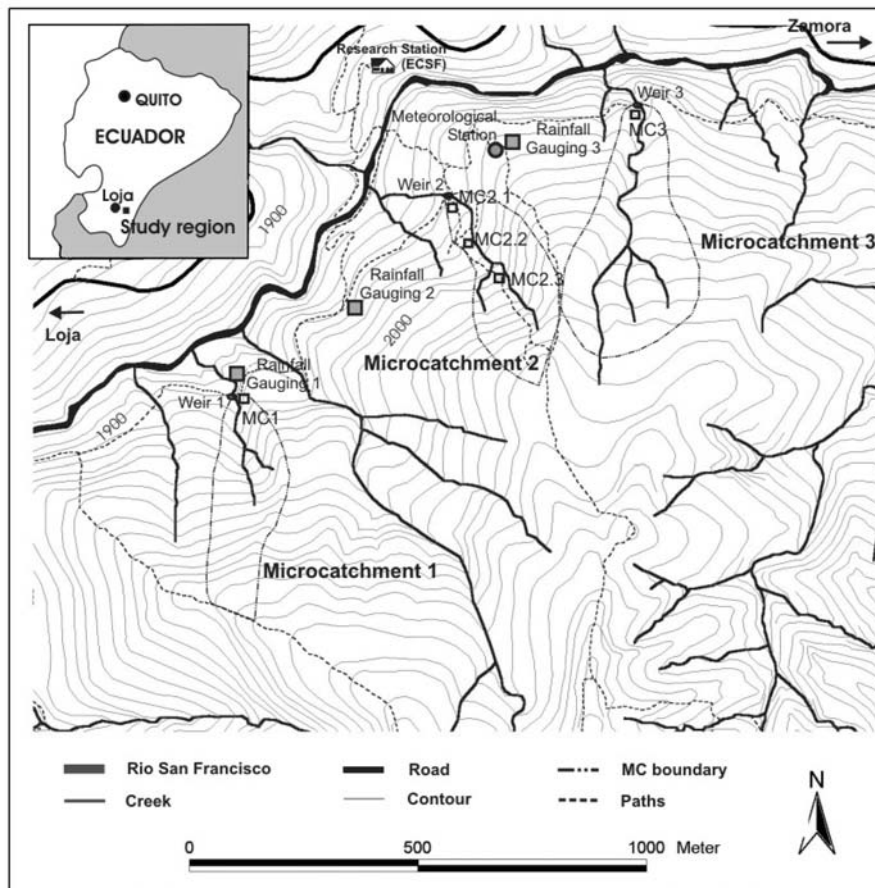


Figure 1. Location of the study area.

Within the monitored period between May 1999 and April 2002, on average 2448 mm y^{-1} of precipitation fell on the study area; 2107 mm fell during the first hydrological year (May 1999 to April 2000), 2643 mm y^{-1} during the second (May 2000 to April 2001), and 2594 mm y^{-1} during the third (May 2001 to April 2002). Additional climate data were available from a meteorological station (P. Emck, personal communication) between MC2 and MC3 (Figure 1). June tended to be the wettest month with 302 mm of precipitation on average, in contrast to 78 mm in each of November and January, the driest months. The mean temperature at 1950 m a.s.l. was 15.5 °C. The coldest month was July, with a mean temperature of 14.5 °C, the warmest November with a mean temperature of 16.6 °C.

Recent soils have developed on postglacial landslides or possibly from periglacial cover beds (Wilcke et al. 2001). Soils are Humic Eutrudepts on transect MC1, Humic Dystrudepts on transects MC2.1, MC2.2, and MC2.3, and Oxyaquic Eutrudepts on transect MC3 (USDA-NRCS 1998). All soils are shallow, loamy-skeletal with high mica contents. The organic layer consisted of Oi, Oe, and frequently also Oa horizons and had a thickness between 2 and 43 cm (mean of 16 cm; Wilcke et al. 2002). The thickness increased with increasing altitude giving Histosols (mainly Terric Haplosaprists) above ca. 2100 m. Selected soil properties are summarized in Table 1. The underlying bedrock consists of interbedding of paleozoic phyllites, quartzites and meta-sandstones (the ‘Chiguinda unit’ of the ‘Zamora series’ in Hungerbühler 1997).

Table 1. Selected mean soil properties at five study transects in an Ecuadorian lower montane forest (taken from Wilcke et al. 2001; $n = 3$ on each transect, except effective cation-exchange capacity (ECEC) and base saturation (BS), which were only analyzed in one combined sample per transect).

Horizon	Transect	ECEC (mmol _c kg ⁻¹)	BS (%)	pH (H ₂ O)	C (g kg ⁻¹)	N (g kg ⁻¹)	P (g kg ⁻¹)	S (g kg ⁻¹)
O	MC1			6.3	404	26	1.2	3.0
	MC2.1			4.4	408	23	1.0	3.0
	MC2.2			4.4	338	20	0.9	2.3
	MC2.3			4.7	403	24	1.1	2.9
	MC3			6.2	394	24	1.2	2.8
A	MC1	47	95	5.1	28	3.2	0.7	0.5
	MC2.1	83	6.3	4.3	44	3.6	0.7	0.5
	MC2.2	92	10	3.9	62	4.7	0.7	0.6
	MC2.3	49	62	4.7	22	2.3	0.7	0.4
	MC3	150	95	5.3	52	4.8	0.9	0.6
B	MC1	39	22	5.1	12	1.6	0.6	0.3
	MC2.1	68	6.1	4.8	19	1.8	0.4	0.3
	MC2.2	135	4.8	4.4	37	2.8	0.5	0.4
	MC2.3	37	35	4.8	12	1.5	0.6	0.3
	MC3	35	81	5.8	21	2.4	0.6	0.4

Microcatchments 2 and 3 are entirely forested, whereas the upper part of microcatchment 1 has been used for agriculture until about 10 years ago. This part is currently undergoing natural succession and is covered by grass and shrubs. The study forest can be classified as 'bosque siempreverde montaño' (evergreen montane forest, Balslev and Øllgaard 2001) or as Lower Montane Forest (Bruijnzeel and Hamilton 2000). More information on the composition of the forest can be found in Wilcke et al. (2001) and Homeier (2004).

Field sampling

Water samples were collected between May 1999 and April 2002 for N and between May 2000 and April 2001 for P and S analyses on a weekly basis. For P and S analyses, weekly samples were combined to monthly samples in the field laboratory.

Each gauging station for incident precipitation consisted of five samplers. Solution sampled by rainfall collectors was 'bulk precipitation' (Whitehead and Feth 1964), since collectors were open to dry deposition between rainfall events (Parker 1983). However, the contribution of dry deposition to rainfall collectors was assumed to be small because of the small sampling area compared to the 'aerosol trapping capacity' of the entire forest (Parker 1983).

Each of the five transects was equipped with five throughfall collectors (in May 2000 three more collectors were added on each transect). All throughfall samplers had a fixed position that was arbitrarily chosen and evenly distributed along the transects. To rove samplers after each sample collection, as suggested by Lloyd and Marques (1988), to improve the representativity of the sample would have resulted in an unacceptable damage to the study forest that was only accessible on very steep machete-cleared and rope-secured paths. More information on our throughfall measurement can be found in Fleischbein et al. (2005).

We furthermore installed three collectors for lateral flow (cutting the slope at a right angle in the organic layer) and litter leachate (collection of water vertically percolating through the organic layer) at lower, central, and upper positions along the transects and three suction lysimeters for soil solution sampling at each of the 0.15 and 0.30 m depths in the mineral soil at central position of the transect. A combined sample for each transect was produced by bulking the single samples directly in the field. Soil solution was sampled since May 2000 after equilibration of the lysimeters in the soil for 4 months. Stream water samples were weekly taken from the center of the streams at the outlet of each catchment.

Throughfall and rainfall collectors consisted of fixed 1-l polyethylene sampling bottles and circular funnels with a diameter of 115 mm. The opening of the funnel was at 0.3 m height above the soil. The collectors were equipped with table tennis balls to reduce evaporation. Incident rainfall collectors were

additionally wrapped with aluminum foil to reduce the impact of radiation. Stemflow collectors were made of polyurethane foam and connected with plastic tubes to a 10-l container (Likens and Eaton 1970). In each catchment, four trees of the uppermost canopy layer and one tree fern belonging to the second tree layer were used for stemflow measurements. The species were selected to be representative of the study forest although this was difficult because of its high plant diversity. A list of the selected species is given in Fleischbein et al. (2005). Collectors for lateral flow samples consisted of a halved 30 cm-long and 10 cm-wide plastic pipe covered with a polyethylene net (0.5 mm mesh width), which was connected to 1-l polyethylene sampling bottles. The collectors were installed within the organic layers with the open side perpendicular to the soil surface to catch water moving through the organic layer parallel to the soil surface. Litter leachate was sampled by zero tension lysimeters, consisting of plastic boxes (0.20×0.14 m sampling area) covered with a polyethylene net (0.5 mm mesh width). The boxes were connected to 1-l polyethylene sampling bottles with a plastic tube. The lysimeters were installed from a soil pit below the organic layer parallel to the surface. The organic layer was not disturbed, most roots in the organic layer remained intact (Wilcke et al. 2001). Mineral soil solution was sampled by suction lysimeters (mullit suction cups, $1\mu\text{m} \pm 0.1\mu\text{m}$ pore size) with a vacuum pump. Vacuum was held permanently and pressure was adjusted to the matric potential. The lysimeters do not collect the soil solution quantitatively (Jemison and Fox 1992).

