Biogeochemical Consequences of Hydrologic Conditions in a Tropical Montane Rain Forest in Ecuador

Dissertation zur Erlangung
des Doktorgrades an der Fakultät
Biologie/Chemie/Geowissenschaften
der Universität Bayreuth

vorgelegt von

Rainer Goller

aus Bayreuth

Bayreuth, August 2004

Die vorliegende Arbeit wurde am Lehrstuhl für Bodenkunde und Bodengeografie der Universität Bayreuth (Lehrstuhlinhaber: Prof. Dr. W. Zech) erstellt.

Vollständiger Abdruck der von der Fakultät Biologie/Chemie/Geowissenschaften genehmigten Dissertation zur Erlangung des Grades eines Doktors der Naturwissenschaften (Dr. rer. nat.).

Tag der Einreichung: 18. August 2004
Tag des wissenschaftlichen Kolloquiums: 22. Dezember 2004

Prüfungsausschuss:
Prof. Dr. K. Bitzer
Prof. Dr. B. Huwe
PD Dr. G. Lischeid
PD Dr. W. Wilcke (1. Gutachter)
Prof. Dr. W. Zech (2. Gutachter)

Contents

List of tables

List of figures

List of abbreviations

a.s.l.	above sea level
BS	base saturation
C.V.	coefficient of variance
DIN, DIP and DIS	dissolved inorganic nitrogen, phosphorus, and sulfur
DOC, DON, DOP and DOS	dissolved organic carbon, nitrogen, phosphorus, and sulfur
DOM	dissolved organic matter
DWM	discharge−weighted mean
ECEC	effective cation exchange capacity
ECSF	Estaciòn Cientifica San Francisco
FDR	frequency domain reflectometry
HSD	Honest Significant Difference
IAEA	International Atomic Energy Agency
LF	lateral flow (in the organic layer)
LL	litter leachate
MC	microcatchment
RF	rainfall
S.D.	standard deviation
SF	stemflow
SS−15 and SS−30	soil solutions at 0.15 and 0.30 m mineral soil depth
SW	stream water
TDN, TDP, and TDS	total dissolved nitrogen, phosphorus, and sulfur
TF	throughfall
TOC	total organic carbon
USDA−NRCS	United States Department of Agriculture – National Resource Conservation Service
V−SMOW	Vienna Standard Mean Ocean Water
VWM	volume−weighted mean

Acknowledgements

A lot of people gave their support to this ‘gigantic’ project called Ph. D. thesis with either their expertise and/or understanding. I’m very grateful to all of them.

PD Dr. Wolfgang Wilcke for the supervision of my thesis. He introduced me to the deeper regions of soil science and ecosystem research and provided the ‘scientific frame’ of my thesis. Furthermore, he gave me valuable criticism and improvement on my writing.

Prof. Dr. Wolfgang Zech for the chance to join this exiting project in such an amazing part of the world and for his confidence and support during my work.

The helpful and friendly atmosphere at the Institute of Soil Science and Soil Geography was established by the following people:

the secretaries Mrs. Cornelia Schreiber and Mrs. Gabriele Wittke, Dr. Ludwig Haumaier and the laboratory staff with the ‘chiefs of the kitchen’ Rußi and Marcella, Andrea Bergmann, Tanja Gonter, Martina Haider, Andrea Hartmann, Karin Jeschke, Gela Mergner, Andrè Wetzel (the RFA master), and Ute Zimmer,

my scientific colleagues Uwe Abramowski, Sonja Brodowski, Holger Ciglasch, Jörg Dilling, Florian Fritsche, Bruno Glaser, Klaus Kaiser, Martin Krauß, Volker Laabs, Julia Lilienfein, Ingo Lobe, Andreas Möller, Marion Schrumpf, Dawit Solomon, Thorsten Ullrich, Anja Winkler, and Syafrimen Yasin for valuable scientific discussion and a good time together sharing similar problems.

For specific advise Prof. Bernd Huwe, Dr. Karsten Kalbitz, Dr. Gunnar Lischeid, Dr. Melanie Leng and Prof. Heinz−Jürgen Tobschall.

The members of the technical garage, GEO I, for quickly constructing reliable equipment for unreliable climatic conditions briefly before leaving Germany for my trips to Ecuador.

Dr. Gunther Ilgen and the ‘laboratory girls’ Kerstin Moser, Bettina Popp, and Petra Dittrich from the Zentrale Analytik des Bayreuther Instituts für terrestrische Ökosystemforschung (BITÖK) for lots of water analyses and always finding a way to push them through.

The huge ‘crowd’ of students, who gave their great support in the field and in the lab for collecting and analyzing thousands of samples.

The German Research Association for funding this study (FOR402/1−1 TP2 and

FOR402/2 TP B10).

My Ecuador colleague ‘from the start’ Katrin Fleischbein and also Jens Boy for a nice time in Ecuador and good cooperation in managing this ‘monstrous’ project with all its tricky details.

It is hard to describe how the time in Ecuador opened my eyes for new views and things concerning many parts of my life. Especially my stays on our lovely research base, the Estacion Cientifica San Francisco (ECSF), were accompanied by a lot of ‘crazy’ and very kindly people, who will make this experience unforgetable. Muchissimas gracias para los todos amigos, especially Dirk Süßenbach (el Rey, cumpadre!) and Jürgen Homeier (‘Rainer, da sind ja Früchte dran!’)!! Muchas gracias a ‘Pablo Rapido’ por su trabajo muy bueno en nuestro proyecto y su humor especial (‘Räuber!’). Muchas gracias tambien a Sonya Sotomayor por su ayuda rapida en muchas cosas y siempre haber una sonrisa amable (‘Soy yo!’). Para todas las horas milagrosas en Ecuadorrr! (tambien, quando el tiempo era muy mal en la estacion) muchissimas gracias para nuestra ‘Mama ecuadoriana’ Doña Maria Feijoo Pinera y su familia muy amable, Angel, Jefe, Karina, Rocio y mi amigo Roberth. Suerte por la futura!

Für ihr anhaltendes Interesse und ‘Mitfühlen’ während des Fortgangs meiner Arbeit möchte ich mich bei meinen Eltern bedanken, Helga und Rudolf Goller.

Um die ‘harten Tage’ im Leben leichter zu nehmen, braucht es manchmal nur ein strahlendes Lächeln. Vielen Dank an meine wundervollen Mädels, Heike & Sarah ...

Summary

Tropical montane forests regulate the hydrological cycles of high−elevation areas being an important service for the local population. The objectives of my work were (1) to determine the major hydrological flow paths, (2) to quantify concentrations of dissolved organic C and organic and inorganic forms of N, P, and S, and (3) to identify the major controls of the dissolved C, N, P, and S dynamics in a tropical montane forest in south Ecuador.

Three 8−13 ha large microcatchments (MCs) under montane forest at an altitude of 1900−2200 m above sea level were selected. Scientific equipment was installed on five transects, about 20 m long with an altitude range of 10 m. Three unforested sites near the microcatchments were used for rainfall gauging. Within the three monitored years between May 1999 and April 2002, on average 2448 mm of precipitation fell on the study area. The $\delta^{18}O$ of rainfall shows large variations (-12.6 ‰ to +2.1 ‰) related to different air−masses. The $\delta^{18}O$ values of throughfall and lateral flow are similar to those in rainfall. Variations in $\delta^{18}O$ values of the soil solution and the stream water are smaller (-9.1 ‰ to -3.0 ‰ and -5.8 ‰ to -8.7 ‰) than those of rainfall, throughfall, and lateral flow. The $\delta^{18}O$ values in stream water increased immediately after an intense rainstorm event to isotope values similar to those of rainfall and lateral flow. This indicated that during elevated rainfall the water flows rapidly in the organic layers to the stream channel paralleling the surface. During this time the water content of the organic layer was higher than of the upper mineral soil. Results from an isotope two−component hydrograph separation for the three microcatchments showed that new rain water ('event water') contributed 44−81 % to the total stormflow runoff during one selected peak discharge.

The canopy was a small and the organic layer the major source of DON, DOP, and DOS, which were almost completely retained in the mineral soil. The organically bound forms contributed, on average in all solutions, 54 %, 78 %, and 59 % to the total concentrations of N, P, and S, respectively. The contribution of organically bound forms to total nutrient concentrations was element−specific and differed among the ecosystem fluxes. The portions of DON (23−81 %) were similar and those of DOP (5−100 %) highly variable in all solutions. There were high DOS portions in the aboveground fluxes (51−100 %) and lower portions in the mineral soil (8−47 %). The pH was positively correlated with the DOC and organic N, P, and S concentrations at the scale of pedons. Increasing DOC concentrations in stream water following rainstorms indicated that rainstorms were an important control of the dissolved organic matter dynamics on a regional scale.

During the passage of the water through the forest, dissolved inorganic N (DIN) and DIP concentrations increased between the canopy and the mineral soil and strongly decreased in the mineral soil. In contrast, DIS concentrations were highest in the mineral soil and stream water. Thus, the organic layer was the major source for DIN, the canopy for DIP and the mineral soil for DIS. The mineral soil was a sink for DIN and particularly for DIP. Soil drying and rewetting promoted the release of inorganic N. High discharge levels following heavy rainstorm events were associated with pulses of NO_3−N and partly also NH_4−N concentrations in stream water. Nitrate−N concentrations in the stream water were positively related to runoff conditions. The DIP and DIS concentrations in throughfall and stemflow were negatively correlated to the respective water fluxes, whereas DIS concentrations in the mineral soil solutions of both studied soil depths were positively related to the rainfall volume. DIN and DIP concentrations and fluxes tended to be positively related to the pH of the organic layer. My results demonstrate that nutrient dynamics were mainly controlled by hydrological conditions in the studied steep forested catchments. Furthermore, small ecosystem inputs and outputs indicated tight cycles of dissolved N, P and S in the study forest, except for DIS.

