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TOC, TON, TOS and TOP in rainfall, throughfall, litter percolate and soil solution of a montane rainforest succession at Mt. Kilimanjaro, Tanzania

MARION SCHRUMPF[1,*], WOLFGANG ZECH[1], JOHANNES LEHMANN[2] and HERBERT V.C. LYARUU[3]
*[1]Department of Soil Science, University of Bayreuth, D-95440 Bayreuth, Germany; [2]Department of Crop and Soil Sciences, Cornell University, Ithaca, NY 14853, USA; [3]Botany Department, University of Dar es Salaam, Tanzania; *Author for correspondence (e-mail: mschrumpf@bgc-jena.mpg.de; phone: +49(0)3641-576182; fax: +49(0)3641-577100)*

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Abstract. Organic nutrients have proven to contribute significantly to nutrient cycling in temperate forest ecosystems. Still, little is known about their relevance in the tropics. In the present study, organic C, N, S and P were analysed in rainfall, throughfall, litter percolate and soil solution of a montane rainforest at Mt. Kilimanjaro, Tanzania. The aim was to determine the amounts of organic nutrients in different water pathways and to assess the influence of forest disturbance on organic nutrients by comparing mature forests, secondary forests and shrub vegetation in clearings. Concentrations of all studied elements increased from rainfall to throughfall and litter percolate and then exhibited a rapid decrease in the mineral soil. Concentrations of organic P were above the detection limit only in the litter percolate. Organic N (ON) as a fraction of total N increased from 50% in rainfall (0.19 mg l^{-1}) to 66% (0.45 mg l^{-1}) in throughfall followed by a decline to 39% in the litter percolate (0.77 mg l^{-1}) of the mature forest. Similarly, proportions of organic S and P amounted to 43 and 34%, respectively, in the litter percolate in mature forest. For ON, this proportion further decreased to less than 10% in the soil solution. The latter was probably attributable to a high sorption capacity of the studied Andisols, which led to overall low organic element concentrations in the soil solution (OC: 1.2 mg l^{-1}, ON: 0.05 mg l^{-1} at 1 m soil depth) as compared to other temperate and tropical forest ecosystems. Organic element concentrations were higher in litter percolate and soil solution under the clearings, but there were no differences in the relative contribution of these elements. Organic nutrient forms at Mt. Kilimanjaro appeared to be much less susceptible to leaching than their inorganic forms.

Introduction

Nutrient cycles in forests are closely linked to the hydrological cycle because water acts as the main transporting agent and solvent (Bruijnzeel 1989). Apart from dissolved inorganic nutrients, the importance of dissolved organic matter (DOM) in nutrient cycles has been increasingly emphasized in the past two decades. Dissolved forms of organic N (DON), P (DOP) and S (DOS) contribute significantly to total dissolved N, P and S in throughfall, litter percolate

and soil solution, and their fluxes often exceed the fluxes of corresponding inorganic forms (Homann et al. 1990; Qualls and Haines 1991a; Michalzik et al. 2001). While nitrate commonly is particularly mobile, Hedin et al. (1995) and Perakis and Hedin (2002) showed that N losses in unpolluted watersheds in southern Chile were nearly exclusively comprised of DON, which was formerly not included in forest ecosystem models. Similarly in another south Chilean forest ecosystem, DON comprised more than half of total N in rainfall, throughfall, soil solution and stream flow (Oyarzún et al. 2004). Smolander and Kitunen (2002) pointed out that DON amounted to 62–83% of total N in the soil solution of a Norway spruce stand. In addition to its role for N leaching in forest ecosystems, DON may be a potential N source for plants that can directly assimilate low molecular weight amino acids (Neff et al. 2003). Apart from DON, also DOP has proven to be a major P form in forest floor leachates and in soil solutions of temperate forests (Qualls et al. 2000; Kaiser et al. 2003).

Humus and the litter layer were identified as main sources for DOM in forest ecosystems, with some contribution also from microbial biomass and root exudates (Kalbitz et al. 2000). DOM concentrations and fluxes are controlled by abiotic factors like temperature, soil moisture, soil mineral composition and pH (Andersson et al. 2000; Kaiser and Guggenberger 2000; Kalbitz et al. 2000; Solinger et al. 2001), as well as by biotic factors such as microbial activity and the abundance of fungi (Guggenberger et al. 1994; Kalbitz et al. 2000). The effect of the vegetation cover on fluxes and quality of DOM is still a matter of controversy (Michalzik et al. 2001).

In his review, Chantigny (2003) draws attention to the knowledge gap about the role of DOM in the nutrient cycle of tropical forest ecosystems. Most studies on DOM in the tropics focused on dissolved organic carbon (DOC), while less is known about fluxes of DON, DOP and DOS (McDowell and Asbury 1994; Lesack and Melack 1996; Williams and Melack 1997; McDowell 1998; Schroth et al. 2001; Wilcke et al. 2001; Schwendenmann and Veldkamp 2005). Möller (2001) showed that NO_3–N concentrations exceeded DON in the soil solution of a tropical montane rain forest in Thailand. Only Goller (2005) studied the fate of DOC, DON, DOP and DOS in rainwater in their passage through montane rainforest ecosystems from throughfall to stream water in three micro-catchments in Ecuador. He observed a high contribution of DON and DOS to total N and S in rainfall and throughfall, while their proportion in litter percolate and soil solutions exhibited a high variability within and between the studied headwaters. For example the contribution of DON to total N ranged between 26 and 88% in the soil solution. Apart from the study by Goller (2005), DOS was to our knowledge not included in any published studies on nutrient cycling in the tropics. The study by Roose and Lelong (1981) is the only published assessment on the relevance of DOM in Sub-Saharan Africa known to us.

Deforestation, slash and burn agriculture and other land use changes are common practices in the humid tropics and often increase the risk of land

degradation. Studies of soil chemical changes accompanying these conversions were reviewed by Bruijnzeel (1998), but most of them excluded DOM. Increased concentrations of DOC in soil solution, ground water and stream water were observed in central Amazonia after cutting and burning a rainforest catchment (Williams et al. 1997). Klinge (1997) observed an increase in DON concentrations after clearing a tropical rainforest plot in Amazonia, which was further enhanced after the plots were burned. Land use changes are accompanied by changes in the vegetation cover and thus the amount and quality of litter, which in turn affect DOM leaching from the canopy as well as from the forest floor (Chantigny 2003). Therefore, land use changes can lead to long-term effects on DOM concentrations and fluxes.

The forests of Mt. Kilimanjaro in Tanzania were subject to selective logging and fire during the past decades, which led to a fragmentation of the lower forest belt and changes in plant species composition (Lamprey et al. 1991; Mwasaga 1991; Lambrechts et al. 2002). The aims of this study were (1) to analyse the relevance of organic nutrients in the nutrient cycles of a tropical montane rain forest at Mt. Kilimanjaro, (2) to determine how the concentrations of organic components in rainwater change during the passage through vegetation and soil, and (3) to assess possible effects of changes in the vegetation cover caused by logging. Therefore, concentrations of the inorganic and organic compounds of total organic carbon (TOC), total organic nitrogen (TON), total organic sulphur (TOS) and total organic phosphorus (TOP) were analysed in rainfall, throughfall, litter percolate, soil solution and stream water in mature forest sites, secondary forest sites and early successional shrub vegetation.