Hydrometric measurements

Rainfall, throughfall and stemflow were measured weekly by recording single volumes for each collector. Soil moisture conditions were characterized by determining the matric potentials by manual-reading tensiometers. At each transect, one tensiometer was installed at each of the 0.15 and 0.30 m mineral soil depths at one selected position approximately in the center of each transect. Matric potentials were read each week directly in the field by means of a manual display unit (Infields 5, UMS, Germany).

Water levels of catchment runoff were recorded hourly with a pressure gauge (water level sensor) at the outlet of each microcatchment. Unfortunately, logger breakdowns occurred during the runoff measurement likely because of the frequently wet conditions in the studied forest. Data gaps were closed by means of the hydrological modeling program TOPMODEL (Beven et al. 1995) as described in Fleischbein (2004).

Water analyses

The pH and Cl^- concentration were measured immediately after collecting in an aliquot of the unfiltered sample solution (pH 330 pH meter with Sentix 41 glass electrode, WTW, Germany and Cl^- -specific ion electrode Ionplus

9617BN, Orion). For all further analyses, samples were filtered in the field laboratory (ashless white ribbon paper filters, pore size, 4–7 μm , Schleicher & Schuell) and stored frozen until export to Germany.

Water samples were analyzed colorimetrically with a segmented continuous flow analyzer (SAN^{Plus}, Skalar Analytical B.V., Netherlands) for concentrations of dissolved inorganic nitrogen ($\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N} + \text{NO}_2\text{-N}$, hereafter referred to as $\text{NO}_3\text{-N}$), and total dissolved nitrogen (TDN) concentrations (after UV oxidation to NO_3). Additionally, total dissolved phosphorus (TDP) and sulfur (TDS) concentrations (ICP-OES, Integra XMP, GBC Scientific Equipment Pty. Ltd., Australia) and PO_4^{3-} and SO_4^{2-} concentrations (ion chromatography, DX-100, Dionex) were determined.

Calculations and statistical evaluations

Carbon and N fluxes were calculated for rainfall, throughfall and stemflow by multiplying the respective annual volume-weighted mean (VWM) concentrations with the annual water fluxes. Water fluxes in the soil were not quantified. We therefore could not calculate VWM values and instead showed the median in the tables. Carbon and N fluxes with surface runoff were calculated by multiplying flow-weighted mean (FWM) concentrations with the measured or modeled annual surface runoff and referring the annual flux to the surface area of the catchments. Phosphorus and S fluxes were calculated by multiplying unweighted annual mean concentrations with annual water fluxes.

The concentrations of DON were calculated as difference between those of TDN and $\text{NH}_4\text{-N} + \text{NO}_3\text{-N}$, the concentrations of DOP as difference between those of TDP and $\text{PO}_4\text{-P}$, and the concentrations of DOS as difference between those of TDS and $\text{SO}_4\text{-S}$. Some samples had concentrations below the detection limit of the analytical methods (0.025 mg l^{-1} for $\text{NH}_4\text{-N}$, 0.050 mg l^{-1} for $\text{NO}_3\text{-N}$, 0.075 mg l^{-1} for TDN, 0.28 mg l^{-1} for $\text{PO}_4\text{-P}$, 0.2 mg l^{-1} for TDP, 0.32 mg l^{-1} for $\text{SO}_4\text{-S}$, and 0.3 mg l^{-1} for TDS). This was the case in 17% of the samples for $\text{NO}_3\text{-N}$, 3% for $\text{NH}_4\text{-N}$, 1% for TDN, 42% for $\text{PO}_4\text{-P}$, 32% for TDP, 20% for $\text{SO}_4\text{-S}$, and 16% for TDS. For calculation purposes, values below the detection limit were set to zero. Thus, our annual means underestimate the real element concentration.

Correlation analyses followed the least squares method. We removed not more than one outlier from any data row. To compare mean dissolved nutrient concentrations in solution between the study transects, the nonparametric Wilcoxon matched-pairs test for connected data rows was used. To compare means of data sets with different size, we used the Spjotvoll & Stolne modification of the parametric Tukey's Honest Significant Difference (HSD) post-hoc test after checking the homogeneity of variances with the Levenné test. Significance was set to $P < 0.05$ for the post-hoc test and to $P < 0.01$ for the Wilcoxon test. Statistical analyses were performed with STATISTICA for Windows 5.5 (StatSoft 2000, Tulsa).

Results

Dissolved organic C concentrations

The vertical distribution of the annual VWM DOC concentrations across the ecosystem showed a consistent pattern at all five measurement transects (Table 2 and Figure 2a). The concentrations of DOC were low in rainfall and increased in the order throughfall < stemflow < lateral flow < litter leachate except at transect MC2.2, where DOC concentrations were higher in lateral flow than in litter leachate. During the passage through the mineral soil, DOC concentrations decreased continuously with increasing depth. There was a particularly pronounced decrease in DOC concentrations between litter leachate and mineral soil solution. The DOC concentrations in stream water were low and comparable to those in rainfall.

The DOC concentrations in rainfall and throughfall showed a seasonal variation with considerably higher concentrations in the drier period between November and February (in 2000 also in March, Figure 3). Similar variations of the DOC/Cl ratios (data not shown) and the lack of correlation between volume of rainfall and DOC concentrations ($r < 0.1$) indicated that the variations in DOC concentrations could not be attributed to dilution/concentration effects.

Table 2. Annual volume-weighted mean concentrations of DOC in rainfall (RF), throughfall (TF), and stemflow (SF), median concentrations in lateral flow (LF), litter leachate (LL), and soil solutions at 0.15 (SS-15) and 0.30 m (SS-30) mineral soil depth (where the flux is not known), flow-weighted mean concentrations in stream water (SW) in an Ecuadorian lower montane forest between May 1999 and April 2002 (between May 2000 and April 2002 for RF at MC1 and MC3).

	DOC (mg l ⁻¹)							
	RF	TF	SF	LF	LL	SS-15	SS-30	SW
MC1	4.0	12c	15b	36b	35b	20b	12b	5.2b
MC2.1	4.5	11d	14c	24c	37b	27a	15a	4.6c
MC2.2	n.a. ^a	12c	n.a.	37abc	27c	7.2d	6.6c	n.a.
MC2.3	n.a.	15b	n.a.	40a	40ab	10c	6.3d	n.a.
MC3	4.5	17a	19a	28abc	55a	20b	14ab	5.6a
<i>Tropical forests</i>	4.3 ⁷	6.2 ⁴	9.2 ¹	–	30 ²	5 ⁶	–	1.6–3.8 ¹
<i>Temperate forests</i>	1.1 ³	2.7–60 ⁵	–	–	20–90 ⁵	–	2–35 ⁵	–

Different letters indicate significant differences of the means between transects (Wilcoxon matched-pairs test, $P < 0.01$). Literature values are given for reference.

^an.a.: not available.

¹Frangi and Lugo (1985), ²Hafkenscheid (2000), ³Likens et al. (1983), ⁴McDowell (1998), ⁵Michalzik et al. (2001), ⁶Möller (2001), ⁷Schrumpf (2004).

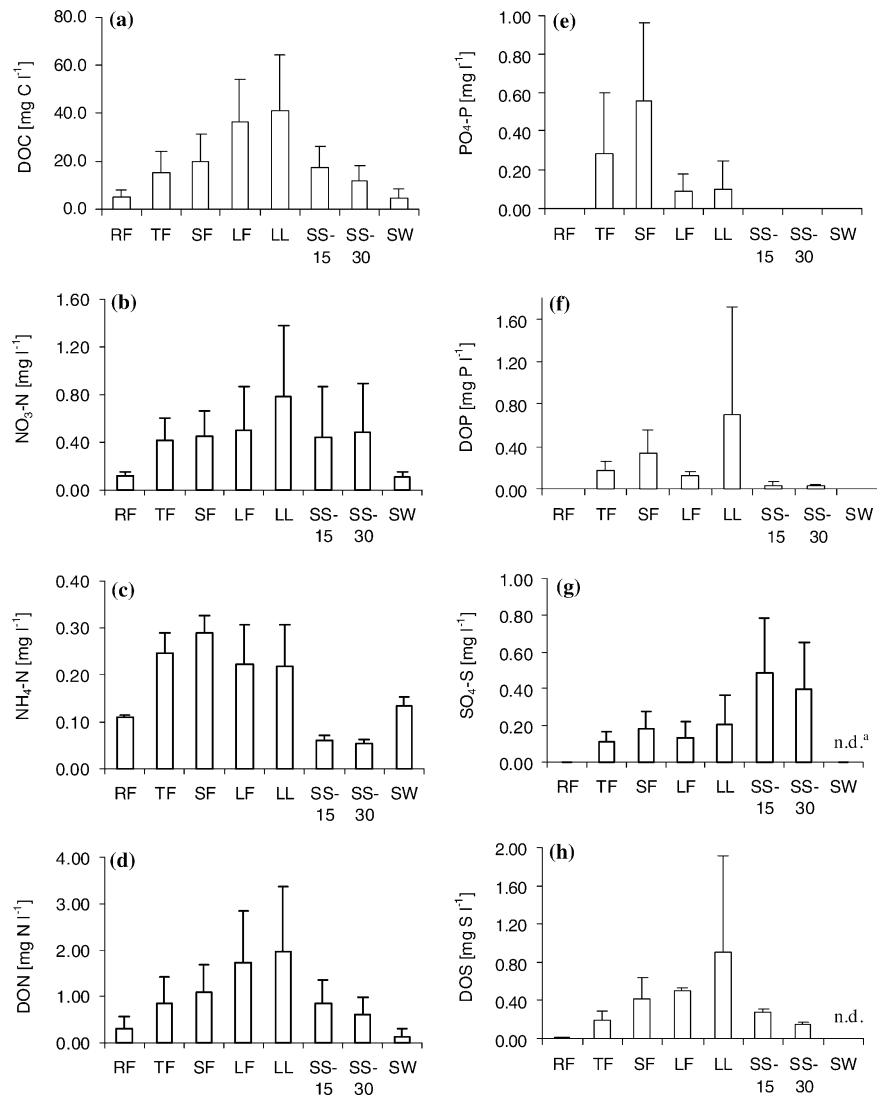


Figure 2. Mean vertical distribution of (a) DOC, (b) NO₃-N, (c) NH₄-N, (d) DON, (e) PO₄-P, (f) DOP, (g) SO₄-S, and (h) DOS concentrations through the forest ecosystem. n.d.^a: not detectable. For explanations of the x axis abbreviations see Table 2.