Zusammenfassung

Die Regulation des Wasserkreislaufs durch tropische Bergwälder ist eine wichtige ökologische Dienstleistung für die örtliche Bevölkerung. Die Ziele meiner Arbeit waren (1) die Ermittlung der Hauptfließwege des Wassers, (2) die Quantifizierung der Konzentrationen von organischem C (DOC), organischem N, P und S (DON, DOP und DOS) und anorganischen N, P und S (DIN, DIP und DIS) in den Ökosystemflüssen und (3) die Identifizierung der wichtigsten Steuergrößen der gelösten C−, N−, P und S−Dynamik in einem tropischen Bergwald in Südecuador. Dazu bearbeitete ich drei 8−13 ha große Einzugsgebiete auf 1900−2200 m ü. NN. Auf fünf 20 m langen Transekten (mit einer Höhendifferenz von 10 m) wurden Messgeräte installiert. Der Freilandniederschlag wurde auf drei Freiflächen erfasst.

Zwischen Mai 1999 und April 2002 fielen durchschnittlich 2448 mm Niederschlag. Der $\delta^{18}O$−Wert des Niederschlags variierte stark (-12,6 ‰ bis +2,1 ‰) zwischen unterschiedlichen Luftmassen. Bestandesniederschlag und Lateralfluss zeigten ähnliche $\delta^{18}O$−Werte wie der Freilandniederschlag. Die $\delta^{18}O$−Werte in Mineralbodenlösung (-9,1 bis -3,0 ‰) und Bachwasser variierten weniger (-5,8 bis -8,7 ‰) als in Freiland- und Bestandesniederschlag und Lateralfluss. Nach einem Starkregen stiegen die $\delta^{18}O$−Werte im Bachwasser schnell an und erreichten ähnliche Werte wie in Regenwasser und Lateralfluss. Dies zeigt, dass während Starkregens Wasser schnell oberflächenparallel in der organischen Auflage zum Vorfluter floss. Eine Zwei−Komponenten−Ganglinienseparierung auf ^{18}O−Basis ergab einen Beitrag des oberflächennahen Abflusses von 44−81 % in den drei Einzugsgebieten zum gesamten Abfluss für ein ausgewähltes Ereignis.

Der Kronenraum fungierte als eine geringe, die organische Auflage als die Hauptquelle für DON, DOP und DOS, die nahezu vollständig vom Mineralboden zurückgehalten wurden. Die Anteile der organisch gebundenen Formen an den Gesamtkonzentrationen von N, P und S betrugen im Durchschnitt 54, 78 und 59 % und zeigten sowohl elementspezifische als auch flussabhängige Variationen. Die Anteile von DON (23−81 %) zeigten geringe, die von DOP (5−100 %) starke Schwankungen in allen Lösungen. Die DOS−Anteile waren in allen oberirdischen Flüssen hoch (51−100 %) und deutlich geringer im Mineralboden (8−49 %). Der pH-Wert korrelierte auf der Ebene einzelner Böden positiv mit den DOC−, DON−, DOP− und DOS−Konzentrationen. Ansteigende DOC−Konzentrationen im Bachwasser während Spitzenabflusses zeigen, dass Starkregen die Austräge an gelöster organischer Substanz in regionalem Maßstab steuern.

Die DIN− und DIP−Konzentrationen stiegen beim Durchgang durch die Waldkrone an und nahmen im Mineralboden stark ab. Im Gegensatz dazu waren die DIS−Konzentrationen im Mineralboden und im Bachwasser am größten. Folglich fungierte die organische Auflage als Hauptquelle für DIN, der Kronenraum für DIP und der Mineralboden für DIS. Gleichzeitig war der Mineralboden eine Senke für DIN und insbesondere für DIP. Der Wechsel von Austrocknung und Wiederbefeuchtung der Böden erhöhte die Freisetzung von DIN. Durch Starkregen ausgelöste hohe Abflüsse waren mit Spitzenkonzentrationen an NO_3−N und teilweise auch NH_4−N im Bachwasser verbunden. Die DIP− und DIS−Konzentrationen im Bestandesniederschlag und Stammabfluss korrelierten negativ mit den zugehörigen Wasserflüssen; die DIS−Konzentrationen in den Mineralbodenlösungen korrelierten dagegen positiv mit den Regenvolumina. Der pH−Wert der organischen Auflage beeinflusste die DIN− und DIP−Konzentrationen im Streuperkolat positiv.

Meine Ergebnisse zeigen, dass wässrige C−, N−, P− und S−Flüsse in den steilen bewaldeten Einzugsgebieten überwiegend von den hydrologischen Bedingungen gesteuert werden. Geringe Ein− und Austräge an gelöstem N, P und S, mit Ausnahme von DIS, weisen auf einen weitgehend geschlossenen Elementkreislauf hin.

Resumen

Los bosques tropicales de montaña regulan el ciclo hidrológico de las áreas altas, prestando un importante servicio a las poblaciones locales. Los objetivos del presente trabajo fueron: (1) determinar las sendas mayores del flujo hidrológico, (2) cuantificar las concentraciones en solución de C orgánico y de las formas orgánicas e inorgánicas de N, P, y S; y (3) identificar los factores principales que controlan la dinámica del C, N, P y S disueltos, en un bosque tropical de montaña en el sur del Ecuador.

Se seleccionaron tres microcuencas (MCs) de 8 a 13 ha de extensión, cubiertas de bosque de montaña, en un rango de altitud de 1900−2200 m s.n.m. Se instalaron equipos científicos en cinco transectos, de cerca de 20 m de longitud con un rango de altitud de 10 m. El registro de la precipitación se realizó en tres sitios deforestados, cercanos a las microcuencas. A lo largo de los tres años de monitoreo, entre mayo de 1999 y abril de 2002, en el área de estudio se registró un promedio de precipitación de 2448 mm. El $\delta^{18}O$ de la lluvia presentó grandes variaciones (-12.6 ‰ to +2.1 ‰), relacionadas con diferentes masas de aire. Los valores de $\delta^{18}O$ de la precipitación que atraviesa el dosel y del flujo lateral, fueron similares a aquellos de la lluvia. Las variaciones de los valores de $\delta^{18}O$ en la solución del suelo y en la corriente de salida (-9.1 ‰ a -3.0 ‰ y -5.8 ‰ a -8.7 ‰), fueron menores que aquellos de la lluvia, la precipitación que atraviesa el dosel y el flujo lateral. Los valores de $\delta^{18}O$ en la corriente de salida se incrementaron inmediatamente después de un aguacero intenso, a valores isotópicos similares a aquellos de la lluvia y del flujo lateral. Esto indica que durante las lluvias intensas, el agua fluye rápido paralelamente a la superficie en la capa orgánica a la corriente de salida. Durante este tiempo, el contenido de agua de la capa orgánica fue más alto que en la parte superior del suelo mineral. Los resultados de un hidrograma de separación de dos componentes isotópicos para las tres microcuencas, mostraron que el agua nueva de lluvia (evento de agua) contribuyó con el 44−81 % de la escorrentía total del flujo de tormenta, durante una descarga pico seleccionada.

El dosel fue una pequeña y la capa orgánica la mayor fuente de NOD, POD y SOD, los cuales fueron casi completamente retenidos en el suelo mineral. Las formas orgánicamente enlazadas contribuyeron, en promedio en todas las soluciones, con 54 %, 78 %, y 59 % de las concentraciones totales de N, P y S, respectivamente. La contribución de las formas orgánicamente enlazadas al total de las concentraciones de nutrientes fue elemento−específica y presentó diferencias entre los flujos del ecosistema. Las proporciones de NOD (23−81 %) fueron similares; en tanto que, aquellas de POD (5−100 %) fueron altamente variables en todas las soluciones. Se encontraron elevadas porciones de SOD en los flujos sobre el suelo (51−100 %) y menores en el suelo mineral (8−47 %). El pH se correlacionó positivamente con el COD y con las concentraciones orgánicas de N, P y S a la escala de los pedones. El incremento de las concentraciones de COD en la corriente de salida después del aguacero, indican que las lluvias torrenciales fueron un importante control de la dinámica de la materia orgánica disuelta a escala regional.