Materials and methods

Study area

The study site was located in the forest belt at the south-western slopes of Mt. Kilimanjaro above Machame village at an altitude between 2100 and 2300 m. The soils developed on layered volcanic ashes and were classified as Fulvudands, Epiaquands and Placaquands (Soil Survey Staff 2003). The soils are acidic and characterised by large stocks of organic carbon and high contents of acid oxalate extractable Fe and Al (Tables 1 and 2). The Kilimanjaro region experiences a bimodal rainfall distribution with rainy seasons from March to June and November–December. Long-term studies by the East African Meteorological Department between 1945 and 1958 at an altitude of 2100 m at Mt. Kilimanjaro registered mean annual rainfall amounts of 1840 mm with values varying from 1200 to 3815 mm (Hedberg 1964). Along an altitudinal transect at the most humid southern slopes, Røhr and Killingtveit (2003) reported a rainfall maximum of more than 3500 mm at 2200 m. Temperature measurements in the study area on 50 days from May to October

Table 1. Mean soil chemical characteristics under mature forests, secondary forests and plots with shrub vegetation (± standard error, $n = 3$).

	pH		C	N	S	CEC	$Al_o + 1/2\ Fe_o$	Al_d	Fe_d
	H_2O	$CaCl_2$	(g kg^{-1})			($cmol_c$ kg^{-1})	(g kg^{-1})		
Mature forest									
0–0.15	4.2 ± 0.1	3.7 ± 0.0	178.6 ± 6.0	10.4 ± 0.3	1.6 ± 0.1	9.3 ± 1.4	39.7 ± 5.2	18.4 ± 2.0	62.6 ± 3.8
0.15–0.30	4.7 ± 0.0	4.3 ± 0.1	125.3 ± 13.6	6.3 ± 0.4	1.4 ± 0.1	2.7 ± 0.4	65.1 ± 5.9	43.4 ± 6.2	67.0 ± 9.1
0.30–0.60	4.7 ± 0.0	4.5 ± 0.0	105.3 ± 12.9	4.7 ± 0.5	1.3 ± 0.2	1.0 ± 0.3	61.6 ± 7.4	29.1 ± 4.4	42.8 ± 15.4
0.60–1.00	4.6 ± 0.0	4.8 ± 0.1	69.9 ± 8.0	3.0 ± 0.4	1.4 ± 0.2	0.6 ± 0.1	57.5 ± 9.5	27.2 ± 6.1	42.2 ± 12.2
1.00–1.50	4.6 ± 0.1	4.9 ± 0.1	66.1 ± 19.1	2.5 ± 0.8	1.3 ± 0.2	0.6 ± 0.4	69.2 ± 7.0	26.7 ± 8.7	32.8 ± 12.9
Secondary forest									
0–0.15	4.2 ± 0.1	3.9 ± 0.1	146.8 ± 9.0	9.9 ± 0.6	1.2 ± 0.1	8.0 ± 0.9	34.5 ± 9.5	29.1 ± 2.8	80.6 ± 4.6
0.15–0.30	4.7 ± 0.1	4.4 ± 0.0	106.0 ± 8.0	6.3 ± 0.1	1.2 ± 0.1	1.9 ± 0.1	63.8 ± 16.0	52.3	68.0
0.30–0.60	4.9 ± 0.0	4.8 ± 0.1	93.1 ± 6.4	5.7 ± 0.4	1.2 ± 0.0	1.0 ± 0.2	51.6 ± 21.5	33.9 ± 7.6	59.7 ± 14.3
0.60–1.00	5.0 ± 0.1	4.9 ± 0.0	66.9 ± 7.0	3.5 ± 0.1	2.3 ± 0.2	0.5 ± 0.1	58.1 ± 3.4	36.9 ± 3.0	78.2 ± 2.0
1.00–1.50	5.1 ± 0.1	5.1 ± 1	45.9 ± 3.5	2.2 ± 0.2	2.7 ± 0.6	0.5 ± 0.1	60.8 ± 5.6	23.0 ± 10.6	54.2 ± 17.5
Shrub vegetation									
0–0.15	4.2 ± 0.2	3.8 ± 0.0	168.7 ± 9.2	11.9 ± 0.7	1.5 ± 0.1	9.1 ± 0.8	40.4 ± 6.0	23.0 ± 0.4	67.5 ± 3.3
0.15–0.30	4.6 ± 0.1	4.4 ± 0.1	114.6 ± 5.8	7.6 ± 0.4	1.4 ± 0.1	3.0 ± 0.4	63.2 ± 2.2	38.6 ± 2.0	66.0 ± 1.0
0.30–0.60	4.8 ± 0.1	4.7 ± 0.0	84.8 ± 3.7	5.4 ± 0.3	1.7 ± 0.1	1.0 ± 0.3	68.5 ± 7.6	41.0 ± 0.4	71.1 ± 2.6
0.60–1.00	5.3 ± 0.6	5.3 ± 0.5	69.3 ± 6.5	4.2 ± 0.6	2.3 ± 0.3	0.5 ± 0.1	69.2 ± 10.6	45.2 ± 5.1	80.0 ± 3.7
1.00–1.50	4.9 ± 0.2	5.0 ± 0.1	57.4 ± 9.7	3.3 ± 0.8	2.8 ± 0.3	0.3 ± 0.1	70.1 ± 7.6	35.0 ± 0.9	64.3 ± 0.7

CEC: effective cation exchange capacity; Al_o, Fe_o: acid oxalate extractable Al and Fe; Al_d, Fe_d: dithionite extractable Al and Fe.

Table 2. Mean C and N stocks in the organic soil horizons and the mineral soil up to a soil depth of 1.0 m (±standard error). Different letters indicate significant differences between vegetation types (Scheffé-test, $p < 0.05$).

	Organic soil horizons (t ha^{-1})			Mineral soil (t ha^{-1})			Total (t ha^{-1})		
	Mf	Sf	Sv	Mf	Sf	Sv	Mf	Sf	Sv
C	$164^{b} \pm 22$	$62^{a} \pm 13$	$98^{ab} \pm 18$	$565^{a} \pm 44$	$471^{a} \pm 33$	$474^{a} \pm 8$	$729^{b} \pm 54$	$533^{a} \pm 35$	$572^{ab} \pm 13$
N	$10.3^{b} \pm 1.2$	$3.7^{a} \pm 0.8$	$6.3^{ab} \pm 1.3$	$25.6^{a} \pm 2.8$	$27.4^{a} \pm 0.4$	$30.0^{a} \pm 1.4$	$35.9^{a} \pm 3.1$	$31.1^{a} \pm 0.9$	$36.4^{a} \pm 1.1$

Mf: Mature forest; Sf: Secondary forest; Sv: Shrub vegetation.

2000 revealed a median daily minimum temperature of 8.7 °C and a maximum of 14.8 °C in the forest.

The mature forest reaches a canopy height of up to more than 40 m, is dominated by the tree species *Ocotea usambarensis* (Engl.) and characterised by a high epiphyte density and diversity (mainly ferns and mosses). The secondary forests originated most probably from the main logging phase during the Second World War, when a sawmill was located close to the study sites (Wood 1964). At approximately 60 years of age, they overall exhibited a lower stand height (maximum 32 m), smaller stem diameters (maximum 0.7 m in the secondary forest vs. 1.6 m in the mature forest), and a lower epiphyte density compared to the mature forest. The dominant tree species in the canopy layer is the pioneer *Macaranga kilimanjarica* (Pax), accompanied by young *Ocotea usambarensis* trees. The prevailing shrub and herb vegetation on the early successional sites is dominated by *Rubus steudneri* (Schweinf.), bracken fern (*Pteridium aquilinum* L.) and some lianas. The sites were cleared by selective logging and had an approximate age of up to greater than 10 years according to regional foresters. Although no direct evidence for recent fires on the plots were observed, it seems likely that fires are among the causes for the seemingly impeded forest regeneration on these sites (Hemp 2002).

Study design

Sites with shrub vegetation and secondary forests were studied at three plots and mature forests at four plots. Each plot was 400 m^2 and had a slope of $< 10°$ with generally southward direction. As no mature forest plot of sufficient size was left at the lower slopes of the study area up to an elevation of 2150 m, these plots had to be chosen at slightly higher altitudes than the secondary forests and the plots with shrub vegetation. Thus, the minimum vertical distance between the mature forest plots and the other plots was 140 m. Because of a fire experiment on some plots with shrub vegetation, one clearing had to be replaced by another one in the second study year. Next to each plot, a soil pit was dug, described and chemically characterised. All plots were tested for homogeneity using soil coring. Rainfall was collected at 2100 and 2250 m using five collectors placed in clearings 1.5 m above the ground and all plots were equipped with 8–10 randomly distributed throughfall collectors. Rain collectors as well as throughfall collectors consisted of 2-l collection bottles and a sharp-rimmed funnel with a diameter of 115 mm, all made of polyethylene. The collection bottles of the throughfall collectors were partly buried in the ground so that the rims of the funnels were approximately 0.3 m above the ground surface. The bottom of the funnel was covered by a 1-mm polyethylene net to reduce the contamination of the samples with litter and insects. Additionally, a table-tennis ball was placed in the funnel mouth to reduce

evaporation losses. The funnels were cleaned after sampling if necessary and collection bottles were cleaned twice a year using a brush and deionized water.