Dissolved N concentrations

Annual VWM NH₄-N and NO₃-N concentrations were low in rainfall, mineral soil solutions, except for NO₃-N, and stream water. They were distinctly higher in the aboveground fluxes (throughfall, stemflow, lateral flow, and litter leachate).

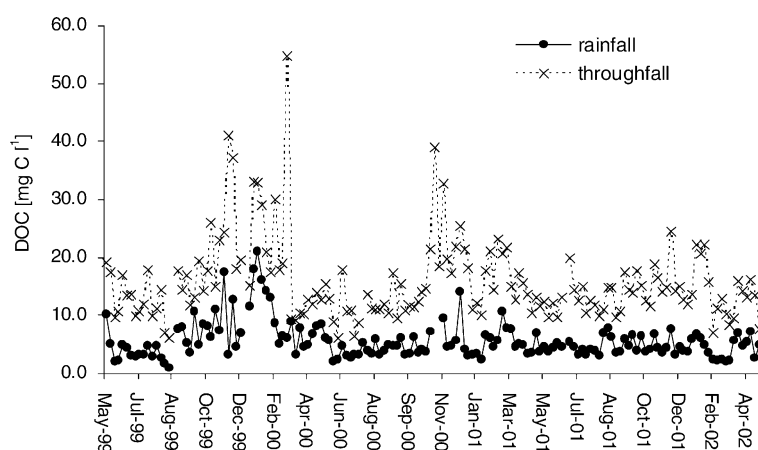


Figure 3. Temporal courses of the mean weekly DOC concentrations in rainfall and throughfall between May 1999 and April 2002.

Highest concentrations occurred in the organic layer at all five measurement transects (Table 3 and Figure 2b–c). The vertical distribution of annual VWM DON concentrations was similar to those of DOC (Table 4 and Figure 2d). The DON concentrations increased during the passage of the water through the ecosystem in the superficial water fluxes and decreased through the mineral soil to the stream, where DON concentrations were similarly low as in rainfall.

Similar to DOC, the $\text{NO}_3\text{-N}$ and DON concentrations in rainfall at the three gauging sites and throughfall at the five measurement transects were considerably higher in the drier period between November and February. The mean weekly $\text{NO}_3\text{-N}$ concentrations in rainfall and throughfall increased by about 10 times from wetter to drier periods. Again, $\text{NO}_3\text{-N}/\text{Cl}$ and DON/Cl ratios (data not shown) showed a similar variation as $\text{NO}_3\text{-N}$ and DON concentrations and rainfall or throughfall volumes and $\text{NO}_3\text{-N}$ or DON concentrations were not correlated ($r < 0.1$) excluding dilution/concentration effects as explanation for the variation in concentrations. Mean weekly $\text{NH}_4\text{-N}$ concentrations in rainfall and throughfall showed a slightly different temporal course with increased concentrations during the drier, but also during the wettest periods of the three monitored years in May 2000 and June 2001 (data not shown).

The annual VWM concentrations of DON in the aboveground fluxes (rainfall, throughfall and stemflow) contributed, on the average of the three monitored years, between 45 and 60% to the VWM concentrations of TDN. Spatial variations in DON contributions to TDN concentrations between the rainfall gauging sites and the five transects were smaller in aboveground fluxes and stream water than in the soil solutions (Table 5).

Temporal variations in DON contributions during the three-year period were small in all ecosystem fluxes at all five transects with coefficients of variance (CV) ranging between 1 and 30%, except for the mineral soil solutions at

Table 3. Three-year means of annual volume-weighted mean concentrations of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ in rainfall (RF), throughfall (TF), and stemflow (SF), median concentrations in lateral flow (LF), litter leachate (LL), and soil solutions at 0.15 (SS-15) and 0.30 m (SS-30) mineral soil depth (where the total volume is not known), flow-weighted mean concentrations in stream water (SW) in an Ecuadorian lower montane forest between May 1999 and April 2002 (except for SS and partly RF, between May 2000 and April 2002).

	$\text{NO}_3\text{-N}$ (mg l^{-1})															
	RF	TF	SF	LF	LL	SS-15	SS-30	SW	RF	TF	SF	LF	LL	SS-15	SS-30	SW
MC1	0.11	0.23	0.28	0.22	0.23	0.07	0.06	0.12	0.10a	0.61a	0.50b	0.42b	0.45bc	0.06c	0.10c	0.16a
MC2.1	0.11	0.23	0.26	0.13	0.12	0.05	0.05	0.15	0.10b	0.24b	0.21c	0.10c	0.31d	0.003d	0.000d	0.08b
MC2.2	n.a. ^a	0.21	n.a.	0.18	0.14	0.05	0.05	n.a.	n.a.	0.22b	n.a.	0.35b	0.41cd	1.0a	0.88a	n.a.
MC2.3	n.a.	0.24	n.a.	0.22	0.33	0.05	0.05	n.a.	n.a.	0.48a	n.a.	0.55a	1.0b	0.41b	0.64b	n.a.
MC3	0.11	0.32	0.33	0.36	0.27	0.08	0.07	0.13	0.16a	0.54a	0.63a	1.1a	1.7a	0.70a	0.82ab	0.09b
<i>Tropical montane forests</i>																
	0.05 ¹ –	0.07 ¹ –			0.1–0.2 ³	0.03–	0.02–	0.01 ⁵	0.05 ¹ –	0.02 ³ –			0.0–0.2 ³	1.5 ⁶	1.4 ⁶	0.06 ⁵
	0.86 ²	1.16 ²				0.04 ⁶	0.04 ⁶		0.11 ⁴	0.20 ⁴			0.92 ⁶			0.56–
					0.27 ⁶		0.82 ⁵	0.05–0.06 ⁶								0.60 ⁶
							(40 cm)									(40 cm)

Different letters indicate significant differences of the data rows between transects according to the Wilcoxon matched-pairs test ($P < 0.01$). Literature values for RF and TF representing ranges of selected tropical montane forests summarized by Hafkenscheid (2000) and single values for LL, SS, and SW are given for reference.

^a n.a.: not available; ¹ Clark et al. (1998); ² Veneklaas (1990); ³ Hafkenscheid (2000), Cambi- and Histosol; ⁴ Asbury et al. (1994); ⁵ McDowell and Asbury (1994), Ultisol; ⁶ Schrumpf (2004), Andisol.

0.15 and 0.30 m depth at transect MC3, which showed a greater variation between May 2000 and April 2002 (CV: 58%).

Dissolved P concentrations

The mean annual PO₄-P and TDP concentrations were below the detection limit in rainfall and stream water and extremely low in mineral soil solution. They were distinctly higher in the aboveground fluxes with highest concentrations in throughfall and stemflow. Dissolved organic P concentrations could only be reliably calculated for throughfall, stemflow, lateral flow, and litter leachate (Table 6 and Figure 2e–f). The vertical ecosystem profile of DOP concentrations was slightly different from that of DON and DOC. Litter leachate had the highest DOP concentrations of the superficial water fluxes. Stemflow had higher DOP concentrations than throughfall and lateral flow, which had similar DOP concentrations.

Table 4. Annual volume-weighted mean concentrations of DON and TDN in rainfall (RF), throughfall (TF), and stemflow (SF), median concentrations in lateral flow (LF), litter leachate (LL), and soil solutions at 0.15 (SS-15) and 0.30 m (SS-30) mineral soil depth (where the total volume is not known), flow-weighted mean concentrations in stream water (SW) in an Ecuadorian lower montane forest between May 1999 and April 2002 (between May 2000 and April 2002 for RF at MC1 and MC3).

	DON (mg l ⁻¹)							
	RF	TF	SF	LF	LL	SS-15	SS-30	SW
MC1	0.20a	0.67b	0.85b	1.9ab	2.0b	1.2a	0.80b	0.10b
MC2.1	0.19b	0.57c	0.71c	1.0d	1.4c	0.87b	0.52c	0.14b
MC2.2	n.a. ^a	0.62c	n.a.	1.4c	1.2d	0.39d	0.36d	n.a.
MC2.3	n.a.	0.70a	n.a.	2.1a	2.2b	0.55c	0.34d	n.a.
MC3	0.21a	0.89a	1.0a	1.5b	2.9a	1.3a	0.94a	0.21a
<i>Tropical forests</i>								
	0.0–0.4 ¹ 0.21 ⁸	0.45 ⁸	–	–	1.1 ²	0.25 ⁷	–	0.15 ³
<i>Temperate forests</i>								
	0.17 ⁶	0.25–1.1 ⁵	–	–	0.4–2.5 ⁵	–	0.2–1.1 (B horizon) ⁵	0.05 ⁴
	TDN (mg l ⁻¹)							
MC1	0.40	1.5	1.6	2.8	3.1	1.5	1.0	0.36
MC2.1	0.39	1.0	1.2	1.4	2.0	0.99	0.60	0.34
MC2.2	n.a.	1.0	n.a.	2.3	1.9	1.5	1.3	n.a.
MC2.3	n.a.	1.4	n.a.	3.2	4.5	1.0	1.1	n.a.
MC3	0.48	1.8	2.0	3.6	5.3	2.3	1.9	0.39

^an.a.: not available.