Durante el paso del agua a través del bosque, las concentraciones de N inorgánico disuelto (NID) y de PID se incrementaron entre el dosel y el suelo mineral, disminuyendo fuertemente en el suelo mineral. Por el contrario, las concentraciones de SID fueron las mayores en el suelo mineral y en la corriente de salida. Consecuentemente, la capa orgánica fue la mayor fuente de NID, el dosel de PID y el suelo mineral de SID. El suelo mineral fue sumidero para el NID y particularmente para el PID. El secado y humedecimiento del suelo promovió la liberación de N inorgánico. Los elevados niveles de las descargas después de los aguaceros intensos, se asociaron con los ritmos de las concentraciones de NO_3−N y parcialmente también de NH_4−N en el agua de la corriente de salida. Las concentraciones de N−nitrato en la corriente de salida se relacionaron

positivamente con las condiciones de la escorrentía. Las concentraciones de PID y SID en la precipitación que atraviesa el dosel y en el flujo del tallo, se correlacionaron negativamente a los flujos de agua respectivos; mientras que, las concentraciones de SID en las soluciones del suelo mineral, a las dos profundidades estudiadas, fueron positivamente relacionadas al volumen de la lluvia. Las concentraciones de NID y de PID y los flujos, tendieron a correlacionarse positivamente con el pH de la capa orgánica. Los resultados demuestran que la dinámica de los nutrientes fueron principalmente controlados por las condiciones hidrológicas en las microcuencas boscosas y de pendiente pronunciada estudiadas. Además, pequeñas entradas y salidas en el ecosistema indican ciclos cerrados para el N, P y S disueltos en el bosque estudiado, excepto para el SID.

1 General introduction

1.1 Background

Starting in the early 1960ies (Bormann et al. 1963), forest ecosystems have been studied to improve the understanding of the functioning of forests and their significance for the nearby living human population. While numerous extensive ecosystem studies have been conducted in forests of the northern hemisphere in the past decades (Matzner & Ulrich 1981; Zöttl 1987; Likens & Bormann 1995; Matzner 2004), investigations of forest ecosystems in tropical regions, especially in montane areas, where forests are often primary and less affected by anthropogenic deposition from the atmosphere, are comparatively few and mostly only cover short time periods.

Nevertheless, tropical montane forests are under increasing pressure, since the demand for new land for human purposes has reached even less accessible regions (Aldridge et al. 1997). As a consequence, forests are cleared for agricultural use (mainly vegetable cropping and grazing), fuelwood and charcoal production, harvesting of timber and non−timber products (e.g. orchids and bromeliads), infrastructural projects, and mining (Aldridge et al. 1997; Bruijnzeel 2001; Hamilton et al. 1995). In Ecuador, according to a threat analysis published by the UNEP−WCMC (United Nations Environment Programme − World Conservation Monitoring Center), the greatest threats to cloud forest are conversion to agricultural and grazing land (Aldridge et al. 1997). This holds also true for the study area in south Ecuador, since Paulsch et al. (2001) found in an analysis of the land−use induced vegetation structure in the Rio San Francisco valley that local land−use dynamics appear as initial burning of the primary forest (sometimes removing valuable trees previously) and subsequently planting pasture or maize. Since these sites lose their agricultural value because of the invasion by ferns after a short time, the burning of further primary forest areas continues. Reforestation activities are rare and, if realized, frequently consist of the planting of exotic tree species like eucalyptus and pine in monocultures.

While the destruction of huge areas of tropical lowland forests, like the Amazonian rain forests, has received wide public attention (Wuethrich 1993), the creeping disappearance

of tropical montane forests, often appearing as small, fragmented pieces and located in remote mountainous areas, remains more clandestine (Bubb et al. 2004). Hamilton et al. (1995) estimated that about 90 % of the tropical montane cloud forests in the north Andes have been lost through human activities.

This process is irreversible in many regions because of the rapid erosional loss of the soil cover, which is the prerequisite for forest growth. The loss of the forest cover in these regions is not only serious because of its immense inherent biodiversity and associated gene pool (Bubb et al. 2004), but also causes severe effects on the local population, since the water protecting function of the forest is removed (Bruijnzeel 2001). This function includes the balance of water yields during drier and wetter periods and regions (Bruijnzeel 1990; Bruijnzeel & Proctor 1995), e.g. during extreme rainfall and drought periods following the 'El Niño' and 'La Niña' phenomena in the northern Andean region (Foley et al. 2002), the maintenance of high water quality for the downslope population because of the filtration effect of the forest, and the protection of the soil from erosion and the accompanying loss of nutrients from the often little fertile soils (Aldridge et al. 1997). Furthermore, the reduction of soil erosion diminishes the risk of landslides, which are a great threat for human communities and infrastructure in these regions (Bremer 1999, Daugherty 1973). On a global scale, it can be assumed that tropical montane forests contribute to the reduction in the atmospheric concentration of the climatically active CO_2 because of the sequestration of considerable carbon amounts, which is reported for neotropical forests in general by Malhi & Grace (2000).

As a consequence of the ecological importance and the services provided for the local population, the preservation and restoration of this valuable ecosystem is of high interest for local and global concerns. This requires a more detailed insight into the biogeochemical cycles of this ecosystem, particularly the cycling of plant nutrients and its controls. Moreover, the need for more scientific data from tropical montane forests in order to expand the information base for these highly threatened ecosystems is highlighted in the recommendations for future work by Aldridge et al. (1997) from the WCMC.

The soil scientific subproject, which was the frame of my thesis, is part of the DFG (German Research Association) research unit 402: 'Functionality in a Tropical Mountain

Rainforest: Diversity, Dynamic Processes and Utilization Potentials under Ecosystem Perspectives'. The focus of my subproject is the biogeochemistry and hydrology of a tropical montane rain forest in the southern Ecuadorian Andes. This region is known as one of the 'phytobiodiversity hotspots' of the world (Barthlott et al. 1996). The multidisciplinary approach of biological, geoscientific, and forest scientific research groups intends to provide a comprehensive understanding of the functioning of this complex tropical ecosystem, which is the prerequisite for its sustainable use and protection.

1.2 Hydrologic and element cycles of tropical montane forests

Tropical montane forests are specifically characterized by two major features: i) high water input via rainfall including the frequent occurrence of rainstorm events and ii) the location on steep montane slopes. These environmental factors strongly influence the cycling of nutrients in tropical montane forest ecosystems, because water is the major transport medium for nutrients and its movement is significantly influenced by topographic conditions (Likens & Bormann 1995; Bonell et al. 1998). A large part of water−carried nutrients is dissolved and therefore directly available for plants. Figure 1 illustrates the hydrological cycle of a tropical cloud forest.

The input of nutrients to a forest originates from two major pathways: wet and dry deposition. The former mainly consists of dissolved electrolytes, which are precipitated onto the forest canopy with the incident rain water or with stripped water from fog and clouds. The latter is termed 'occult precipitation' (Zadroga 1981) and is described as a typical characteristic of many tropical montane forests, which has led to the term 'montane cloud forest' in the literature for forests under frequent or persistent cloud or fog cover, e.g. in coastal fog belts and at higher mountainous regions (Bruijnzeel 2001; Bubb et al. 2004; Hamilton et al. 1995; Stadtmüller 1987). Mechanisms of dry deposition include sedimentation, absorption and impaction of particulate and gaseous compounds (Bruijnzeel 1990, Parker 1983). Dry deposition can be significant in industrialized regions because of elevated emissions of particles and gases from vehicles and industrial facilities, in coastal areas, and also in arid regions owing to wind−blown dust (Parker 1983). In contrast, in

regions distant from anthropogenic and natural sources and further subject to frequent rainfall events, dry deposition is assumed to play a smaller role for the element input into ecosystems than in more anthropogenically affected regions (Parker et al. 1983; Lin et al. 2000).