Four to five collectors for litter percolate were installed below the root mat in the Oa layer at each plot. The collectors consisted of plastic boxes (285 mm side length, 80 mm height), covered with a 1-mm polyethylene mesh. A silicone plastic tube connected the lysimeter to a buried 2-l polyethylene sampling bottle in a closed bucket. No tension was applied. The amount of water collected in the lysimeters may have been underestimated compared to water percolating through the litter layer in the undisturbed soil next to the collector, since water potential rarely reaches saturation in the litter layer which is necessary for the water to drip into the collection container.

Suction cups (SKL 100, ceramic cup K100, UMS Munich) were used to collect the soil solution from three soil depths in three replicates (0.15, 0.30 and 1.00 m) per site. Soil solution was extracted using a constant pressure of 400 hPa overnight. By applying tension, additional solution is extracted that would not be obtained with free draining lysimeters, probably leading to different water amounts and also solute concentrations. In the suction lysimeters and litter percolate collectors soil solution was collected once or twice a week. Therefore, and also because suction cups can be easily by-passed by macropore flow in the soil during high rainfall events (Addiscott 1994), there was a risk of failing to quantify amounts and composition of single infiltration peaks. Direct comparisons between free draining lysimeters in the litter layer and suction cups in mineral soil may be limited, but since with 400 hPa applied pressures were comparatively low and as soil properties were overall comparable among sites, the determined concentrations can nevertheless be used to assess possible vegetation effects. Close to the mature forest sites, water from a perennial headwater was regularly collected as grab samples.

Most equipment was installed in March 2000, and sampling started in May 2000. Sampling of litter percolate collectors was only possible from November 2000 onwards for organizational reasons. These data are therefore missing for the first half year. Sampling was done twice a week in the first study year. Water amounts were separately measured for all collectors, while for chemical analysis, a composite sample of each site was prepared for rainfall, throughfall and litter percolate. Samples of soil solution were combined from all three replicate cups in one collection bottle for each soil depth and site so that no individual analysis of single suction cups within each site was feasible. From June 2001 onwards, sampling was continued on a weekly basis. During this time, mature forest sites were sampled 2 days after the other sites because of problems with the pumps. As rainfall regimes and thus soil water contents and composition could in principle change within short time scales, the comparison of samples taken at different days may have caused challenges in comparisons among sites. However, analyses of individual samples at higher resolution for some periods and the measurement of composite samples of the first year revealed that the seasonal variation of the soil solution concentrations in the mature forests was low compared to the secondary forest sites and especially

the plots with shrub vegetation. Thus, the assumption was made that the median concentration of the composite samples obtained from weekly measurements in the mature forest during the second year should be very close to the median that might have been obtained by sampling on a different day at the secondary forest sites and the plots with shrub vegetation. Therefore, only mean or median concentrations for total years but no individual fortnight samples or time series were statistically compared between vegetation types.

The water samples were combined into 14-d samples irrespective of sampling scheme. For rainfall, throughfall and litter percolate, volume weighted samples were prepared, while arithmetic means were used for soil solutions and the stream water samples, since no reliable data on fluxes were available. Samples were stored frozen. Prior to analysis, rain and litter percolate samples were filtered through ash-free filter papers with a pore size < 2 μm (Schleicher and Schuell, blue band 589[3]). Thus, measured concentrations of organic forms of C, N, S and P could not be referred to as dissolved. Instead the term 'total organic' (TO) was used.

TOC was determined using a TOC analyser (Elementar High TOC and Shimadzu TOC-5050). For the determination of total N, NH_4–N, NO_3–N and NO_2–N, a Segmented Flow Analyser (SANplus, SA 2000/4000, Skalar Analytical BV, The Netherlands) was used. Total N was digested using alkaline persulfate and ultraviolet (UV) to convert NH_4–N and organic N to NO_3–N. The same equipment was used for analysis of total P (P_{tot}, persulfate-UV digestion) and PO_4–P. Since concentrations for PO_4–P and total P were usually below the detection limit (0.04 mg l^{-1} for total P and 0.05 mg l^{-1} for PO_4–P) in rainfall, throughfall and soil solution, only one quarter of these samples was analysed randomly after the first half year, to check if there was a change. Total S (S_{tot}) was measured using an ICP-OES (Integra XMP, GBC Scientific Equipment Pty. Ltd., Australia) and an IC was used for the determination of SO_4–S. Detection limits were 0.3 mg l^{-1} for SO_4–S and total S.

TON, TOP and TOS were calculated as difference between total amounts and inorganic forms ($TON = N_{tot} - NH_4\text{–}N - (NO_3\text{–}N + NO_2\text{–}N)$, $TOP = P_{tot} - PO_4\text{–}P$, $TOS = S_{tot} - SO_4\text{–}S$).

Data analyses and statistics

TOC and TON concentrations were analysed for the entire sampling period from May 2000 to September 2002. TOS was only measured for 1 year, starting from December 2000 when litter percolate collectors were installed and calibrated. Thus, for comparisons among all dissolved elements, the latter time period (December 2000–December 2001) was used. Annual means were calculated as flux weighted means for rainfall and throughfall, while for litter percolate, soil solution and stream water, the median was used as no reliable data on the corresponding water fluxes were available. If values were below the detection limit, they were set as zero for the calculation of means. The same

was done when calculations of organically bound elements resulted in negative values, so that total values were rather conservative. The annual means of the different sites were compared by solution type using one-way analyses of variance (ANOVA), followed by a post-hoc separation of means by the Scheffé-test ($p < 0.05$). Correlation analyses were conducted as Pearson Product-Moment Correlations. For these analyses, values below the detection limit were excluded. Statistical analyses were all conducted using the program STATISTICA 5.0 (Statsoft, Inc., Tulsa, OK).

Results

Hydrology

Rainfall amounts in the first study year from June 2000 to May 2001 were 2480 mm at 2250 m and 2600 mm at 2100 m. In the following year, rainfall amounts were lower and varied between 1960 and 2210 mm, respectively, at both elevations. Rainfall interception, which was determined as the difference between bulk precipitation and throughfall amounts, accounted for 3–9% of incident rainfall in the plots with shrub vegetation, 27–32% in the secondary forest and 18–30% in the mature forest.

Changes of organic nutrient concentrations in water upon passage through vegetation and soil

Mean concentrations of field replicates for the 14-d mixed samples during 1 year form the basis for the box-whisker-plots in Figure 1. Hence, the diagrams show the concentration range throughout the year, but not the variability between the plots. As rainfall concentrations were not volume weighted in these graphs, the median concentrations tended towards larger values as compared to the volume weighted means presented in Table 3.

Annual mean concentrations of total organic elements in rainfall ranged between 3.4 and 5.2 mg l^{-1} for TOC, 0.13–0.30 mg l^{-1} for TON and accounted for 0.4 mg l^{-1} for TOS. The concentrations of these elements in rainfall increased during the passage through the vegetation cover, which was most pronounced on the forested sites (Table 3, Figure 1). Although water fluxes in throughfall were higher in the plots with shrub vegetation, TOC fluxes were significantly lower as compared to the two forest types (Table 4). As half of the analysed rainfall samples were below the detection limit for TOS and were calculated as being absent in these cases, total TOS fluxes on an annual basis are likely to be underestimated. In more than half of the samples, TOP was not detectable and thus it was not included in rainfall and throughfall analyses.