Different letters indicate significant differences of the means between transects (Wilcoxon matched-pairs test, $P < 0.01$). Literature values are given for reference.

¹Eklund et al. (1997), ²Hafkenscheid (2000), ³Hedin et al. (1995), ⁴McDowell and Asbury (1994), ⁵Michalzik et al. (2001), ⁶Michalzik & Matzner (1999), ⁷Möller (2001), ⁸Schrumpf (2004).

Mean monthly $\text{PO}_4\text{-P}$ concentrations in throughfall (0.61 mg l^{-1}), stemflow (1.1 mg l^{-1}), lateral flow (0.77 mg l^{-1}), and litter leachate (0.48 mg l^{-1}) of the measurement transects were highest in November 2000, the driest month of the monitored year. The mean monthly concentrations of $\text{PO}_4\text{-P}$ in throughfall and stemflow and of DOP in throughfall were negatively correlated with the respective water fluxes ($\text{PO}_4\text{-P}$: throughfall $r = -0.74$, stemflow $r = -0.69$, DOP: throughfall $r = -0.44$).

Annual means of DOP contributions to TDP increased, on the average of all five transects, in the order stemflow (41%) < throughfall (49%) < lateral flow (71%) < litter leachate (97%) with high variations between the five study transects in throughfall (range: 18–84%) and lateral flow (46–100%).

Dissolved S concentrations

The mean annual $\text{SO}_4\text{-S}$ concentrations were low in the aboveground fluxes with similar values between canopy and organic layer solutions and markedly higher in the mineral soil solutions. While $\text{SO}_4\text{-S}$ concentrations in stream water were similar to those of the aboveground ecosystem fluxes, the rainfall showed the lowest $\text{SO}_4\text{-S}$ concentrations of all ecosystem fluxes (Table 7 and

Table 5. Mean contributions of DON, DOP, and DOS to TDN, TDP, and TDS concentrations in rainfall (RF), throughfall (TF), stemflow (SF), lateral flow (LF), litter leachate (LL), soil solutions at 0.15 (SS-15) and 0.30 m (SS-30) mineral soil depth, and stream water (SW) in an Ecuadorian lower montane forest between May 1999 and April 2002 for DON and May 2000 and April 2001 for DOP and DOS, respectively.

	RF	TF	SF	LF	LL	SS-15	SS-30	SW
<i>DON contribution (%)</i>								
MC1	50	45	52	70	66	82	77	29
MC2.1	50	55	60	74	68	88	88	41
MC2.2	n.a. ^a	59	n.a.	62	61	26	27	n.a.
MC2.3	n.a.	49	n.a.	65	50	54	32	n.a.
MC3	45	51	52	42	55	57	49	53
<i>DOP contribution (%)</i>								
MC1	n.d. ^b	n.d.	36	46	87	n.d.	n.d.	n.d.
MC2.1	n.d.	64	47	100	100	n.d.	n.d.	n.d.
MC2.2	n.a.	84	n.a.	75	100	n.d.	n.d.	n.a.
MC2.3	n.a.	30	n.a.	63	n.d.	n.d.	n.d.	n.a.
MC3	n.d.	18	39	n.d.	100	n.d.	n.d.	n.d.
<i>DOS contribution (%)</i>								
MC 1	n.d.	58	59	78	94	39	47	n.d.
MC2.1	n.d.	51	74	76	62	38	30	n.d.
MC2.2	n.a.	91	n.a.	94	83	n.d.	n.d.	n.a.
MC2.3	n.a.	67	n.a.	85	50	37	23	n.a.
MC3	n.d.	61	82	88	100	35	27	n.d.

^an.a.: not available, ^bn.d.: not detected.

Table 6. Annual mean concentrations of PO₄-P, DOP, and total dissolved P (TDP) in rainfall (RF), throughfall (TF), stemflow (SF), lateral flow (LF), litter leachate (LL), soil solutions at 0.15 (SS-15) and 0.30 (SS-30) m mineral soil depth, and stream water (SW) in an Ecuadorian lower montane forest between May 2000 and April 2001.

	PO ₄ -P (mg l ⁻¹)										DOP (mg l ⁻¹)										TDP (mg l ⁻¹)															
	RF	TF	SF	LF	LL	SS-15	SS-30	SW	RF	TF	SF	LF	LL	SS-15	SS-30	SW	RF	TF	SF	LF	LL	SS-15	SS-30	SW	RF	TF	SF	LF	LL	SS-15	SS-30	SW				
MC1	<0.005	n.d. ^a	0.56	0.11	0.05	n.d.	<0.005	<0.005	0.005	n.d.	0.30	0.10	0.36	n.d.	0.03	0.005	0.005	0.58	0.86	0.21	0.41	0.004	0.03	0.005	0.005	0.58	0.86	0.21	0.41	0.004	0.03	0.005				
MC2.1	<0.005	0.07	0.15	<0.005	0.02	<0.005	<0.005	<0.005	<0.005	0.10	0.13	0.15	0.02	0.07	0.02	<0.005	<0.005	0.18	0.28	0.15	0.04	0.07	0.02	<0.005	<0.005	0.18	0.28	0.15	0.04	0.07	0.02	<0.005				
MC2.2	n.a. ^b	0.06	n.a.	0.03	0.01	n.d.	<0.005	n.a.	n.a.	0.30	n.a.	0.09	0.21	n.d.	0.02	n.a.	n.a.	0.37	n.a.	0.12	0.22	0.004	0.02	n.a.	n.a.	0.37	n.a.	0.12	0.22	0.004	0.02	n.a.				
MC2.3	n.a.	0.28	n.a.	0.20	n.d.	<0.005	<0.005	n.a.	n.a.	0.11	n.a.	0.16	n.d.	0.004	0.01	n.a.	n.a.	0.39	n.a.	0.36	n.d.	0.00	0.01	n.a.	n.a.	0.39	n.a.	0.36	n.d.	0.00	0.01	n.a.				
MC3	n.d.	0.73	0.97	n.d.	0.32	<0.005	<0.005	n.d.	n.d.	0.15	0.57	n.d.	2.20	0.01	0.06	n.d.	0.02	0.88	1.54	0.43	2.52	0.01	0.06	0.01	0.02	0.88	1.54	0.43	2.52	0.01	0.06	0.01				
Literature																																				
	0.002 ¹ –	0.004 ⁴ –																																		
	0.034 ²	0.090 ²	0.002 ⁵	0.06 ³																																
			(TDP)	0.03–																																
				0.20 ⁶																																

Literature values are given for reference.

^an.d.: not detected, ^bn.a.: not available; ¹Clark et al. (1998), ²Veneklaas (1990), ³Hafkenscheid (2000), ⁴Asbury et al. (1994), ⁵McDowell and Asbury (1994), ⁶Kaiser et al. (2000) – all literature data refer to tropical montane forests except Kaiser et al. (2000): temperate forests in Germany.

Figure 2g). The vertical distribution of DOS concentrations across the ecosystem paralleled those of DON and DOC (Figure 2h).

Similar to N and P concentrations, the mean monthly $\text{SO}_4\text{-S}$ concentrations in throughfall (0.20 mg l^{-1}), stemflow (0.39 mg l^{-1}), lateral flow (0.57 mg l^{-1}), and litter leachate (1.1 mg l^{-1}) of the study transects were highest in November 2000. Sulfate-S concentrations in mineral soil solutions showed a continuous decline from high values ($0.44\text{--}1.1 \text{ mg l}^{-1}$) during the wetter period between May and August 2000 to relatively constant values ($0.22\text{--}0.50 \text{ mg l}^{-1}$) during the remaining monitored period, whereas monthly $\text{SO}_4\text{-S}$ concentrations in stream water remained relatively stable during the entire monitored period ($0.09\text{--}0.21 \text{ mg l}^{-1}$). Similar to $\text{PO}_4\text{-P}$ and DOP, concentrations of $\text{SO}_4\text{-S}$ in throughfall and stemflow and of DOS in throughfall correlated negatively with the respective water fluxes ($\text{SO}_4\text{-S}$: throughfall $r = -0.65$, stemflow $r = -0.68$, DOS: throughfall $r = -0.78$).

The DOS contributions to the mean annual TDS concentrations increased, on the average of all five transects, in the order throughfall (66%) < stemflow (71%) < litter leachate (78%) < lateral flow (84%). In the mineral soil, portions of DOS were markedly lower with similar means between the two studied soil depths (37% at 0.15 m and 32% at 0.30 m; Table 5).

Relations between DOC, DON, DOP, and DOS concentrations

Weekly and monthly DOC and DON, DOP, and DOS concentrations were not correlated except that there were correlations between DOP and DOS for stemflow at transects MC1 ($r = 0.97$, $n = 6$), MC2.1 ($r = 0.94$, $n = 6$), and MC3 ($r = 0.92$, $n = 8$) and litter leachate at transect MC2.2 ($r = 0.99$, $n = 5$). Nevertheless, there were strong positive correlations between annual mean concentrations of DOC and DON ($r = 0.95$, $n = 34$), DOC and DOP ($r = 0.65$, $n = 33$), and DOC and DOS ($r = 0.89$, $n = 33$) for all ecosystem fluxes.