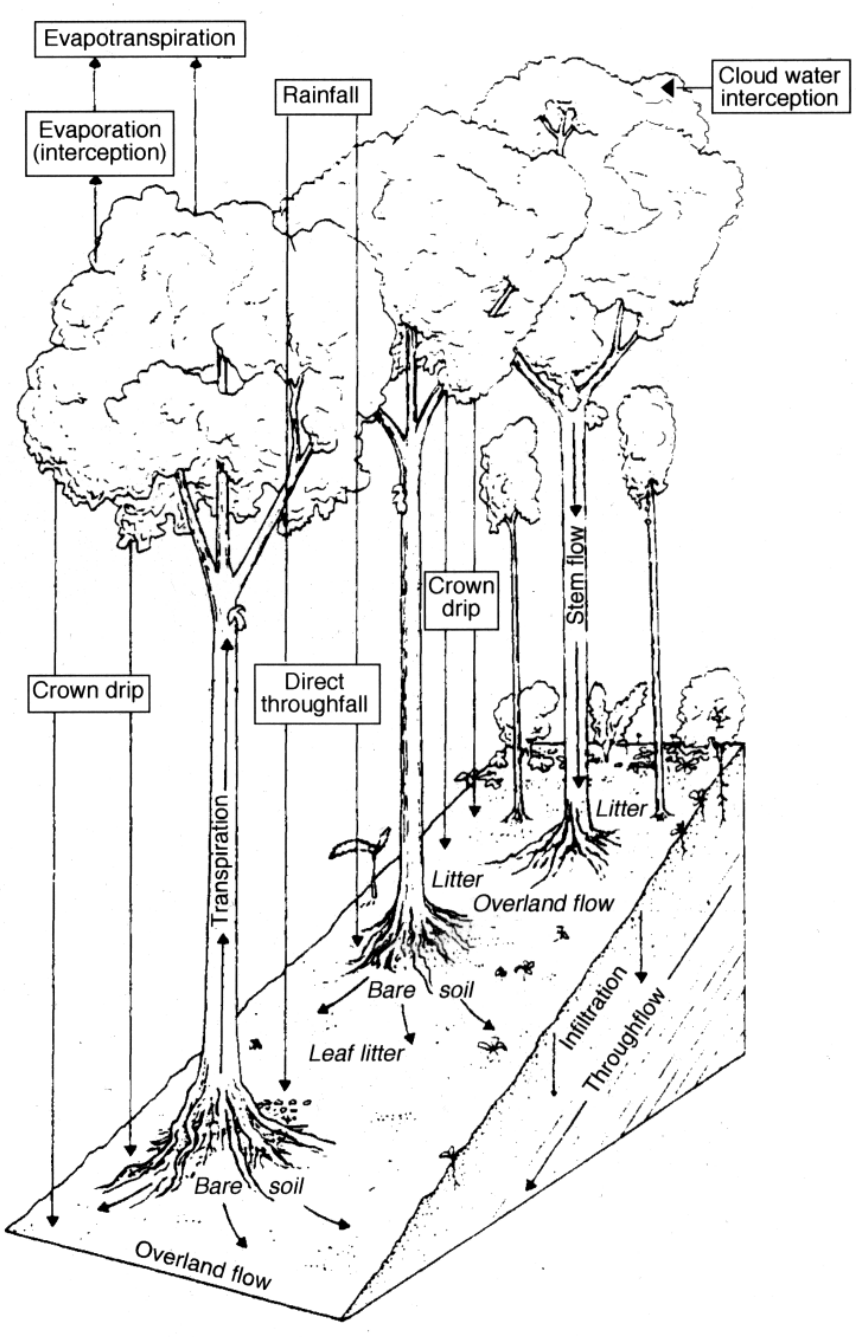

Figure 1: Hydrological cycle in a cloud forest (from Douglas 1978).

While a variable part of the incoming water is intercepted by the canopy and afterwards directly evaporates back to the atmosphere (0 to 42 % of total annual rainfall in tropical

montane forests (Cavelier et al. 1997, Scatena 1990), the other portion passes through the canopy and reaches the forest floor as throughfall (direct throughfall and crown drip) and stemflow. According to Bruijnzeel (1990), annual throughfall comprised 75−86 % of the total annual rainfall in six studied tropical montane forests. During the passage through the canopy the concentration of solutes is altered by canopy interactions. These interactions include element uptake and release by plants, particularly epiphytes (Cavelier & Goldstein 1989; Veneklaas 1990), and microbes on plant tissues (Lovett & Lindberg 1984), and furthermore the washout of dry deposition (Lindberg et al. 1986).

According to Vitousek & Sanford (1986), the majority of studies in tropical forests found a net leaching of most nutrients from the forest canopy. Although element concentrations in stemflow are often even higher than in throughfall, the total input flux via stemflow is small, since the annual contribution comprises only 1−2 % of the incident rainfall (Bruijnzeel 1990). This might nevertheless have a considerable impact on the small area around the stems (Herwitz 1986, Hafkenscheid 2000, Proctor 1987, Wilcke et al. 2001). The chemical composition of throughfall and stemflow is of high ecological significance, since these fluxes supply directly bioavailable nutrients to the forest soil.

During the passage through the forest canopy and the upper soil regions, a portion of the infiltrating water is taken up by the forest plants and given back to the atmosphere via transpiration.

After falling on the forest floor, the water percolates through the soil organic layer, normally in vertical directions until it reaches less permeable zones, like clayey horizons or bedrock, where the flow paths may be diverted to lateral directions (Guehl 1983) whereby the flow velocity remains low (‘throughflow’ according to Kirby & Chorley 1967). However, high water input during rainstorm events may lead to an excess of the infiltration capacity of the underlying soil layers (Bruijnzeel 1990) resulting in rapid lateral interflow (‘quickflow’ in Ward 1984; ‘subsurface stormflow’ in Dunne 1978). This has been found to be a common runoff process on steep slopes in tropical regions (Bruijnzeel 1990; Schellekens et al. 2004). The frequently observed increase in solute concentrations in the litter percolate of tropical montane forests is caused by the leaching of soluble substances from the organic layer, which frequently is thick and contains high concentrations of easily

soluble elements (Bruijnzeel et al. 1993; Hafkenscheid 2000; Steinhardt 1979; Wilcke et al. 2001, 2002).

Under normal hydrological conditions (i.e. under non−stormflow conditions), the water percolates slowly through the soil matrix of the mineral subsoil, which is characterized by a markedly higher bulk density and the abundance of sorption sites at mineral surfaces. The adsorption to soil particles and the uptake by plant roots lead to a decrease of nutrient concentrations in the mineral soil solution (Stevenson & Cole 1999). The presence of preferential flow paths through macropores in the soil (e.g. root pipes, soil cracks, stone surfaces) and the location on steep hillslopes can initiate a 'bypassing' of the mineral soil matrix (Qualls et al. 2002) resulting in 'nutrient pulses' in the stream water of small water catchments (Lodge et al. 1994) because of the preferred leaching of some elements. This special runoff mechanism is promoted by extraordinary water input volumes and near−waterlogged soil conditions (Buttle 1998). Thus, the amounts of nutrients that are leached from the ecosystem are strongly affected by the current hydrological conditions (Burt 1986).

Because of the 'filtration function' of the soil, element concentrations in stream water are generally low, except for elements that are released by mineral weathering (McDowell 1998; McDowell & Asbury 1994). Under baseflow conditions, solute concentrations in the stream water remain relatively constant because of the high infiltration capacity and permeability and the rapid adjustment of chemical equilibriums in forested soils (Likens & Bormann 1995).

1.3 Research objectives

Many ecosystem studies in tropical montane forests were conducted for only a one−year period and/or biweekly up to monthly sampling intervals. This is attributable to the remote locations with difficult environmental conditions on steep slopes and resulting logistic problems, like accurate sample treatment and quick sample transport to the analytical laboratory. Nevertheless, to be able to assess the temporal variability of the element dynamics on smaller (influence of rainstorms) and greater (seasonal patterns) time scales, a higher

sampling resolution and longer total monitoring periods are necessary. Therefore, this study covers a three−year monitoring period with weekly sampling intervals.

The investigation of the functional linkage between the hydrological and the biogeochemical cycle in a tropical montane forest in south Ecuador was the overall objective of my work. In detail the specific aims were

- to determine the major hydrological flow paths in the study forest in relation to weather conditions and elucidate their influence on the nutrient dynamics
- to quantify concentrations of the dissolved organic forms of C, N, P, and S and their contributions to total N, P, and S in the ecosystem fluxes and compare them to those in temperate and other tropical forests
- to quantify concentrations and fluxes of the dissolved inorganic forms of the plant nutrients N, P, and S in the ecosystem fluxes across an ecosystem profile and to set up an input−output budget for three small forested catchments
- to identify the major controls of the dissolved C, N, P, and S dynamics in the study forest

2 Materials and Methods

2.1 Study site

2.1.1 Location

The study site 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 in the province Zamora−Chinchipe at 4° 00` S and 79° 05` W (Figure 2). On the forested north−exposed side of the valley of the Rio San Francisco, three 30−50° steep microcatchments (MC1−3) under montane forest at an altitude of 1900−2200 m above sea level (a.s.l.) were selected (Figure 2). All catchments are drained by small tributaries to the Rio San Francisco which flows into the Amazon basin.

The study area is characterized by high relief energy because of the steep slopes with a mean inclination of 38° and locally extreme values of 70° (R. Stoyan, personal communication). The maximum difference in elevation of the area covers 1340 m between the bottom of the valley of the Rio San Francisco (1800 m a.s.l) and the highest peak, the 'Cerro de Consuelo' (3140 m a.s.l).

2.1.2 Bedrock

The southern Cordillera Real is mainly built up by the 'Zamora series', consisting of palaeozoic metamorphic rocks of widely varying metamorphic grade (Litherland et al. 1994). The study site is underlain of an interbedding of folded mainly low metamorphic phyllites, quartzites, and metasandstones, which is called 'Chiguinda unit' of the 'Zamora series' according to Litherland et al. (1994).

2.1.3 Soils

Recent soils have developed on postglacial landslides or possibly from periglacial cover beds (Wilcke et al. 2001, 2003). The dominating soil type in all catchments was a Humic Dystrudept (USDA−NRCS 1998) occupying 38 %, 60 %, 28 % of the area of MC1, 2 and 3, respectively (Yasin 2001). Different soil types have developed dependent on their topog-

raphic position. While on the ridge tops soil types were Humic Dystrudepts, Aquic Dystrudepts, and Terric Haplosaprists, in the valley bottoms Oxyaquic Eutrudepts, Oxyaquic Dystrudepts, Aquic Eutrudepts, and Histic Humaquepts were found (Yasin 2001). All soils are shallow, loamy−skeletal with high mica content (Yasin 2001).

The organic layer consisted of Oi, Oe, and Oa horizons ('Moder' according to the German soil classification, AG Boden 1994) in most parts of the study catchments and had a thickness between 2 and 43 cm (average of 16 cm; Wilcke et al. 2002).