Overall, largest concentrations of total organically bound elements were measured in the litter percolate (Table 3; Figure 1). In the plots with shrub vegetation, TOC, TON and TOP concentrations in litter percolate were

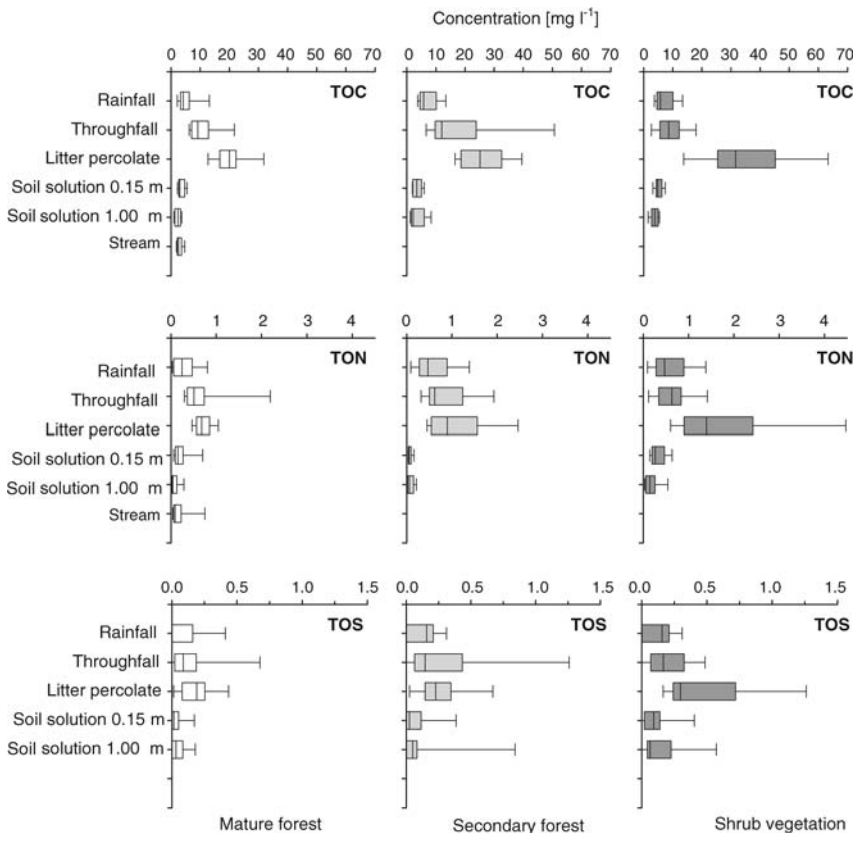

Figure 1. Changes in TOC, TON and TOS concentrations in percolating water on the passage through three vegetation types at Mt. Kilimanjaro. Boxes (25th and 75th percentile, line represents median) include mean concentrations per vegetation type of 2 week mixed samples from Dec 2000 to Nov 2001 and represent the temporal variability of solute concentrations. Outliers above and below the 90th and 10th percentile (whiskers) are not shown.

significantly larger than those under mature forest. As water fluxes were probably higher in the litter percolate of the plots with shrub vegetation due to higher throughfall amounts, it can be assumed that also the fluxes of these elements in litter percolate were higher at the plots with shrub vegetation as compared to the forest sites, although it was not possible to quantify this result. In the soil solution, TOP was not detectable at any depth. Also the median TOS concentration was in the range of the detection limit only for the plots with shrub vegetation. For TOC and TON, concentrations declined by a factor of 5–10 from litter percolate to soil solution (Table 3, Figure 1). Mean TOC concentrations in the topsoil solution were significantly higher in the plots with shrub vegetation as compared to the secondary forest plots only in the second study year, while for TON, these differences were significant for both years. Such differences were not significant for the deeper soil layers. Median

Table 3. Mean concentrations of total organically bound elements. The mean was calculated from annual volume-weighted mean concentrations for rainfall and throughfall and from annual median concentrations at individual sites for litter percolate, soil solution and stream water (± standard error, $n = 3$ for clearings and secondary forest, $n = 4$ for mature forest). Different letters indicate significant differences between vegetation types (Scheffé-test, $p < 0.05$).

		TOC (mg l^{-1})		TON (mg l^{-1})		TOS (mg l^{-1})	TOP (mg l^{-1})
		year 1	year 2	year 1	year 2	year 1*	year 2
Rainfall	2100 m	5.18	4.29	0.21	0.30	0.04	ND
	2250 m	4.34	3.41	0.13	0.24	0.04	ND
Throughfall							
	Mf	$7.40^{a} \pm 0.76$	$11.4^{a} \pm 1.14$	$0.39^{a} \pm 0.06$	$0.50^{a} \pm 0.05$	$0.06^{a} \pm 0.02$	ND
	Sf	$10.9^{b} \pm 0.20$	$13.1^{a} \pm 0.96$	$0.49^{a} \pm 0.07$	$0.58^{a} \pm 0.04$	$0.08^{a} \pm 0.01$	ND
	Sv	$5.22^{a} \pm 0.27$	$5.26^{b} \pm 0.66$	$0.35^{a} \pm 0.03$	$0.43^{a} \pm 0.04$	$0.09^{a} \pm 0.01$	ND
Litter percolate							
	Mf		$21.22^{a} \pm 2.08$		$0.77^{a} \pm 0.07$	$0.18^{a} \pm 0.03$	$0.04^{a} \pm 0.00$
	Sf		$24.43^{ab} \pm 2.09$		$0.88^{a} \pm 0.11$	$0.23^{a} \pm 0.02$	$0.06^{ab} \pm 0.01$
	Sv		$30.81^{b} \pm 0.51$		$1.48^{b} \pm 0.12$	$0.29^{a} \pm 0.03$	$0.09^{b} \pm 0.01$
Soil solution 0.15 m							
	Mf	$2.33^{a} \pm 0.20$	$2.67^{ab} \pm 0.25$	$0.09^{a} \pm 0.01$	$0.14^{ab} \pm 0.02$	ND	ND
	Sf	$2.97^{a} \pm 0.67$	$2.02^{a} \pm 0.28$	$0.05^{b} \pm 0.01$	$0.09^{a} \pm 0.01$	ND	ND
	Sv	$4.36^{a} \pm 0.62$	$4.30^{b} \pm 0.71$	$0.17^{c} \pm 0.01$	$0.31^{b} \pm 0.11$	0.07 ± 0.01	ND
Soil solution 1.00 m							
	Mf	$1.54^{a} \pm 0.05$	$1.26^{a} \pm 0.15$	$0.03^{a} \pm 0.01$	$0.06^{a} \pm 0.01$	ND	ND
	Sf	$3.19^{a} \pm 0.54$	$1.73^{a} \pm 0.25$	$0.04^{a} \pm 0.02$	$0.08^{a} \pm 0.02$	ND	ND
	Sv	$3.69^{a} \pm 1.55$	$1.99^{a} \pm 0.46$	$0.04^{a} \pm 0.02$	$0.14^{a} \pm 0.07$	0.08 ± 0.04	ND
Stream			2.88		0.09	ND	ND

Year 1: June 2000–June 2001, year 2: June 2001–June 2002, year 1*: Dec. 2000–Dec. 2001.
ND: Median concentration was below the detection limit of S and P. MF: Mature forest; SF: Secondary forest; Sv: Shrub vegetation.

concentrations of TOC and TON in stream water sampled close to the mature forest sites were slightly larger than concentrations measured in solutions sampled with the deepest suction cups under mature forest.