Influence of pH

Although there were no correlations between the pH and the concentration of any studied C, N, P, and S form in the weekly solution samples, there was a general trend of lowest mean annual $\text{NO}_3\text{-N}$, DON, $\text{PO}_4\text{-P}$, DOP, and DOS concentrations in the organic layer and mineral soil solutions of the more acid soils in MC2 and highest mean annual concentrations in the solutions of the least acid soil in MC3 (Tables 1, 3, 4, 6 and 7). The differences in mean annual concentrations are mostly significant for the N forms whereas no statistical comparison of the measurement transects was possible for P and S forms because of the small data set. Soil pH and DOC, $\text{NH}_4\text{-N}$, and $\text{SO}_4\text{-S}$ concentrations were not correlated.

Table 7. Annual mean concentrations of $\text{SO}_4\text{-P}$, DOS, and total dissolved S (TDS) in rainfall (RF), throughfall (TF), stemflow (SF), lateral flow (LF), litter leachate (LL), soil solutions at 0.15 (SS-15) and 0.30 m (SS-30) mineral soil depth, and stream water (SW) in an Ecuadorian lower montane forest between May 2000 and April 2001.

	$\text{SO}_4\text{-S}$ (mg l^{-1})										DOS (mg l^{-1})										TDS (mg l^{-1})												
	RF	TF	SF	LF	LL	SS-15	SS-30	SW	RF	TF	SF	LF	LL	SS-15	SS-30	SW	RF	TF	SF	LF	LL	SS-15	SS-30	SW	RF	TF	SF	LF	LL	SS-15	SS-30	SW	
MC1	<0.005	0.14	0.29	0.14	0.05	0.32	0.20	n.d. ^a	0.02	0.17	0.38	0.52	0.90	0.20	0.16	n.d.	0.02	0.32	0.67	0.66	0.96	0.52	0.36	0.15	0.02	0.32	0.67	0.66	0.96	0.52	0.36	0.15	
MC2.1	<0.005	0.11	0.10	0.17	0.23	0.54	0.32	n.d.	0.01	0.11	0.25	0.31	0.37	0.33	0.12	n.d.	0.01	0.22	0.36	0.48	0.60	0.87	0.44	0.04	0.01	0.22	0.36	0.48	0.60	0.87	0.44	0.04	
MC2.2	n.a. ^b	0.02	n.a.	0.02	0.11	n.d.	n.d.	n.a.	n.a.	0.23	n.a.	0.32	0.55	n.d.	n.d.	n.a.	n.a.	n.a.	0.34	0.66	0.38	0.49	n.a.	n.a.	n.a.	n.a.	0.34	0.66	0.38	0.49	n.a.		
MC2.3	n.a.	0.09	n.a.	0.26	n.d.	0.21	0.29	n.a.	n.a.	0.18	n.a.	0.80	0.70	0.11	0.07	n.a.	n.a.	n.a.	1.06	n.d.	0.32	0.36	n.a.	n.a.	n.a.	n.a.	1.06	n.d.	0.32	0.36	n.a.		
MC3	n.d.	0.18	0.16	0.08	0.42	0.88	0.77	n.d.	0.02	0.28	0.63	0.56	1.97	0.46	0.25	n.d.	0.07	0.46	0.79	0.65	2.39	1.34	1.02	0.05	0.07	0.46	0.79	0.65	2.39	1.34	1.02	0.05	
<i>Literature</i>																																	
	0.14 ²⁻	0.28 ⁴⁻						0.78 ⁵					0.05 ⁻	0.13 ⁻	0.28 ⁸																		
	1.51 ³	2.67 ¹											1.4 ⁶	0.15 ⁷																			

Literature values are given for reference.

^an.d.: not detected, ^bn.a.: not available; ¹Veneklaas (1990), ²Hafkenscheld (2000), ³Asbury et al. (1994), ⁴Cavelier et al. (1997), ⁵McDowell and Asbury (1994), ⁶Homann et al. (1990), ⁷Kaiser and Guggenberger (2003), ⁸Houle et al. (2001) – references 1–5 refer to tropical montane forests, references 6–8 to temperate forests.

Influence of soil water regime

The mean weekly $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ concentrations in litter leachate responded negatively to rainfall and to soil matric potential (i.e. negatively to soil moisture content). Exceptions were short periods at the beginning of May 2000 and between the end of May and June 2001, which were characterized by high weekly rainfall amounts including the occurrence of heavy rainstorms and strongly increased $\text{NH}_4\text{-N}$ concentrations (Figure 4a–d). The responses of the weekly $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ concentrations in the mineral soil solutions to moisture conditions were similar as in litter leachate. However, temporal variations were smaller than in litter leachate (data not shown).

During periods with low water input for several days up to two weeks (e.g., in November 2000) often associated with elevated solar radiation, a considerable drying of the organic layer and subsequently the upper mineral soil occurred. The latter was demonstrated by substantially decreasing matric potentials in the mineral soil from values near zero indicating almost water saturation to minimum values of -73 and -67 kPa in November 2000 and January 2002, respectively (Figure 4a). During dry periods, weekly DON concentrations in litter leachate and in mineral soil solutions were low (Figure 4d). Periods with strongly decreased DON concentrations in litter leachate were short, normally lasting 1 week to at most 3 weeks in December 2001 followed by a considerable increase in DON concentrations in litter leachate after rewetting of the soil indicated by abruptly increasing matric potentials. Rapid increases in DON concentrations to more than 3.0 mg l^{-1} in litter leachate were always associated with elevated rainfall, partly with first rainfall following drier periods, e.g., on 20 September, 22 November, 27 December 2000, on 23 May, 10 October, 26 December 2001, and on 23 January and 27 February 2002.

The $\text{SO}_4\text{-S}$ and $\text{PO}_4\text{-P}$ concentrations in the soil organic layer solutions were not correlated with soil moisture except that they were highest in the driest month (November 2000). In the mineral soil solution, mean monthly $\text{SO}_4\text{-S}$ concentrations were positively correlated with soil moisture (as indicated by the negative correlation between $\text{SO}_4\text{-S}$ concentrations in the soil solution and the matric potential, $r = -0.38$ at 0.15 m depth and $r = -0.42$ at 0.30 m depth). The $\text{PO}_4\text{-P}$ concentrations in the mineral soil solution were below the detection limit. There was no correlation between soil moisture and DOP and DOS concentrations in organic layer and mineral soil solutions.

In stream water, the mean weekly $\text{NH}_4\text{-N}$ concentrations increased from relatively constant values of about 0.1 mg l^{-1} during most part of the entire monitored period up to $0.8\text{--}1.5 \text{ mg l}^{-1}$ at the beginning of the wet periods in May 2000 and June 2001 directly following the drier periods between November and April. During this time, $\text{NH}_4\text{-N}$ concentration peaks were related to heavy rainstorm events (Figure 5b). The weekly $\text{NO}_3\text{-N}$ concentrations in stream water were positively related to elevated catchment discharge during the wetter periods of the monitored years. Although peakflow events

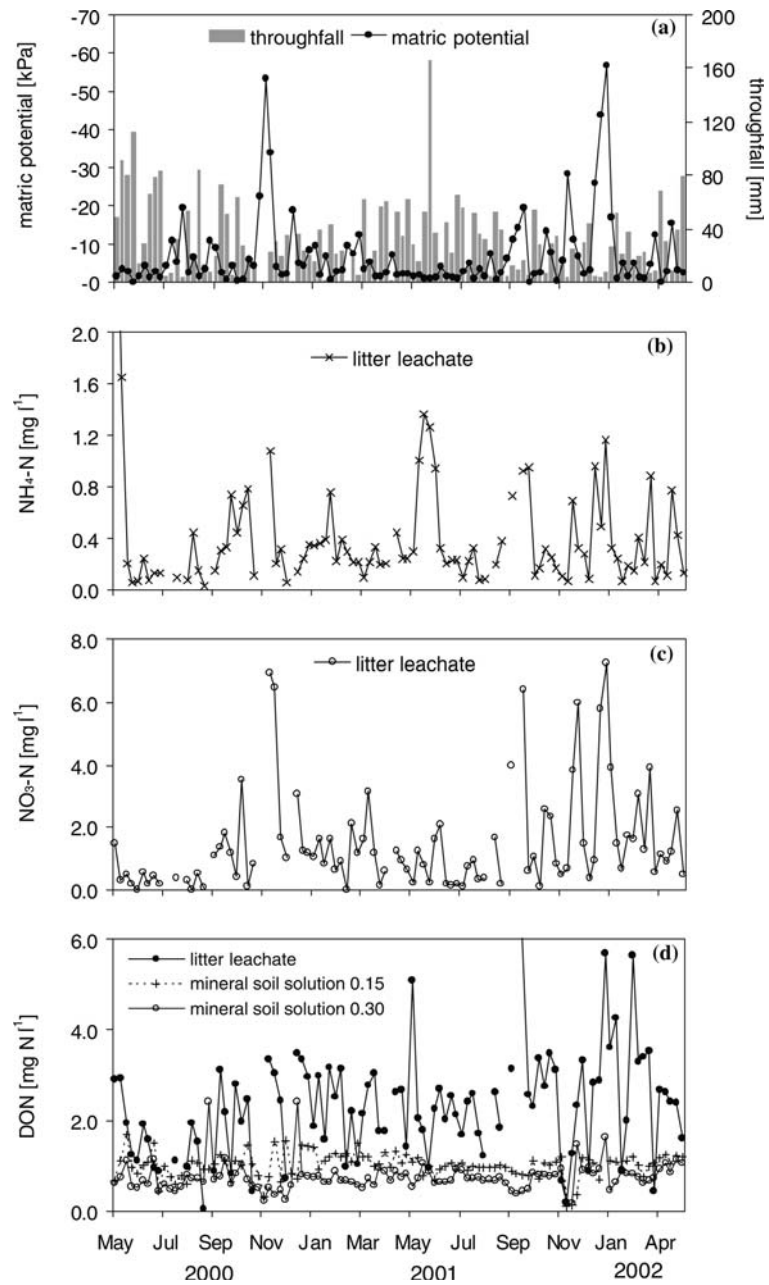


Figure 4. Temporal courses of (a) mean weekly throughfall and matric potentials, (b) mean weekly $\text{NH}_4\text{-N}$ and (c) $\text{NO}_3\text{-N}$ concentrations in litter leachate and (d) mean weekly DON concentrations in litter leachate and mineral soil solutions at five study transects between May 2000 and April 2002.

following rainstorms were partly associated with increased $\text{NO}_3\text{-N}$ and DON concentrations in stream water (see 23 July 1999, 10 May and 5 July 2000, 13 June, 27 June, and 8 August 2001, 6 February and 3 April 2002 in Figure 5c, d), no correlation existed between rainstorm events and increased $\text{NO}_3\text{-N}$ and DON concentrations. Furthermore, the three-year flow-weighted mean $\text{NO}_3\text{-N}$ concentrations in stream water during baseflow were not significantly different from those during stormflow. Mean DOC and DON concentrations in stream water were significantly different between storm and nonstorm subsets (Figure 6a, b).