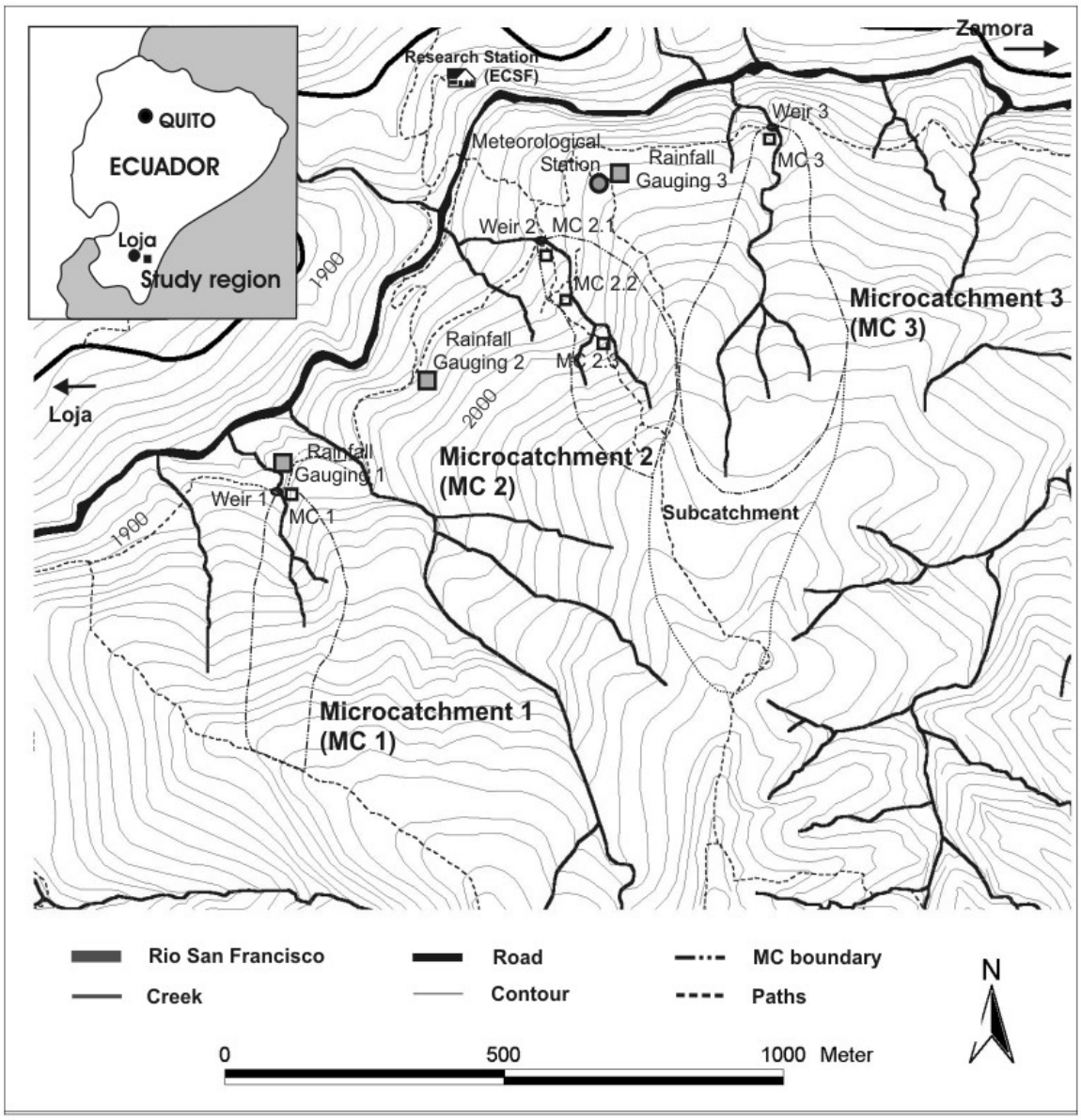

Figure 2: Location of the study area.

Because of the greater thickness and element concentration the elemental storage in the organic layer was high compared with forest soils in other temperate and tropical regions

(Wilcke et al. 2002). The abundance of macropores in the organic layer developed as soil pores and cracks, and root channels (Fleischbein 2004) resulted in a low bulk density (Table 1). The bulk density further increased with depth in the mineral soil ranging between mean 1.1 g cm^{-3} in the A horizon and mean 1.4 g cm^{-3} in the B horizon (Fleischbein 2004). The high stone content of the mineral soil (estimated mean 36 % in the upper 0.5 m, Fleischbein 2004) is considered to provide preferential flow paths (J. Zeilinger, personal communication).

Table 1: Mean and range (in parentheses) of selected properties of 47 O and A horizons collected from three ca. 10 ha−large microcatchments under lower montane forest in south Ecuador. (taken from Wilcke et al. 2002 and Yasin 2001), CEC: cation−exchange capacity and BS: base saturation).

				C	N	P	S
horizon	thickness [cm]	bulk density [g cm^{-3}]	pH (H_2O)	Total concentrations [g kg^{-1}]			
Oi	2.5	0.08	5.0	463	17	0.87	2.0
	(0.5−7)	(0.06−0.09)	(3.9−7.4)	(251−529)	(7.5−28)	(n.d.[a]−4.6)	(1.2−2.8)
Oe	4.1	0.11	4.5	428	23	0.95	2.5
	(0.5−25)	(0.06−0.20)	(3.5−7.1)	(262−516)	(12−32)	(n.d.−1.5)	(1.6−3.6)
Oa	9.1	0.2	3.8	370	23	0.97	3.0
	(0.5−32)	(0.12−0.29)	(3.1−6.7)	(105−503)	(8.3−32)	(0.39−2.2)	(1.3−10)
	CEC [mmolc kg^{-1}]	BS [%]					
A	72	29	4.3	35	4.5	3	1.2
	(15−152)	(1.3−103)	(3.7−6.4)	(2.8−92)	(0.52−58)	(n.d.−102)	(0.12−40)

[a] n.d. : not detected

2.1.4 Vegetation

Microcatchments 2 and 3 are entirely forested, whereas the upper part of MC1 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 forest in microcatchments 2 and 3 seems to be undisturbed. However, there is a disused pathway, which connects Loja and Zamora, as well as high−voltage lines and a small water channel from a nearby power station in the lower part that might be secondary forest.

Bruijnzeel (2001) pointed at the difficulties concerning the distinction of different types of tropical montane forests, which have led to a number of partly overlapping terms. Several key features have been suggested including elevation, abundance of epiphytes, duration of cloud cover, stem thickness and density and tree height.

The study forest can be classified as 'bosque siempreverde montaño' (evergreen montane forest, Balslev and Øllgaard 2002) or as Lower Montane Forest (Bruijnzeel & Hamilton 2000), which is described as a 'tall forest little affected by low clouds but rich in epiphytes' by Bruijnzeel & Hamilton (2000), since this definition was in good agreement with own observations. The most frequent tree families of the study forest are Lauraceae, Rubiaceae, Melastomataceae and Euphorbiaceae. The tallest and species−richest forest is found on lower slopes and in ravines where the canopy reaches 25 m with some emergents of up to 35 m. Characteristic taxa are *Inga* (Mimosaceae), *Miconia* (Melastomataceae), *Hyeronima* (Euphorbiaceae), *Ficus* (Moraceae), *Piper* (Piperaceae), and *Prumnopitys montana* (H.&B.) de Laub (Podocarpaceae). On nearby upper slopes and ridges, forest stature and tree species composition is different with only few trees reaching more than 15 m. Some frequent species are *Alchornea pearcei* Britton ex Rusby (Euphorbiaceae), *Podocarpus oleifolius* D. Don (Podocarpaceae), *Alzatea verticillata* Ruiz & Pav. (Alzateaceae) various Lauraceae, and *Purdiaea nutans* Plancheon (Cyrillaceae). The latter dominates the forest above 2100 m of elevation. The most abundant tree species between 1800 and 2200 m is *Graffenrieda emarginata* (Ruiz & Pav.) Triana (Melastomataceae) which is mainly restricted to upper slopes and ridges. In the undergrowth stratum, the forest has a high percentage of Cyatheaceae. The ground flora is dominated by ferns and large herbs (Homeier et al. 2002; Paulsch 2002; J. Homeier, University of Bielefeld, Germany, personal communication).

2.1.5 Regional climatic conditions

For the eastern Andean slopes at altitudes between 1000 and 3600 m a.s.l., an unimodal distribution of the annual precipitation with a single rainfall maximum between April and September and without a dry season is typical (Bendix & Lauer 1992). The rainfall maximum between April and September is caused by the winds of the equatorial current, which

induces orographic precipitation at the eastern Andean slope. The drier season is caused by the Low Level Jet that reaches the eastern Andean slope between October and March (Bendix & Lauer 1992).

Additional climate data were available from a meteorological station (P. Emck, Friedrich−Alexander−University of Erlangen−Nürnberg, Germany, personal communication) between MC 2 and 3 (Figure 2).

Figure 3: View of microcatchment 2 (MC2) from the opposite valley side. The white line marks the water catchment boundary.

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. The prevailing directions of the synoptic wind recorded at the highest peak of the study area (3140 m a.s.l) were easterly during more than 80 % of the observed time period, while the air circulation was dominated by valley−mountain wind systems. As climate data covers a period of four years and adjacent Ecuadorian weather stations didn't indicate any climatic peculiarities for this

time period, data can be considered as mean local climatic conditions (P. Emck, personal communication). More detailed results of precipitation volumes of the study site are presented in chapter 3.1.

2.2 Methods

2.2.1 Experimental design

The long−term experiences of the extensive ecosystem study at the Hubbard Brook Experimental Forest have led to the suggestion of a 'small watershed approach' for the investigation of the complex biogeochemistry of forest ecosystems, since this method enables quantitative budgets for the most macronutrients (Likens & Bormann 1995). Following this recommendation, three small water catchments ('microcatchments') were equipped with scientific measurement devices. Microcatchment 1 has a size of ca. 8 ha, MC2 of ca. 9 ha (Figure 3), and MC3 of ca. 13 ha (Yasin 2001).