Correlation analyses

TOC fluxes in rainwater were strongly correlated with rainfall amounts ($r = 0.87$, $n = 48$ for 2100 m and $r = 0.82$, $n = 45$ for 2250 m, $p < 0.001$; data not shown). Correlations for TOS fluxes were less strong ($r = 0.75$, $p < 0.005$, $n = 13$ and $r = 0.79$, $p < 0.01$, $n = 10$ respectively). For TON only weak correlations were found ($r = 0.31$ and $r = 0.28$, $p < 0.05$, $n = 45$). Net throughfall fluxes were calculated as the difference between throughfall and rainfall fluxes of individual elements and represent the amount of total organically bound elements added during the passage through the canopy. That flux was only weakly but significantly correlated with rainfall amounts and concentrations for TOC at the forest sites (Table 5). Net TON fluxes showed slightly stronger correlations with rainfall amounts and concentrations for both forest types, indicating increasing net fluxes with increasing precipitation and subsequent lower rainfall concentrations. Such a relationship was not found for the plots with shrub vegetation. For net TOS fluxes, the number of fluxes usable for correlation analyses ($n = 13$ for 2100 m and $n = 10$ for 2250 m) was low as rainfall concentrations were often below the detection limit. Net TOS fluxes were negatively correlated to rainfall amounts at the mature forest and the plots with shrub vegetation, but not at the secondary forest sites. No correlation with rainfall concentrations was observed for net TOS fluxes (Table 5).

The analyses of throughfall fluxes of TOC and TON revealed a close correlation for mature forests ($r = 0.91$, $p < 0.001$, $n = 45$), a weaker one for secondary forests ($r = 0.66$, $p < 0.001$, $n = 47$) and an even weaker one for plots with shrub vegetation due to one outlier ($r = 0.55$, $p < 0.001$, $n = 47$). A weak positive correlation was also observed between TOC fluxes in throughfall and TOS fluxes for mature forests ($r = 0.68$, $p < 0.001$, $n = 21$) and plots with shrub vegetation ($r = 0.70$, $p < 0.001$, $n = 20$) while for secondary forests they were not significant ($r = 0.35$, $n = 21$).

Organic and inorganic fluxes were significantly correlated in throughfall for N, with closest correlations for the mature forest (Figure 2). Correlations between organic and inorganic S forms were also significant and strongest for mature forest, while overall relationships were less strong (Figure 3). Overall, closest correlations were found for N in the mature forest sites. For rainfall, no correlations between organic and inorganic fluxes were found for S and N. The same was true for net throughfall fluxes.

Median TOC concentrations in the litter percolate of all sites were positively correlated to median TON, TOP and TOS concentrations, with the closest correlation for TON (Figure 4). Overall, mature forests, secondary forests and early successional plots showed different amounts of total organically bound

nutrients released as can be seen in Figure 4. In the soil solution at 0.15 m, a similar but weaker correlation was found for TOC and TON ($r = 0.64$, $p < 0.05$, $n = 10$; data not shown). For TOP and TOS most concentrations were below the detection limit in soil solution, and therefore no correlation analyses were possible.

The relevance of organic as compared to inorganic N, S and P forms

The largest proportion of TON as a fraction of total N (N_{tot}) was found for throughfall in the forests (Table 6). At the bottom of the forest floor, the proportion of TON was less than 50% and it further decreased in the mineral

Table 4. Fluxes of total organically bound elements in rainfall and throughfall (±standard error, $n = 3$ for clearings and secondary forest, $n = 4$ for mature forest). Different letters indicate significant differences between vegetation types (Scheffé-test, $p < 0.05$).

	Rainfall (kg ha^{-1} a^{-1})		Throughfall (kg ha^{-1} a^{-1})		
	2100 m	2250 m	Mature forest	Secondary forest	Shrub vegetation
DOC					
June 2000–June 2001	143.9	110.9	$160.0^{ab} \pm 17.3$	$218.5^{a} \pm 6.03$	$137.4^{b} \pm 0.26$
June 2001–June 2002	88.9	59.4	$142.2^{a} \pm 13.6$	$182.3^{a} \pm 9.1$	$102.8^{b} \pm 8.0$
DON					
June 2000–June 2001	5.97	3.36	$8.31^{a} \pm 1.23$	$10.31^{a} \pm 1.42$	$9.59^{a} \pm 0.84$
June 2001–June 2002	6.18	4.15	$6.24^{a} \pm 0.60$	$8.06^{a} \pm 0.35$	$8.11^{a} \pm 0.34$
DOS					
Dec. 2000–Dec. 2001	0.99	1.05	$1.34^{a} \pm 0.49$	$1.57^{a} \pm 0.19$	$2.39^{a} \pm 0.20$

Table 5. Correlation coefficients between net throughfall fluxes (throughfall – rainfall fluxes) of TOC, TON and TOS and rainfall amount and concentration.

	Rainfall amount (mg l^{-1})			Rainfall concentrations of total organically bound elements (mg l^{-1})		
	Mature forest	Secondary forest	Shrub vegetation	Mature forest	Secondary forest	Shrub vegetation
Net throughfall flux						
TOC						
r (n = 40–45)[#]	0.53	0.56	0.01	−0.45	−0.38	−0.09
p	< 0.001	< 0.001	n.s.	< 0.005	< 0.05	n.s.
TON						
r (n = 48)	0.65	0.66	0.11	−0.67	−0.52	0.26
p	< 0.001	< 0.001	n.s.	< 0.001	< 0.001	n.s.
TOS						
r (n = 10–13)	−0.77	−0.45	−0.87	−0.09	0.09	0.21
p	< 0.01	n.s.	< 0.005	n.s.	n.s.	n.s.

[#] Excluding one outlier.

soil, where its proportion was often less than 10%. Except for throughfall, where the percentage of TON was lower at the plots with shrub vegetation ($p < 0.05$), no vegetation effects on the partitioning of TON in organic and inorganic forms was found.

The proportion of TOS as a fraction of total S (S_{tot}) in throughfall was low compared to the litter percolate. In the soil solution under the plots with shrub vegetation, the proportion of TOS was again less than in percolates from the organic horizons similar to N. No effect of the vegetation type on the percentage of TOS was detectable. With around 35% the proportion of TOP as a fraction of total P in the litter percolate under the forests was slightly less than the one of TON (39–43%) and TOS (42–43%).

Discussion

Since different filter papers with varying pore sizes have been used in published studies on the contents of organic nutrients in solutions, direct comparisons

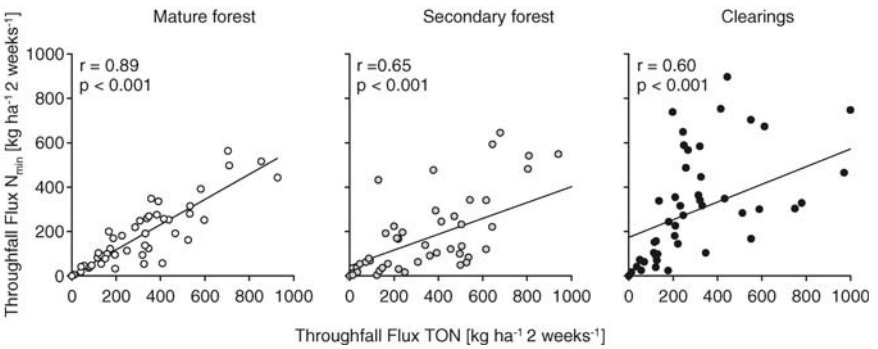

Figure 2. Relationship between organic (TON) and inorganic (N_{min} = NH_4–N + NO_3–N) N fluxes in throughfall at Mt. Kilimanjaro. Time period considered: June 2000–June 2002.

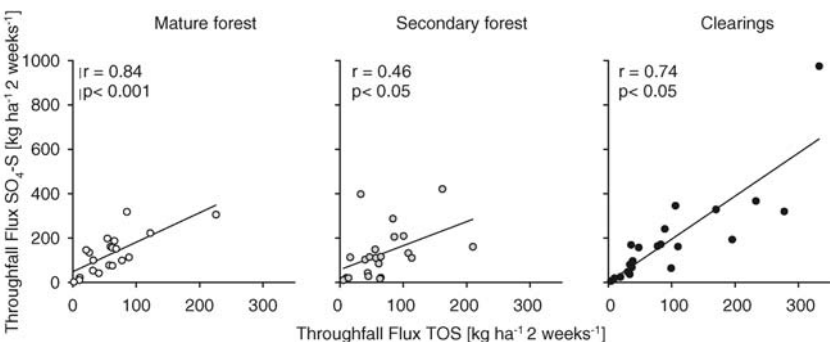

Figure 3. Relationship between organic and inorganic S fluxes in throughfall at Mt. Kilimanjaro. Time period considered: Dec. 2000–Dec. 2001.

between locations have some limitations. In the next paragraphs, the term 'dissolved' will be used for sites using filters with a pore size of < 0.7 μm, while 'total' will be used for filtration with a pore size > 0.7 μm, which was mainly the case in the present study at Mt. Kilimanjaro and in a study in an Ecuadorian montane rain-forest (Goller 2005). Differences were most pronounced in rainfall, throughfall and litter percolate samples, while the utilization of suction cups for the extraction of soil solution excludes particles >1 μm, thus reducing the effects of different filters.