Discussion

C, N, P, and S forms in ecosystem fluxes

Compared with the low values in rainfall, concentrations of all studied C, N, P, and S forms in throughfall and stemflow increased to a larger extent than would be expected as result of the evaporation of intercepted water (25–52%; Tables 2–4, 6, and 7). Thus the canopy was a source of dissolved C, N, P, and S (Figure 2a–h). This is attributable to element leaching from the leaves, phyllosphere organisms, humic material accumulated by epiphytes in the forest canopy, and wash-off of dry deposition (Parker 1983; Vance and Nadkarni 1990).

In the organic layer solutions, the $\text{NO}_3\text{-N}$ concentrations partly further increased (Figure 2b), dissolved $\text{NH}_4\text{-N}$ and $\text{SO}_4\text{-S}$ concentrations did not change (Figure 2c, g), and $\text{PO}_4\text{-P}$ concentrations decreased (Figure 2e). As most roots were concentrated in the organic layer (Wilcke et al. 2002), it can be assumed that a large part of the annual 280–990 mm of transpiration (+ evaporation from the soil, i.e. 22–56% of throughfall + stemflow, Fleischbein 2004) were taken up from the organic layer illustrating that the changes in dissolved $\text{NO}_3\text{-N}$ concentrations in the organic layer solutions relative to throughfall can be explained by concentration effects whereas the organic layer was a sink of $\text{NH}_4\text{-N}$, $\text{SO}_4\text{-S}$, and $\text{PO}_4\text{-P}$.

The concentrations of dissolved organic C, N, P, and S increased considerably during the passage through the organic layer (Figure 2a, d, f, h). Thus the organic layer was the major source of dissolved organic C, N, P, and S. According to Kalbitz et al. (2000), the major DOM generating processes in the organic layer of forest soils are microbial decomposition of soil organic matter (SOM) and leaching of DOM from fresh litter. Whereas $\text{PO}_4\text{-P}$ concentrations were lower in litter leachate than in throughfall and stemflow and not detectable in mineral soil solutions, the DOP concentration in litter leachate was the highest of all studied ecosystem fluxes.

In the mineral soil solutions, the concentrations of all studied C, N, P, and S forms, except for $\text{SO}_4\text{-S}$, decreased relative to the organic layer solutions (Figure 2a–f, h). The reasons include gaseous losses of N by denitrification, immobilization of P by uptake into plants and litter-decomposing organisms

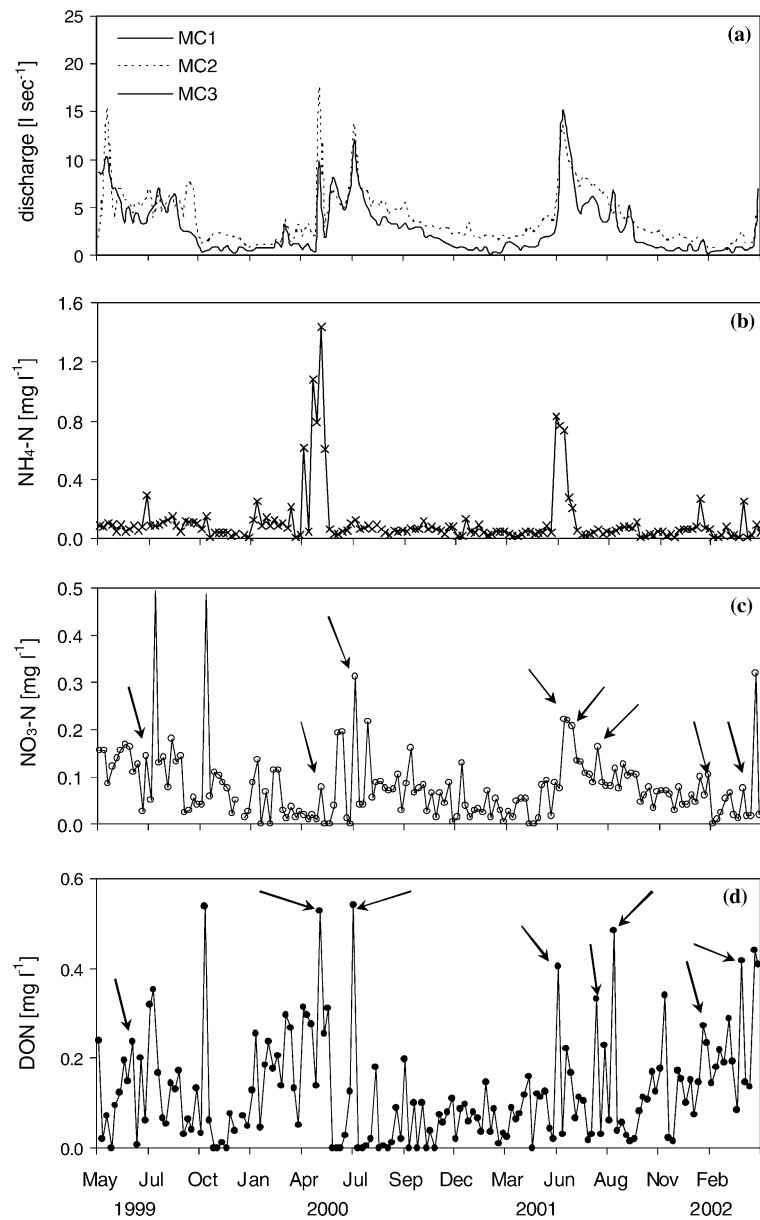


Figure 5. Temporal courses of (a) the discharges of three microcatchments and (b) mean weekly NH₄-N, (c) NO₃-N and (d) DON concentrations in stream water between May 1999 and April 2002. Arrows in 'c' and 'd' indicate increased NO₃-N and DON concentrations during peakflow following rainstorm events.

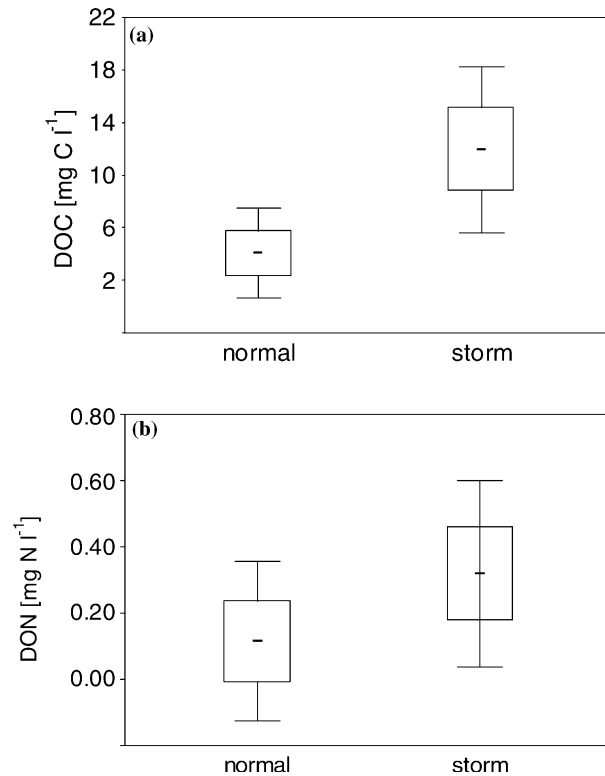


Figure 6. Mean (a) DOC and (b) DON concentrations in stream water of three microcatchments under non-storm and storm conditions between May 1999 and April 2002. Whiskers represent ranges of $1.96 \times$ standard deviation (SD), boxes ranges of $1 \times$ SD, and lines inside the boxes arithmetic means ($n_{\text{storm}} = 15$, $n_{\text{non-storm}} = 141$). Selected dates with storm conditions were characterized by an event with a rainfall intensity higher than 7.5 mm h^{-1} at most one day before sampling or by showing a dominant peak in the hydrograph of at least two MCs.

(Vitousek and Sanford 1986) and sorption of inorganic and organic C, N, and P species. Immobilization of P can be attributed to high P-use efficiency related to the dense root system in the organic layer and upper part of the topsoil supported by the high abundance of arbuscular mycorrhiza in the study forest, which is known to accelerate the P uptake by plant roots (Kottke et al. 2004). The decrease of the dissolved $\text{NO}_3\text{-N}$ concentrations in the mineral soil solution (Table 3) might be attributable to the flushing of $\text{NO}_3\text{-N}$ from the near-surface soil to the surface runoff during rainstorms as a consequence of the steep topography (Goller et al. 2005). A small part of $\text{NO}_3\text{-N}$ leached from the litter layer might also be taken up by the plants. However, Wilcke et al. (2002) have shown that more N is mineralized than required by the vegetation. The increase in $\text{SO}_4\text{-S}$ concentrations in the mineral soil solution relative to the organic layer solution suggests the presence of a S source in the mineral soil.