To assess the aquatic cycle of nutrients through the studied ecosystem, the major ecosystem fluxes in a vertical ecosystem profile were sampled based on a compartment model suggested by Matzner & Ulrich (1981) following the way the water takes through the forest (Figure 4).

Equipment in each microcatchment was installed on transects, about 20 m long with a altitude range of 10 m, on the lower part of the slope at 1900−1910 m a.s.l. (transects MC1, MC2.1, and MC3). Extra instrumentation was installed at 1950−1960 (MC2.2) and 2000−2010 m a.s.l. (MC2.3; Figure 2). All transects were located below closed 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. Each gauging station for incident precipitation consisted of five samplers. Solution sampled by rainfall collectors was 'bulk precipitation' (Whitehead & 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 low 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 evenly distributed on the transect (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 & Marques−Filho (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.

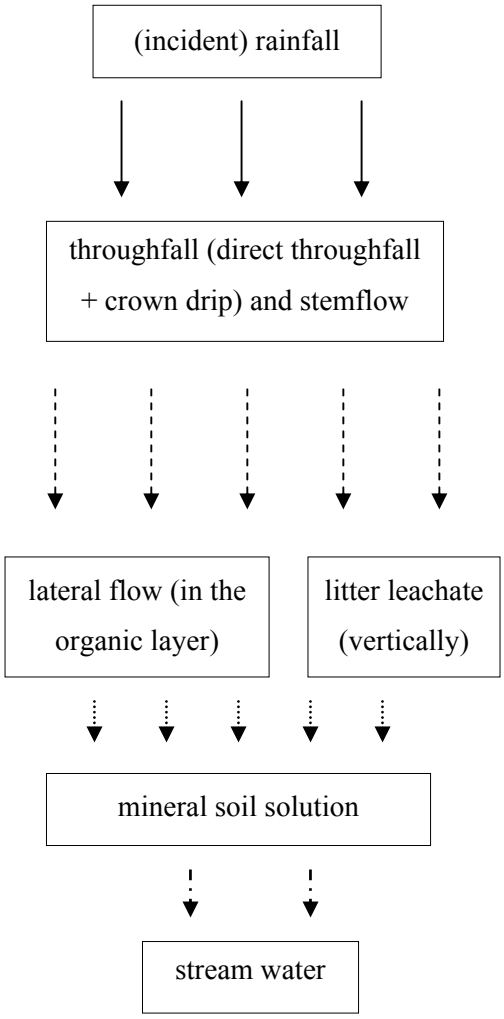

Figure 4: Sampled ecosystem fluxes in the studied tropical montane forest.

Furthermore, three collectors for lateral flow and litter leachate were installed at lower, central, and upper positions along the transects and three suction lysimeters for soil solution sampling at each 0.15 m and 0.30 m depths in the mineral soil at in central position of

the transect. Soil solution was sampled since May 2000 after equilibration of the lysimeters in the soil for four 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 & 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 Table 2.

Collectors for lateral flow samples consisted of a halved 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.

Table 2: Species and diameter at breast height of the trees used for measuring stemflow in three microcatchments (MC1−3) under lower montane forest in south Ecuador.

MC1	dbh [cm]	MC2	dbh [cm]	MC3	dbh [cm]
Heliocarpus americanus L. (s. o.)	78	*Heliocarpus americanus* L. (s. o.)	123	*Heliocarpus americanus* L. (s. o.)	116
Sapium aereum Klotzsch ex M. Arg	90	*Sapium aereum* Klotzsch ex M. Arg	70	*Sapium aereum* Klotzsch ex M. Arg	108
Cecropia villosa C. C. Berg & P. Franco, sp. nov.	95	*Cecropia villosa* C. C. Berg & P. Franco, sp. nov.	122	*Cecropia villosa* C. C. Berg & P. Franco, sp. nov.	111
Turpinia occidentalis (Sw.) G. Don.	44	*Piptocoma discolor* (Kunth) Pruski	72	*Ocotea* s.p.	33
Cyathea caracasana (Klotzsch) Domin	66	*Cyathea caracasana* (Klotzsch) Domin	75	*Cyathea caracasana* (Klotzsch) Domin	74

Litter leachate was sampled by zero tension lysimeters, consisting of plastic boxes (0.20

x 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). Lateral flow and litter leachate collectors were positioned at the lower, central, and upper part of each transect. A combined sample for every transect was produced by bulking the single samples directly in the field.

Mineral soil solution was sampled by suction lysimeters (mullit suction cups, 1 µm ± 0.1 µm pore size) with a vacuum pump. Vacuum was applied only one (moist conditions) or two times (dry conditions) per sampling week, respectively. Pressure was adjusted to the matric potential. The lysimeters do not collect the soil solution quantitatively (Jemison & Fox 1992). Stream water samples were taken from the center of the streams at the outlet of each microcatchment.

2.2.2 Field sampling

Dissolved nutrient samples

Water samples were collected between May 1999 and April 2002 for DOC, DIN and DON and between May 2000 and April 2001 for DOP, DOS, DIP and DIS on a weekly basis. For P and S analyses, weekly samples were combined to monthly samples in the field laboratory.

Isotope samples

Between August 2000 and August 2001 water samples of rainfall, throughfall, lateral flow, soil solution at 0.15 m and 0.30 m depth in the mineral soil, and stream water at the outlet of each microcatchment for isotope analyses were collected. Sampling was carried out bi-weekly for isotopes, and each sample represented an average of the previous week except that of stream water. Rainfall, throughfall, lateral flow, and soil solution sampling was accomplished by mixing the single volumes of each collector at each transect and rainfall gauging site, respectively. Furthermore, an ‘event sample’ was taken immediately after the rainstorm event on 19 September 2000 to examine how the isotope values changed. Water

samples for ^{18}O and D analyses were stored in 10 and 100 ml glass bottles, the bottles were tightly sealed with an aluminium cap containing a barrier septum immediately after collecting in the field in order to prevent evaporation. Samples were stored at ca. 7 °C in a refrigerator until the analysed.

2.2.3 Hydrometric measurements

Rainfall, throughfall and stemflow were measured weekly by recording single volumes for each collector. Furthermore, rainfall data in hourly resolution were available from the meteorological station between MC2 and 3 (Fig. 2) and three rain gauges under the canopy next to each of the three weirs at the outlets of the catchments. Soil moisture conditions were determined by five frequency−domain−reflectometry (FDR) probes on transect 2.1 (MC2). FDR−probes (Theta−probe ML2x, Delta−T Devices Ltd.) were installed in O, A, and B horizon (3 probes in 0.10 m vertical distance in B horizon) and connected to a datalogger (DT 50, UMS) for hourly registration of volumetric soil water content. Because of uncertainties associated with the conversion of the measured FDR−signal in organic material (Veldkamp & O'Brien 2000) the actual value of the volumetric water content of the organic horizon might be underestimated. Nevertheless, since the output signal of the FDR−probes is linearly related to the water content (Gaskin & Miller 1996), the curve of the water content in the organic layer represents the correct temporal course.

Additionally, matric potentials were determined two times per week by manual−reading tensiometers installed at 0.15 and 0.30 m depth of the mineral soil at one selection position approximately in the center of each transect. Matric potentials were read 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). In MC1, the gaps comprised 253, in MC2 261, and in MC3 298 days. TOPMODEL has successfully been used in humid tropical catchments to examine the relative contributions of various flow

paths during storm events (Molicova et al. 1997; Chappell et al. 1998), to model the runoff conditions (Campling et al. 2002), and to assess the water balance (Kinner & Stallard 2004). For the study catchments, TOPMODEL was parameterized with a range of climatic, topographic, and soil hydrologic variables measured in the study area to set up a water budget by Fleischbein (2004). The model validation based on the comparison of calculated runoff data from a four−year period (April 1998 to April 2002) with manually measured weekly runoff data (Fleischbein 2004).

2.2.4 Hydrochemical analyses

Hydrogen and oxygen isotope analyses of water samples from the first 2.5 months were conducted at the Alfred−Wegener−Institute for Polar and Marine Research, Potsdam. Measurements were carried out with a Finnigan MAT Delta−S mass spectrometer using standard methods. Analytical precision was better than +/-0.06 ‰ for $\delta^{18}O$ and +/-1.3 ‰ for δD. The remaining samples were analyzed at the NERC Isotope Geosciences Laboratory, UK. Isotope samples were analyzed using the equilibration method for oxygen (Epstein & Mayeda 1953), and Zn−reduction method for hydrogen (Coleman et al. 1982; Heaton & Chenery 1990) and measurements were made on a VG SIRA mass spectrometer. Analytical precision was typically +/-0.05 ‰ for $\delta^{18}O$ and +/-2.0 ‰ for δD.

Isotopic ratios ($^{18}O/^{16}O$ and D/H) are generally expressed in delta units, $\delta^{18}O$ and δD ‰, and defined in relation to the international standard, V−SMOW (Vienna Standard Mean Ocean Water):

$$\delta^{18}O_{sample} = \left(\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O/^{16}O)_{reference}} - 1 \right) \text{x } 1000 \text{ in ‰}$$

Since the initial data showed that $\delta^{18}O$ and δD fell on a local meteoric water line, and therefore had a consistent relationship, further samples were analyzed only for $^{18}O/^{16}O$ ratios apart from some soil solution samples, which were analyzed for δD to examine possible evaporative effects. I used O and H isotope data in precipitation from Amaluza, Ecuador from the IAEA GNIP database (IAEA 2001) for comparison with my own data.