Comparison of DOC and DON from ecosystem analyses in temperate and tropical forest ecosystems

For the temperate zone and especially the northern hemisphere, a number of studies have examined concentrations and fluxes of DOC and DON in forest ecosystems (McDowell and Likens 1988; Qualls et al. 1991b; Michalzik and Matzner 1999). Only a few studies have been undertaken in the tropics (see some examples in Tables 7 and 8).

The high TOC concentrations and fluxes in rainwater of the Ecuadorian (Wilcke et al. 2001) and the Tanzanian montane rainforest might be a result of differences in pore sizes of filters used prior to analyses. Ecuadorian and Tanzanian samples were filtered using a coarser filter (4–7 and 2 μm, respectively) compared to the studies in Thailand (0.45 μm; Möller 2001) and Puerto Rico (0.7 μm; McDowell 1998). Hence, a larger quantity of particulate organic nutrients was included in the first two studies. In a subtropical region in Taiwan, Liu and Sheu (2003) also observed high concentrations and fluxes of DOC in rainfall, though using a 0.45 μm filter.

Throughfall DOC concentrations in temperate forests show a high variability being in the same order of magnitude as the throughfall concentrations of tropical forests presented in Table 7. DOC throughfall fluxes at tropical sites were rather at the higher end of those obtained at temperate sites, which is probably due to higher throughfall amounts in the tropics (Table 8).

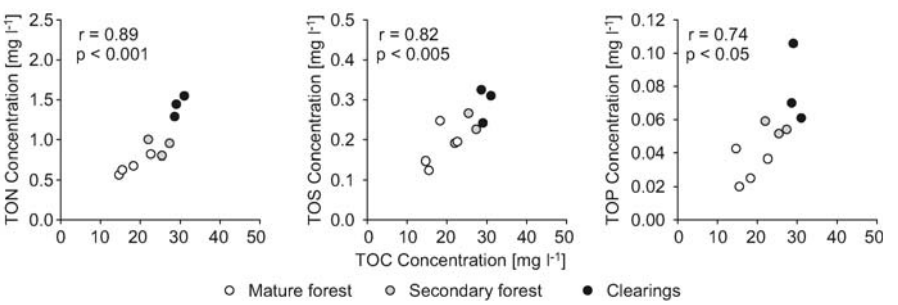

Figure 4. Correlation between median concentrations of TOC and TON, TOC and TOP at individual plots for the time from Dec. 2000–Dec. 2001 ($n = 10$).

Table 6. Mean percentage of total N, S and P present as TON, TOS and TOP in different water pathways under different vegetation types. Percentages were calculated from volume weighted mean concentrations for rainfall and throughfall and median values for other water samples. Means for the period from June 2001 to June 2002 were used for TON and TOP, while Dec. 2000–Dec. 2001 was used for TOS (± standard error, $n = 3$ for clearings and secondary forest, $n = 4$ for mature forest).

	Percentages of N_{tot}, S_{tot} and P_{tot} as TON, TOS and TOP								
	TON (%)			TOS (%)			TOP (%)		
	Mf	Sf	Sv	Mf	Sf	Sv	Mf	Sf	Sv
Rainfall	48	53	53	34	34	34	ND	ND	ND
Throughfall	66 ± 3	77 ± 9	57 ± 3	34 ± 3	37 ± 2	36 ± 1	ND	ND	ND
Litter percolate	39 ± 2	43 ± 3	33 ± 11	43 ± 5	42 ± 2	44 ± 9	34 ± 4	35 ± 9	21 ± 5
Soil solution (0.15 m)	8 ± 2	7 ± 1	11 ± 3	ND	ND	17 ± 5	ND	ND	ND
Soil solution (0.30 m)	7 ± 1	10 ± 3	7 ± 1	–	–	–	–	–	–
Soil solution (1.00 m)	5 ± 1	14 ± 4	16 ± 5	ND	ND	23 ± 2*	ND	ND	ND
Stream water	12	–	–	–	–	–	–	–	–

ND: Not detectable; Mf: Mature forest; Sf: Secondary forest; Sv: Shrub vegetation; *: $n = 2$.

Table 7. DOC and DON concentrations in temperate and tropical forest ecosystems. Values put in parenthesis present soil depths where solution samples were extracted.

	RF (mg l^{-1})	TF (mg l^{-1})	LP (mg l^{-1})	SS (mg l^{-1}) (m)	SS (mg l^{-1}) (m)
DOC					
Range of different temperate forests[a]		3–35	20–90	18–75 A horizons	2–35 B horizons
StRF Taiwan[b]	4.7	8.3		21 (0.15)	10 (0.6)
LRF Ivory Coast[c#]	1.3	7.4		8.7 (0.3)	8.1 (2.0)
LRF Costa Rica[d]		1.8	8.1	3.9 (0.2)	0.7 (1.5)
MRF Puerto Rico[e]	1.0	6.2		5.3 (0.4)	2.4 (0.8)
MRF Thailand[f]	1.5	3.3–4.4		4–6^{+} (0.15)	2—3^{+} (0.8)
MRF Ecuador[g#]	4–4.5	11–17	27–55	7.2—27 (0.15)	
MRF Tanzania[h#]	3.4—5.2	7.4–13	21–24	2.0–3.0 (0.15)	1.3–3.2 (1.0)
DON					
Range of different temperate forests[a]		0.25–1.11	0.4–2.45		0.2–1.1 B horizons
LRF Brazil[i*]	0.15	0.48		0.4^{+} (0.25)	0.2–0.3^{+} (1.1)
MRF Thailand[f]	0.22	0.22–0.25		0.2–0.3^{+} (0.15)	
MRF Ecuador[g#]	0.19–0.21	0.57–0.89	1.2–2.9	0.39–1.3 (0.15)	
MRF Tanzania[h#]	0.13–0.30	0.39–0.58	0.77–0.88	0.05–0.14 (0.15)	0.03–0.08

RF: rainfall; TF: throughfall; LP: litter percolate; SS: soil solution; StRF: Subtropical rainforest; LRF: Lowland rainforest; MRF: Montane rain forest; [#]total organic C and N; [+]values taken from graph.
[a]Michalzik et al. (2001).
[b]Liu and Sheu (2003).
[c]Roose and Lelong (1981).
[d]Schwendenmann and Veldkamp (2005).
[e]McDowell (1998).
[f]Möller (2001).
[g]Goller (2005) range for 3 catchments.
[h]This study.
[i]Klinge (1997)* values calculated as difference between total N and inorganic forms presented in the study.

TOC concentrations in litter percolate at Mt. Kilimanjaro were at the lower end of values measured for temperate forests and are also lower than in a tropical montane rain forest in Ecuador with similar rainfall amounts (Wilcke et al. 2001; Goller 2005). DOC concentrations measured in the litter percolate of a Costa Rican rainforest were even lower, which can partly be explained by higher rainfall amounts (4070 mm) leading to a dilution of solutes in percolating water (Schwendenmann and Veldkamp 2005). Overall DOC concentrations of soil solutions at the tropical sites were lower than the concentrations in temperate regions. In A horizons at Mt. Kilimanjaro, TOC concentrations were an order of magnitude lower compared to temperate sites and significantly lower than at other tropical sites. Still, comparisons of concentrations among different studies are limited by the fact that they are dependant on water fluxes. Therefore, future studies on belowground water chemistry in the tropics should also include approximations of nutrient fluxes.