This assumption is further supported by the observation that the concentrations of $\text{SO}_4\text{-S}$ varied little in stream water during the monitored year indicating a continuous $\text{SO}_4\text{-S}$ release from the soils. Furthermore, the concentrations of $\text{SO}_4\text{-S}$ in the stream water of microcatchments MC1 and MC2 were consistently higher than in rainfall (Table 7). Given the high density of roots in the organic layer and the marked decrease in dissolved N and P concentrations between the organic layer and the mineral soil solutions, it seems unlikely that the higher $\text{SO}_4\text{-S}$ concentration in the mineral soil than in the litter leachate can be attributed to incomplete S uptake by the plants. This is further unlikely as there are even indications of insufficient S supply for plant nutrition in the organic layer (Wilcke et al. 2002). A possible source of $\text{SO}_4\text{-S}$ in the mineral soil may be the weathering of S minerals, e.g. pyrite, which probably occur in the parent material (shists and phyllites). Furthermore, temporary water logging of the soil might result in the precipitation of reduced S forms that are released during drier periods. The decrease in DOC, DON, and DOP concentrations during the passage from the forest floor to the subsoil at all transects is the result of progressive retention of DOM in the mineral soil (Stevenson and Cole 1999; McDowell 2003). The main reason is the adsorption of DON and DOC to Al and Fe oxides and hydroxides (Kaiser et al. 1996; Qualls et al. 2002). Guggenberger and Kaiser (2003) recently suggested that biofilms covering soil particle surfaces also retain DOM. Furthermore, part of DON is taken up by plants, e.g. via mycorrhiza, or after mineralization to inorganic N (Kalbitz et al. 2000; Neff et al. 2003).

The low concentrations of all C, N, P, and S forms in the stream water, except for $\text{SO}_4\text{-S}$, in addition to low element concentrations in rainfall indicated a largely closed nutrient cycle within the study forest. However, denitrification particularly in near-river areas which we did not quantify might also partly explain low N concentrations in stream water.

Comparing our results with other forest ecosystem studies, the concentrations of $\text{NH}_4\text{-N}$, $\text{PO}_4\text{-P}$, and $\text{SO}_4\text{-S}$ in rainfall were at the lower end of the range in other tropical forests (Tables 3, 6, and 7); those of $\text{NO}_3\text{-N}$, DOC, and DON were comparable to the published range (Tables 2–4). Compared with temperate forests, DOC concentrations in rainfall were high and DON concentrations were similar (Likens et al. 1983; Michalzik and Matzner 1999). Elevated DOC concentrations in rainfall probably result from the extended forest area in the Amazon basin and transport with the mainly easterly winds (Forti and Neal 1992).

The $\text{PO}_4\text{-P}$ and $\text{NO}_3\text{-N}$ concentrations in throughfall were higher than published for other tropical montane forests; $\text{NH}_4\text{-N}$ concentrations were well within this published range (Tables 3 and 6). For DOP, the concentrations in throughfall plus stemflow of the studied forest were about 15 times higher than in a temperate deciduous forest reported by Qualls et al. (1991) indicating strong P leaching from the canopy. The DON and DOC concentrations in throughfall were higher than those of other tropical forests and at the upper end of the range reported for temperate forests (Tables 2–4). In contrast, $\text{SO}_4\text{-S}$ concentrations in

throughfall were at the lower end of the range of other tropical montane forests. The DOS concentrations in throughfall and stemflow were lower than in a temperate coniferous forest in Quebec (Houle et al. 2001; Table 7).

Our result that the organic layer was the major source of dissolved organic C, N, P, and S corresponds with findings of Qualls and Haines (1992), Kaiser et al. (2000), and Kaiser and Guggenberger (2003). The decrease in DOC, DON, and DOP concentrations during the passage from the forest floor to the subsoil is similar to findings of Qualls and Haines (1992) that more than 95% of the DON and DOC input were retained during the passage through a temperate forest ecosystem. The DOP concentration in litter leachate of the studied forest was about 12 times higher than reported by Hafkenscheid (2000) for a tropical montane forest in Jamaica and also much higher than in temperate forests (Qualls et al. 1991; Kaiser et al. 2000; Table 6). The DOS concentration in litter leachate was in the range of those in eight temperate forested water catchments in North America (Homann et al. 1990).

In contrast to Amazonian lowland forests, where – similar to temperate forests – $\text{NO}_3\text{-N}$ concentrations are often high in mineral soil solution (Tamm 1991), in the studied montane forest, $\text{NO}_3\text{-N}$ concentrations were highest in litter leachate and distinctly lower in the mineral soil (Table 3). Ammonium concentrations in soil solutions were generally low and comparable to other tropical montane forests (Table 3). The DOC and DON concentrations were higher than at other tropical forest sites but comparable to those in temperate forests (Tables 2 and 4). This may be related with the comparatively high litter fall and organic matter storage of the studied Ecuadorian forest (small litter: $8.5\text{--}9.7 \text{ t yr}^{-1}$, organic C storage: $1.2\text{--}33 \text{ kg m}^{-2}$, Wilcke et al. 2002). The DOS concentrations were slightly lower than in temperate forest soils in south Germany (Kaiser and Guggenberger 2003) and in Quebec (Houle et al. 2001; Table 7).

In stream water, DOC, $\text{NH}_4\text{-N}$, and DON concentrations were at the upper end or higher than those in other tropical forests, $\text{PO}_4\text{-P}$ concentrations were similar, and $\text{NO}_3\text{-N}$ and $\text{SO}_4\text{-S}$ were at the lower end (Tables 2–4, 6, and 7). The DOC concentration under non-storm conditions (4.1 mg l^{-1}) was at the upper end of the range in a forested water catchment in Puerto Rico ($1.6\text{--}3.8 \text{ mg l}^{-1}$), whereas the DOC concentration in surface water during storm conditions (12 mg l^{-1}) was less than half of that in the Puerto Rican catchment (28 mg l^{-1} , Frangi and Lugo 1985).

Contribution of organic species to total element concentrations

Dissolved organic N contributed $> 50\%$ to TDN in almost all ecosystem fluxes (Table 5). The spatial and temporal variations in DON contributions were small in aboveground and much larger in belowground fluxes. In the soil solutions, DON was the dominant N form except at transects MC2.2 and MC2.3, where DON portions in the mineral soil solution were low. The higher

spatial variations in soil solutions coincide with the high heterogeneity of chemical properties of the soil solid phase in the study area (Wilcke et al. 2002). This variation may be explained by a greater number of controls on DOM mobilization in the soil than in the aboveground compartments of the forest (Kalbitz et al. 2000).

The DON contributions in litter leachate at our study site were similar to those reported by Currie et al. (1996) of 56–67% but lower than those reported by Qualls and Haines (1992) of 95% for North American temperate forests. The DON contribution to TDN (mean 41%) in the stream water of the study forest was low compared with other temperate and tropical regions. Lewis et al. (1999) reported a mean DON contribution of 67% in first and second order streams of several undisturbed tropical water catchments mainly in South America. The results of studies on small streams under undisturbed temperate forests cover a wide range of DON contributions to TDN between 50% (Wondzell and Swanson 1996) and 97% (Perakis and Hedin 2002).

The high mean DOP contribution in all ecosystem fluxes to TDP illustrates that the organic form is the major vector of P transport through the studied forest (Table 5). The contributions of DOP to TDP varied considerably in the aboveground ecosystem fluxes and in the lateral flow through the organic layer between the study transects (18–100%). This suggests that aboveground and near-surface fluxes might be significantly influenced by the high plant diversity and quick lateral flow through the topsoil after rainstorms. Similar findings have been reported for a beech forest in Germany by Kaiser et al. (2003).

The mean DOS contribution to TDS (65%) demonstrates that DOS plays a major role in the S dynamics of the studied forest (Table 5). Dissolved organic S was the most abundant S form in all ecosystem fluxes above the mineral soil. This is in agreement with the conclusions of Stevenson and Cole (1999) that most of the aboveground S cycling occurs in the organic form. The DOS contributions in throughfall, stemflow, and litter leachate were higher than DOS portions in eight temperate forests in the northwestern USA of 5–54, 1–50, and 16–46%, respectively (Homann et al. 1990). In the mineral soil, the DOS contributions to TDS were low, which was different from the medium to high contributions of DON to the TDN concentrations. The shift from DOS to $\text{SO}_4\text{-S}$ in the mineral soil solution is attributable to the efficient exchange of $\text{SO}_4\text{-S}$ by DOM (Kaiser and Zech 1998) and to mineral weathering. Strong adsorption of DOS is further supported by the low DOS contribution to TDS in stream water, which were comparable to DOS portions of 12–21% in Canadian water catchments (Mitchell et al. 1986).