The pH and Cl^- concentration were measured immediately after collecting in 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 and Schuell) and stored frozen until export to Germany.

Water samples were analyzed for the concentrations of dissolved organic carbon (DOC) (TOC−5050 Analyzer; Shimadzu Corp., Japan), and for dissolved inorganic nitrogen (NH_4−N and NO_3−N + NO_2−N, hereafter referred to as NO_3−N) and total dissolved nitrogen (TDN) concentrations colorimetrically with a continuous flow analyzer (SAN Plus; Skalar Analytical B.V., Netherlands). Additionally, concentrations of total dissolved phosphorus (TDP) and sulfur (TDS, ICP−OES, Integra XMP, GBC Scientific Equipment Pty. Ltd., Australia), PO_4^{3-}, and SO_4^{2-} (ion chromatography, DX−100; Dionex) were determined. The detection limits of the used analytical methods are summarized in Table 3.

Table 3: Analytical devices and detection limits for water analyses

Elements	Analytical devices	Detection limit [mg l^{-1}]
Cl^-	Cl^-−specific electrode	0.2
DOC	Total organic carbon analyzer	1.0
TDN	Continuous flow analyzer	0.075
NH_4^+−N	Continuous flow analyzer	0.05
NO_3^--N	Continuous flow analyzer	0.025
TDP	Inductively−coupled plasma−atomic emission spectrometer	0.2
PO_4^{3-}	Ion chromatography	0.3
TDS	Inductively−coupled plasma−atomic emission spectrometer	0.3
SO_4^{2-}	Ion chromatography	0.3

2.2.5 Calculations and statistical evaluations

For one selected event, for which the $\delta^{18}O$ values in rainfall and the stream water were

available, a basic isotope two−component hydrograph separation for a rainstorm event was conducted to estimate the contributions of event and pre−event waters to the total stormflow runoff during the event using the mixing equation

$$X = \frac{C_s - C_e}{C_p - C_e}$$

where X is the contribution of event water to total stormflow runoff and C_s, C_p, and C_e are the δ values in total stormflow (s), pre−event (p) and event water (e), respectively.

The following assumptions were made to meet the conditions required for the application of a isotope hydrograph separation:

(i) The $\delta^{18}O$ of the rainfall remained constant from the day before to the day after the event. This was supported by nearly constant $\delta^{18}O$ values in rainfall of 19 and 20 September 2000 (-5.8 to -5.7 in MC1, -5.7 to -5.7 in MC2, and -5.6 to -5.6 ‰ in MC3, respectively).

(ii) The $\delta^{18}O$ of the stream water from 6 September 2000 was used to define the $\delta^{18}O$ signal of pre−event water, since the three weeks before the rainstorm event were relatively dry (22, 21, and 32 mm of rainfall) and the $\delta^{18}O$ of the stream water remained nearly stable (-6.7 to -6.8 in MC1, -6.9 to -7.0 in MC2, and -6.6 to -6.8 ‰ in MC3).

Correlation analyses followed the least squares method. To compare mean dissolved nutrient concentrations in solution between the study transects, the Wilcoxon matched−pairs test for connected data rows was used. To compare means of data sets with different size, I used the Spjotvoll & Stoline modification of Tukey's Honest Significant Difference (HSD) test (StatSoft Inc. 2000). Significance was set to $p<0.05$ for the post−hoc tests and to $p<0.01$ for the Wilcoxon test. Statistical analyses were performed with STATISTICA for Windows 5.5 (StatSoft Inc. 2000).

Nutrient fluxes were calculated for rainfall, throughfall, stemflow, and stream water by multiplying the respective annual volume−weighted means (VWM) with the annual water fluxes. Water fluxes in the soil were not quantified. For the calculation of stream water fluxes a discharge−weighted mean (DWM) concentration for the runoff of each microcatchment was computed by multiplying the mean daily discharges of the sampling week

by the mean weekly concentration of the individual constituents for the corresponding period and dividing the sum of the products by the sum of the discharges.

In most studies, 'DOC' is operationally defined as <0.45 µm in diameter (Thurman 1985). In my study, filters with a pore size of 4−7 µm were used except for mineral soil solution (1 µm). As Michalzik et al. (2001) did not observe a significant change in the concentrations of DOC and DON in litter leachates when filter pore diameters were increased to 25 µm, I considered all organic C, N, P, and S in my solutions as dissolved.

The concentrations of DON were calculated as difference between those of TDN and NH_4−N + NO_3−N, the concentrations of DOP as difference between those of TDP and PO_4−P, and the concentrations of DOS as difference between those of TDS and SO_4−S. In some cases, mainly in fluxes with low concentrations like rainfall and stream water (for N, P, and S) and mineral soil solution (for P and S), measured concentrations of inorganic forms were erroneously higher than measured total concentrations rendering the calculation of organic forms impossible. This happened in 0.6, 10, and 20 % of all samples for N, P, and S, respectively. Furthermore, some samples had concentrations below the detection limit of the analytical methods (0.075 mg l^{-1} for N, 0.2 mg l^{-1} for P, and 0.3 mg l^{-1} for S). This was the case in 7 % of the samples for dissolved inorganic N and TDN and in 29 % for dissolved inorganic P and S. For calculation purposes, negative values of dissolved organic solute concentrations and values below the detection limit were set to zero. Thus, my annual means underestimate the real element concentration.

3 Results

3.1 Hydrological conditions of the study site

3.1.1 Incident rainfall

Within the three−year monitored period between May 1999 and April 2002, on average 2448 mm of precipitation fell on the study area. The rainfall exhibited a typical seasonal pattern with a wetter period between April and September and a drier period between October and March (Figure 5). During the monitored period, three weeks without rainfall occurred between 21 and 27 August 1999 and between 2 and 15 November 2000 (Figure5).

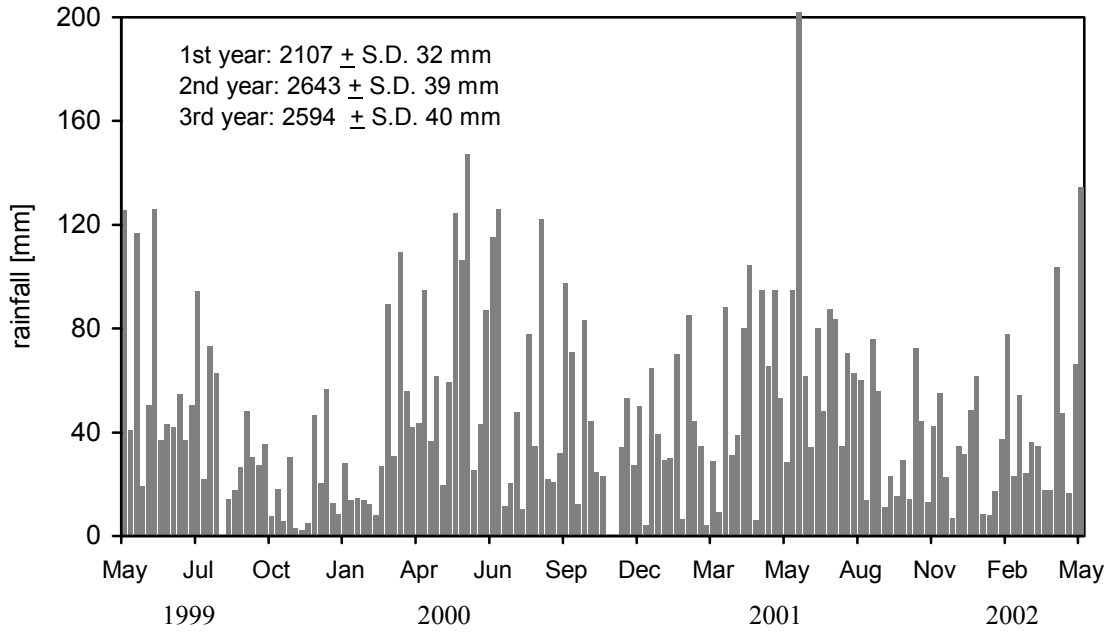

Figure 5: Mean weekly rainfall and total annual rainfall amounts of the study area between May 1999 and April 2002. Standard deviation (S.D.) represents the temporal variation during the three studied years.

The rainfall of the study area was characterized by rain events of varying duration and intensity. According to Fleischbein (2004), who examined the rainfall distribution of the study area in detail for a four−year period between April 1998 and April 2002, the total rainfall was dominated by events with low intensity of <2 mm h^{-1} (83 %). Events with a medium intensity between 2 and 4 mm represented 15.2 %, while only 1.8 % were high intensity rain events (4 to 14 mm h^{-1}).

3.1.2 Soil water regime

As shown in Figure 6, the temporal courses of the mean matric potentials of the mineral soil at the five study transects reflect the annual rainfall distribution of the study site showing lower values during the drier season between October and March and higher values during the wetter season between April and September. Matric potentials quickly responded to rainfall variations indicating a relatively rapid drying and rewetting of the soil at all transects. Weeks with strongly reduced rainfall resulted in a strong decrease of matric potentials, particularly in November 2000 and January 2002, indicating that the water content of the subsoil is markedly affected during dry periods. However, considering the entire two−year period between May 2000 and April 2002, the temporal time course of the matric potentials suggests that the mineral soil was relatively wet during the greater part of the year often reaching nearly water−saturated moisture conditions. This was confirmed by findings of Fleischbein (2004), who found frequent water saturation in the mineral soil at an intensively studied test plot near transect MC2.2.