The number of ecosystem studies in the humid tropics which include DON measurements is small. Rainfall concentrations and fluxes of DON at rainforest sites in Brazil (Klinge 1997) and Costa Rica (Schwendenmann and Veldkamp 2005) were in the same order of magnitude as at Mt. Kilimanjaro (Table 8). Throughfall DON concentrations were lowest at a rainforest site in Thailand (Möller 2001). Other tropical sites were within the range of concentrations observed for temperate forest ecosystems, while fluxes were rather higher (Tables 7 and 8). In the soil solution, TOC and TON

Table 8. DOC and DON fluxes in rainfall and throughfall of selected temperate and tropical forest sites.

	RF (kg ha^{-1} a^{-1})	TF (kg ha^{-1} a^{-1})
DOC		
Range of different temperate forests[a]		40–160
StRF Taiwan[b]	143	189
LRF Costa Rica[c]	22–36	232
LRF Puerto Rico[d]	34	127
MRF Ecuador[e#]	90	143–266
MRF Tanzania[f#]	59–89	142–182
DON		
Range of different temperate forests[a]		1.2–12
LRF Costa Rica[c]	1–6	9
LRF Brazil[g*]	4.6	12
MRF Tanzania[f#]	3.4–6.2	6.2–10

[a]Michalzik et al. (2001).
[b]Liu and Sheu (2003).
[c]Schwendenmann and Veldkamp (2005).
[d]McDowell (1998).
[e]Goller (2005) range for 3 catchments.
[f]This study.
[g]Klinge (1997)* values calculated as difference between total N and inorganic forms presented in the study.
[#]Total organic C and N.

concentrations at Mt. Kilimanjaro were the lowest of all tropical sites summarised in Table 7.

A tropical montane rainforest in Ecuador revealed overall higher OM concentrations in litter percolate and soil solution as compared to the study forest at Mt. Kilimanjaro. Besides TOC and TON (see Table 7), also TOP (0.02–2.20 mg l^{-1}) and TOS (0.37–2.0 mg l^{-1}) concentrations in litter percolate were higher than at Mt. Kilimanjaro. The same was true for TOS in the soil solution at 0.15 m soil depth (0.11–0.46 mg l^{-1}), while TOP was below the detection limit in the soil solution at both studies. The overall larger OM concentrations in the litter percolate and soil solution of the Ecuadorian site might be due to the extraordinarily high accumulation of organic material in the litter layer of these forests (Schrumpf et al. 2001).

Contribution of organic matter to throughfall fluxes at Mt. Kilimanjaro

DOM concentrations usually increase during the passage of rainwater through the forest canopy (Table 7). Tukey (1970) reported that several organic substances including carbohydrates and amino acids can be leached from plant tissues. Also Parker (1983) attributed the DOC increase during the passage of water through a forest canopy to leaching but argued that decomposition of dead organic material in the canopy may also contribute to DOC in throughfall. This might be of special importance in tropical montane rain forests with a high density of epiphytes. Dead organic matter (crown humus and intercepted litterfall) comprised over 60% of total epiphytic material in a montane rainforest in Costa Rica (Nadkarni et al. 2004). The microbial biomass in canopy humus was found to be similar to that of the forest floor (Vance and Nadkarni 1990). Thus, leaching of decomposing parts of epiphytes as well as from canopy humus is likely to contribute to OM concentrations in throughfall of the studied montane rainforest at Mt. Kilimanjaro.

The correlation between net throughfall TOC fluxes and rainfall amounts observed at Mt. Kilimanjaro indicates that, besides wash-off of dry deposits from the canopy, leaching from plant tissues contributes to organic matter in throughfall (Parker 1983). In the mature forest, a close correlation between throughfall fluxes of TOC and TON suggested that both variables were controlled by similar factors. In addition, the significant relationship between organic and inorganic N fluxes in throughfall, especially for the mature forest sites, points out that both fluxes might be determined by similar processes.

Processes that include ion adsorption and exchange are probably influenced by solute concentrations. The negative correlation between net TON throughfall fluxes and rainfall TON concentrations supports this hypothesis. Net throughfall TON fluxes at the plots with shrub vegetation were neither correlated to rainfall amounts nor to rainfall concentrations. Thus, processes determining net throughfall fluxes in the forests might be related to specific

properties of the forested sites such as the presence of epiphytes or specific properties of tree leaves.

Reasons for low TOC and TON concentrations in soil solution at Mt. Kilimanjaro

Concentrations of TOC as well as of TON in the litter percolate at Mt. Kilimanjaro were at the lower limit of concentrations measured at other sites. In the soil solution, concentrations were lower than values obtained in temperate forests. Also, the relative contribution of TON to total N in litter percolate and soil solution was smaller than the proportions in temperate (Qualls et al. 1991b; Smolander et al. 2001) and other tropical (Klinge 1997; Goller 2005) forest ecosystems. This result may be due to low release of organic matter in the forest floor, rapid mineralisation of organic compounds, plant uptake or adsorption to minerals.

In the present study, forest floor percolate was sampled in the Oa horizon below the root mat of the trees. With a total thickness of up to 0.33 m of the soil organic layer, the amount of organic material present is probably sufficiently high to act as a significant source for DOM. Plant roots can present a source (root exudates, decomposing dead roots), but also a sink for DOM due to direct uptake of DON (Neff et al. 2003). While there is evidence for direct plant uptake of amino acids, it is not yet clear whether direct root uptake of dissolved organic N compounds is an important pathway for N acquisition by plants, even for high latitude ecosystems (Jones et al. 2005). Thus, it cannot be ruled out that tropical montane forest plants can use DON constituents but to what extent is rather unclear.

Sorption processes may have affected the OM concentrations in the soil solution and to a minor extent also in the litter percolate, since the Oa horizons already contained a significant amount of mineral particles. According to studies by Kaiser et al. (1996), Fe and Al hydrous oxides are major sorbents for DOM in soils. Andisols, the dominant soil type in the study area, usually contain large amounts of oxalate-extractable Fe and Al and are expected to have a high sorption capacity for DOM. This was also confirmed by studies of Dahlgren et al. (1991) in non-allophanic Andisols of Japan, where large quantities of DOM were immobilized or decomposed in the A1 horizons. In batch experiments, Nambu and Yonebayashi (2000) similarly measured more DOM sorption to Andisols as compared to Inceptisols and Entisols. Neff et al. (2000) studied the influence of soil age on DOM fluxes in a laboratory experiment using O horizons of volcanic ash soils of varying age (from 300 to 4,100,000 years). The soils with an intermediate soil age of 20,000 years had the largest contents of noncrystalline minerals and exhibited the strongest physical control on DOC fluxes. At the oldest sites, the authors observed an increase of biological control on DOM release which was attributed to a decrease in the amorphous constituents at advanced stages of Andisol weath-

ering. Radiocarbon ages (^{14}C) of charcoal in fossil A horizons at the study sites ranged from 10,000 to 16,000 years (data not shown), indicating that the recent topsoil material is comparably young. The soils contained considerable amounts of oxalate-extractable Al and Si and dithionite-citrate-extractable Al, and negative delta pH values indicated a considerable anion sorption capacity in the deeper mineral soil. In summary, these results suggest that a major part of the DOM released in the litter layer and canopy was probably retained by sorption in the mineral soil.

The analysis of the degradability of DOM in different ecosystem fluxes revealed that DOM in throughfall was more readily mineralisable than DOM in litter percolate or in the soil solution (Qualls and Haines 1992). Jones et al. (2004) observed a high turnover of free amino acids in the soil solution, while DON of higher molecular weight, which dominated the total DON pool, turns over more slowly. Even though there were further indications that biodegradation of DOM occurs at deeper soil layers, overall adsorption to soil particles appears to be the process determining the retention of DOM in the subsoil (Kalbitz et al. 2000). Similarly, Schwendenmann and Veldkamp (2005) concluded that sorption to soil particles was the main factor controlling the DOC concentrations in the soil solution of a tropical lowland rainforest in Costa Rica, which is probably also the case at Mt. Kilimanjaro.