Controls of the N, P, and S dynamics

pH

The significantly lower $\text{NO}_3\text{-N}$ concentrations in litter leachate and mineral soil solutions at the most acid transect MC2.1 than at all other transects suggest

reduced microbial activity (Table 3). This confirms findings of Wilcke et al. (2002) in the study forest, who reported a reduced nutrient turnover in the organic layer at transect MC2.1 compared with the transects MC1 and MC3. However, $\text{NO}_3\text{-N}$ concentrations in mineral soil solutions of transect MC2.2, which had a similar pH as transect MC2.1, were the highest of all transects, although $\text{NO}_3\text{-N}$ concentrations in litter leachate were similar to those of transect MC2.1. In spite of the low pH, organic matter is turned over at MC2.2 at a higher rate as indicated by lower annual median DOC/DON ratios in the second and third monitored years in the mineral soil solutions at 0.15 m depth (DOC/DON: 19) and at 0.30 m depth (DOC/DON: 20) at transect MC2.2 than at transect MC2.1 (0.15 m: 32 and 0.30 m: 29). As parent materials (phyllites) and soil types (Humic Dystrudepts) were the same and the depths of the A horizons at transects MC2.1 (103 mm) and MC2.2 (93 mm) comparable, it is not likely that the differences in DOC/DON ratios are attributable to differential sorption of DON. Therefore, we consider the differences in DOC/DON ratios between these two transects as indication of a higher $\text{NO}_3\text{-N}$ release at transect MC2.2 than MC2.1. In contrast, the $\text{NH}_4\text{-N}$ concentration in the soil solutions at the five transects seemed to be independent of the pH.

In many studies, decreasing pH reduced DOC concentrations in litter leachates (Kalbitz et al. 2000). However, this conclusion was mostly drawn from batch experiments, whereas confirmation in field studies is rare. For the mineral soil, some laboratory studies even showed opposite results (Vance and David 1989; Guggenberger et al. 1994). Schindler et al. (1992) found increasing DON concentrations as a consequence of artificial acidification in a lake in Ontario, Canada. The mobilization of DON and DOS in solutions of the mineral soil and partly in the organic layer tended to be positively related to the pH, although there was no correlation between concentrations of the organic nutrients and the pH in weekly samples, which has often been reported for field studies (Kalbitz et al. 2000). The mineralization of N, P, and S in the organic layer was reduced at the most acid transect MC2.1 (Wilcke et al. 2002), suggesting that the release of DOM might also be reduced resulting in low DOC concentrations in the litter leachate.

Hydrologic conditions

Increased concentrations of DOC and all dissolved N species in rainfall coincided with dry periods characterized by a change of the prevailing wind direction from generally E to W at the end of the monitored years (data from a meteorological station on the highest peak of the study area, 'Cerro de Consuelo', 3180 m a.s.l.; P. Emck, personal communication). We suggest that vegetation fires in and dust from the much drier, agriculturally used Loja basin and probably to a smaller extent also from the valley of the Rio San Francisco (own field observations) explain increased C and N concentrations in rainfall.

The elevated DOC and dissolved N input with rainfall was reflected by simultaneously increased DOC and dissolved N concentrations in throughfall

and stemflow indicating that the deposited C and N was transferred to the soil. Increasing $\text{PO}_4\text{-P}$ and $\text{SO}_4\text{-S}$ concentrations in throughfall and stemflow during dry periods, in contrast, are partly attributable to concentration/dilution effects because of reduced water fluxes during drier periods particularly in the canopy. This was indicated by negative correlations between $\text{PO}_4\text{-P}$ and $\text{SO}_4\text{-S}$ concentrations in throughfall and stemflow and the respective water fluxes.

All inorganic N, P, and S concentrations in litter leachate and mineral soil solutions were elevated during dry periods (Figure 4a–c for N). Furthermore, $\text{NH}_4\text{-N}$ concentrations were elevated in wet periods with nearly waterlogged soil conditions (Figure 4b). Soil drying and rewetting is known to enhance the release of inorganic N, P, and S into the soil solution. The inorganic N, P, and S results from the bursting of dead cells during drying and an enhanced mineralization during rewetting favored by the increased exposure of substrate surfaces to microbial attack because of the breakdown of water-stable aggregates (Stevenson and Cole 1999). At the same time, N, P, and S uptake by the vegetation might be reduced, because trees mainly dropped their leaves during the drier period at the end of the year (Wilcke et al. 2002).

The decreasing DON concentrations in the soil solution during dry periods (Figure 4d) may be explained by increased retention of DOM in the soil as a result of the reduced water fluxes, enhanced microbial DOM decomposition, and sorption to soil particles (Savric 2001). This results in an accumulation of ‘potentially soluble’ (Qualls et al. 2002) organic compounds, particularly in the organic layer. The subsequent mobilization of this DOM pool by suddenly increasing water fluxes as consequence of first rainfall after dry periods may lead to elevated DON concentrations in litter leachate (‘rewetting effect’, Kalbitz et al. 2000). This was frequently reported for DOC (e.g., Guggenberger and Zech 1993; Tipping et al. 1999). In the studied forest, the effects of soil drying and rewetting were more pronounced for DON than for DOC (no significant results were observed for DOP and DOS maybe because of the monthly resolution of measurements). This coincides with the findings of Pechtel et al. (2000) in a temperate forest on similar soil types (Inceptisols to Spodosols) in south Germany. The authors conclude that different mechanisms must be responsible for the mobilization of DOC and DON from the forest floor. However, an alternative explanation of the more pronounced response of DON than of DOC to rewetting might be a preferential release of hydrophilic DOM, which is richer in N (Quall and Haines 1991), after dry periods because of its elevated solubility.

The course of the mean weekly $\text{NO}_3\text{-N}$ concentrations in stream water paralleled the hydrographs of the three microcatchments indicating that the export of $\text{NO}_3\text{-N}$ from the study forest was mainly governed by the hydrological runoff conditions (Figure 5a, c). The rapid increase in $\text{NO}_3\text{-N}$ concentrations in stream water at the beginning of the wetter periods indicated an elevated $\text{NO}_3\text{-N}$ input from the catchment soils from an unknown source. Although mean $\text{NO}_3\text{-N}$ concentrations in stream water were not significantly higher during stormflow conditions, the strong increases in $\text{NO}_3\text{-N}$

concentrations in response to discharge peaks, particularly at the beginning of the wetter season (May 2000 and June 2001, Figure 5a, c), suggested that stormflow plays an appreciable role in $\text{NO}_3\text{-N}$ export. The consistent decrease in $\text{NO}_3\text{-N}$ concentrations in stream water following the beginning of wetter periods indicated reduced nitrification and enhanced denitrification because of (near-)waterlogged conditions.

The DOC concentrations in stream water were positively related to the rainfall under nonstorm conditions. Furthermore, peaks of DOC and DON concentrations in stream water mostly corresponded to rainstorms indicating an enhanced DOM export via elevated stream discharge (Figure 5a, of for DON). One reason might be the flushing of soluble organic compounds accumulated during preceding dry periods from the organic layer into the streams (Kalbitz et al. 2000; Qualls et al. 2002). In a previous study, Goller et al. (2005) showed furthermore that during rainstorms flow paths of water in the soil switched rapidly from mainly vertical to mainly near-surface lateral flow, where concentrations of organic C and N are highest. Recent studies in the temperate zone have shown that this happens in small time periods with strong short-time increases of DOC and DON concentrations in stream water (e.g., Jardine et al. 1990; Brown et al. 1999; Hagedorn et al. 2000).

However, the increase in DOC and DON concentrations was not significantly correlated to the increase in discharge. This might be explained by the fact that DOM mobilization depends on a variety of overlapping factors, e.g. the amount of potentially soluble organic matter, rainfall volume and intensity, and the interception capacity of the canopy. Michalzik et al. (1998) pointed out that a high temporal sampling resolution is necessary to detect possible effects of rainfall events on DOM concentrations in ecosystem solutions, because these effects occur on a small time scale of hours to days.

Nevertheless, the significantly higher three-year means of DOC and DON concentrations in stream water during stormflow than under non-storm conditions suggests that the frequently occurring rainstorm events may cause a considerable loss of C and N from the studied catchments (Figure 6a, b). Similar results were reported by Bushaw et al. (1996), who found that stormflow contributed more than 50% to the total DOC and DON export from a forested water catchment in Virginia.

We were not able to evaluate the relation between rainstorms and DOP and DOS concentrations in stream water because of the monthly resolution of our measurements. However, from the correlation between DOC and DOP and DOS concentrations, we infer a similar response of organic P and S to rainstorms as found for DOC.

The close correlations between annual mean concentrations of DON and DOC in all ecosystem fluxes at all transects indicated that the cycling of the dissolved forms of N and C are connected in the studied forest corroborating other studies in temperate and tropical forests (Kalbitz et al. 2000; Michalzik et al. 2001; Qualls et al. 2002).

Conclusions

In the study forest, DOM was the major vector for most fluxes of N, P, and S. Although DON, DOP, and DOS concentrations were all correlated with those of DOC indicating that their biogeochemical dynamics were linked, differences in the contributions of the organic forms to the total nutrient fluxes imply that the cycles of N, P, and S are partly decoupled, particularly in soil.

The canopy was the largest source of dissolved inorganic N and P, the organic layer of DOC, DON, DOP, and DOS, and the mineral soil of dissolved $\text{SO}_4\text{-S}$. The forest canopy also released considerable DOC, DON, DOP, and DOS. The organic layer was a sink for dissolved inorganic N, P, and S and the mineral soil for all studied C, N, P, and S forms except $\text{SO}_4\text{-S}$.

The concentrations of $\text{NO}_3\text{-N}$ and DON in soil solutions tended to be positively related to pH. Hydrological conditions controlled N, P, and S transport and transformation through the ecosystem. Dissolved inorganic N, P, and S concentrations were increased during dry periods probably because of the dying of microorganisms. In contrast, DON concentrations in soil solutions were reduced during dry periods because of sorption followed by a DON pulse from the organic layer after rewetting.

Rainstorms associated with short-time high-intensive rainfall, occurring from time to time at the study site, appeared to be responsible for a considerable increase in C and N and possibly P and S concentrations in catchment runoff. This indicated an elevated export of these elements from the studied forest during periods of stormflow because of fast near-surface lateral water flow.

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