Vegetation effects

The vegetation cover may influence organic matter concentrations and fluxes through differences in leaching properties of plant tissue and decomposability of litter. The contribution of TON to total N in throughfall was greater at forested sites than for plots with shrub vegetation, although TON fluxes did not exhibit any differences. This can be explained by the retention of inorganic N, especially of NO_3–N, in the forest canopies, while N was leached from the shrub vegetation of the clearings, leading to an increased contribution of TON in throughfall at the forest sites. TOC concentrations and fluxes were significantly larger in throughfall of forest sites compared to the other two sites, indicating stronger release or additional sources of organic matter in the forest canopies. Besides stronger leaching due to the larger biomass of the forest canopy, epiphytic humus may contribute to organic matter in throughfall of the forests.

Therefore, more TOC reached the forest floor via throughfall under the forest sites than under the plots with shrub vegetation. Nevertheless, the increase in concentrations of organic C and nutrients from throughfall to litter percolate was more pronounced for the plots with shrub vegetation, indicating a stronger release of organic matter in the litter layer at these sites. Larger inorganic N concentrations in the litter percolate at the plots covered by shrub vegetation at Mt. Kilimanjaro (data not shown) indicate higher N-mineralisation rates and higher microbial activity. This is probably caused by higher temperatures

and lower C/N ratios of the litter in the plots with shrub vegetation (C/N ratio in Oi layer of plots with shrub vegetation: 22, secondary forest 31, mature forest 30). Inorganic and organic N concentrations were significantly correlated in the litter percolate of the plots with shrub vegetation ($r = 0.82$, $p < 0.001$), which points at increased turnover of the litter material at the plots with shrub vegetation.

Johnson-Maynard et al. (1998) studied a suppressed secondary succession of a coniferous forest after the invasion of bracken fern (*Pteridium aquilinum*) on Andisols. They observed significantly larger DOC concentrations in the soil solution of fern-dominated plots with shrub vegetation than under undisturbed forest and suggested that bracken fern is responsible for an increase in Al-humus complexes in the subsoil (Johnson-Maynard et al. 1997). These results would suggest that also the litter of the bracken, which was dominant at the younger plots with shrub vegetation at Mt. Kilimanjaro, could have influenced the release of organic matter in litter percolate. Similar to the observations of Johnson-Maynard et al. (1997), litter accumulation was higher under shrub vegetation as compared to adjacent secondary forest. A high amount of Oi and Oe material consisting of old fern leaves and old *Rubus* twigs was observed on sites covered with shrub vegetation. A greater humus concentration may contradict the former assumption of higher mineralisation rates on the plots with shrub vegetation. It might be that mainly easily decomposable herbs, leaves and lianas as well as old forest humus decomposes on the warmer plots with shrub vegetation while less decomposable parts of the vegetation remain. However, differences in solution concentrations disappeared with increasing depth, likely due to the strongly sorbing soil mineral matrix.

Importance of organic matter for nutrient fluxes

The forest at Mt. Kilimanjaro showed the largest percentage of TON to total N in throughfall compared to soil solution and stream water. Concentrations of NH_4–N and NO_3–N in the mature forest were within the range of other tropical montane rainforest sites (Schrumpf et al. 2006). The contribution of organic matter to total N, P, and S was generally <50% in the litter percolate and was even lower in the mineral soil. This is in contrast to observations made in temperate forest ecosystems. In a deciduous forest in the Appalachian Mountains, DON and DOP concentrations in litter percolate and the soil solution exceeded inorganic forms (Qualls et al. 2000). Similar results were obtained for DON in a Norway spruce stand (Smolander et al. 2001) and for DOP in a German beech forest (Kaiser et al. 2003).

In a tropical montane rainforest in Ecuador, Goller (2005) also observed a high contribution of organic to total nutrient concentrations in litter percolate (50–68% for TON, 87–100% for TOP and 62–100% for TOS). With less than 10%, Schwendenmann and Veldkamp (2005) on the other hand observed an even lower contribution of DON to total N in a lowland rainforest in Costa

Rica than at Mt. Kilimanjaro. In the soil solution, the percentage of DON was similar at both sites (10–20% in Costa Rica vs. 4–16% at Mt. Kilimanjaro). Schwendenmann and Veldkamp (2005) ascribed the low contribution of DON to total N partly to the high observed DOM sorption capacity of the soil, which might also be the reason at Mt. Kilimanjaro. This partly contradicts the observations of Hedin et al. (1995) and Perakis and Hedin (2002), who studied stream N concentrations in a number of Chilean streams and found DON consistently to represent $>95\%$ of total N. Some of the streams were sampled in areas with soils that developed on tephra. These soils probably also contain high amounts of amorphous soil material and have a high retention capacity for organic nutrients, thus reducing the concentrations of DON in the soil solution. Perakis and Hedin (2002) ascribed the high contribution of DON to total N to low input of inorganic N as the study areas were largely unpolluted. The canopy of the forest at Mt. Kilimanjaro retained significant amounts of the deposited N and thus inputs of inorganic N via throughfall were low (2–4 kg ha^{-1} y^{-1} NH_4–N and 0.7–1.0 kg ha^{-1} y^{-1} NO_3–N in the mature forest, Schrumpf et al. 2006). Schwendenmann and Veldkamp (2005) suggested that not only external N inputs, but also the overall N supply of a forest might determine the relevance of NO_3–N to total N losses via leaching. Similar to the site in Costa Rica, also the mature forest at Mt. Kilimanjaro is probably not N-limited (Schrumpf et al. 2006). But the same is true for a montane rainforest in Ecuador, where high litter N concentrations and fluxes indicated that the growth of the rainforest was not N limited, while having high percentages of TON to total N in litter percolate as well as in the soil solution (Wilcke et al. 2002; Goller 2005). Therefore, it seems plausible that the proportion of DON as a fraction of total N is controlled by low NO_3–N concentrations in the soil solution of N-limited forest sites, where also N-inputs via throughfall might be low, while it is controlled by low DON concentrations at sites with a high sorption capacity for DOM.

Relationships between TOC, TON, TOP and TOS

In the mature forest, TOC concentrations were closely correlated to TON in throughfall, litter percolate and the soil solution in the upper mineral soil. Relationships between DOC and DON concentrations and fluxes in different compartments of forest ecosystems have frequently been observed in temperate forests (Michalzik et al. 2001). Nevertheless, some evidence exists that release and fate of DON might be independent of DOC (Kalbitz et al. 2000; Solinger et al. 2001). In litter percolate, mean annual TOC concentrations were related to mean TON, TOS and TOP concentrations at different sites. These results indicated that despite different amounts of organic matter being released in the forest floor under the different vegetation types, there are no major changes in the distribution of organic and inorganic forms.

Conclusions

In the studied montane rainforest at Mt. Kilimanjaro, concentrations and fluxes of OM in rainfall and throughfall were in the same range as reported for other temperate and tropical forest ecosystems. However, belowground OM concentrations were very low, which was attributable to the likely high sorption capacity of the studied Andisols. Therefore, the relative proportions of TON, TOS and TOP as a fraction of total N, S and P in the litter percolate was lower than at many temperate forest sites. The proportion of TON was very low, less than 10% of total N in the mineral soil, indicating that inorganic N is more mobile than organic N and largely responsible for nutrient exports from these montane forest ecosystems.

The highest proportion of TON as a fraction of total N was found in throughfall water below the forest canopies, which was more pronounced as NO_3–N was retained in the canopies. Epiphytic biomass and canopy humus were thought to contribute to throughfall TOM fluxes in the forests. Organic matter release in litter percolate and the topsoil solution under shrub vegetation was greater than at forested sites, which was probably due to higher mineralisation rates and to litter properties specific to the bracken vegetation.

Increased organic matter release following disturbance by logging or fires may not lead to high leaching losses of nutrients and export by streams as a result of the supposedly high sorption capacity of the mineral soil. Higher concentrations of organic nutrients under about 10-years-old shrub vegetation indicate that forest disturbance can lead to long-term effects on DOM release. Sorption analyses need to be conducted to test the hypothesis of the large sorption capacity of the soils and their ability to control organic matter concentrations in the soil solution at the study sites.

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