To study the response of the soil water regime to the incident rainfall in more detail, high resolution data (hourly) of the rainfall (P. Emck, personal communication) and the soil water content in the organic layer and the mineral soil of two periods during the driest and the wettest period of the year were selected (Figures 7 and 8). Generally, the temporal courses of the volumetric soil water content demonstrated the characteristic response of the catchment soils to the local rainfall conditions with steep rising and flat falling limps of the soil water content graphs (Figures 7 and 8). This illustrates a frequent alternation of soil drying and rewetting cycles. Typically, when soil horizons were presaturated, short−time rain events with high rain intensity caused a rapid increase in the soil water content. In the short drier periods between the events, the soil water content quickly reacted with a decline until the next rain event.

Figure 7 illustrates the transition from the wetter season between April and September to the drier season between October and March. In October 2000 the soil horizons were relatively wet because of the high water input during the preceding wetter period. From 21 October, rainfall decreased which was reflected in a decline of the soil water content in all

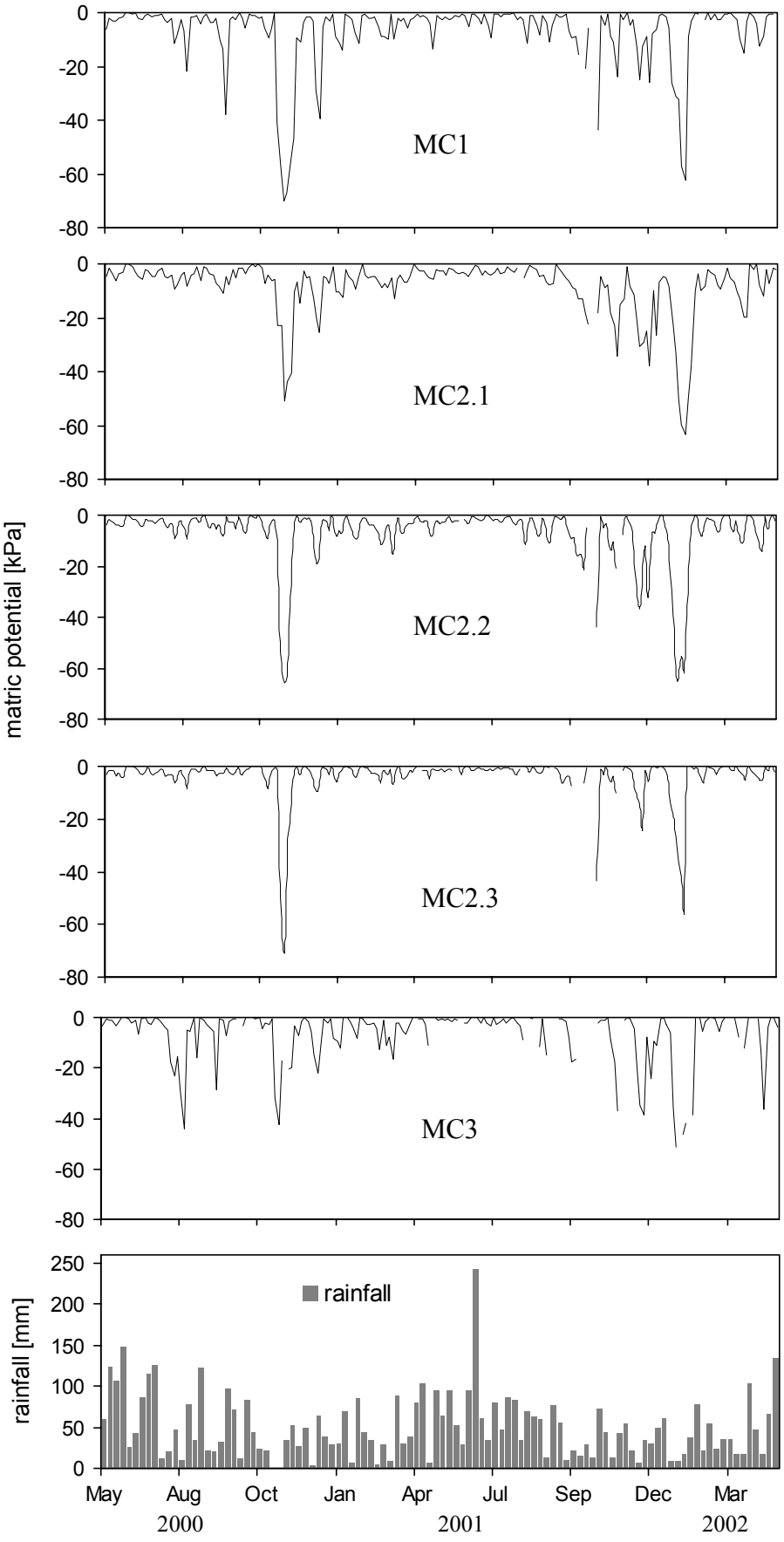

Figure 6: Mean matric potentials of the mineral soil at five study transects and weekly rainfall of the study site between May 2000 and April 2002.

three studied soil horizons (O, A, and B horizons). The decline of the soil water content was interrupted by a short rainy period around the 30 October, which caused a short−term increase in the soil water content only in the A horizon, probably indicating interflow within this soil layer. After this event, three weeks without rainfall followed resulting in a simultaneous drying of the top− and the subsoil to low water contents.

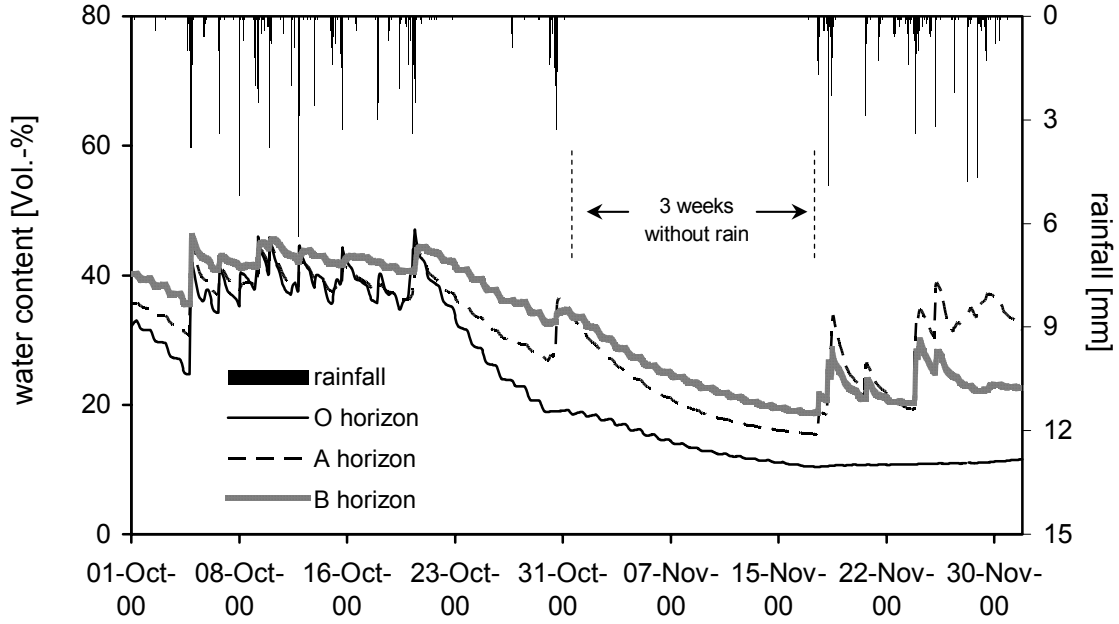

Figure 7: Rainfall volumes and volumetric soil water contents of the O, A, and B horizons on transect MC2.1 during the transition from a wet period to a drier period between 1 October and 1 December 2000.

The first rain on 17 November and subsequently the following events during the end of November 2000 caused a soil water response remarkably only in the A and B horizons, whereas there was no change in the water content of the organic layer. This may be explained with the 'hydrophobicity' of the dry organic layer components (Wilson et al. 1991), which induced a rapid transfer of the first rain water to the deeper soil layers. This finding indicates a refilling of the soil water reservoir after a longer dry period from deeper to higher soil regions. While the soil water contents of the A and the B horizons paralleled each other after the first rain, the soil water content of the A horizon exceeded that of the B horizon when rainfall was continuing after 24 November, again probably indicating interflow in the A horizon.

The soil water dynamics during the wettest period of the year between May and July are shown in Figure 8. The courses of the soil water contents of the O, A, and B horizons are paralleling each other with increasing values in the order O<A<B horizon during the entire monitored period. Fluctuations were highest in the O and smallest in the B horizon. Again, the soil water content increased directly (within 1 hour) after a rain event showing the fastest and strongest response in the O horizon. The different soil water responses on 19 and 27 June 2001 showing a faster increase immediately after the event on 19 June indicated a negative relation between rainfall intensity and the time delay until the soil water content responded to the event. This was confirmed by the quick reactions of the soil water content during the rainstorm events on 26 May, 4 June, 13 July, and 20 July (Figure 8).

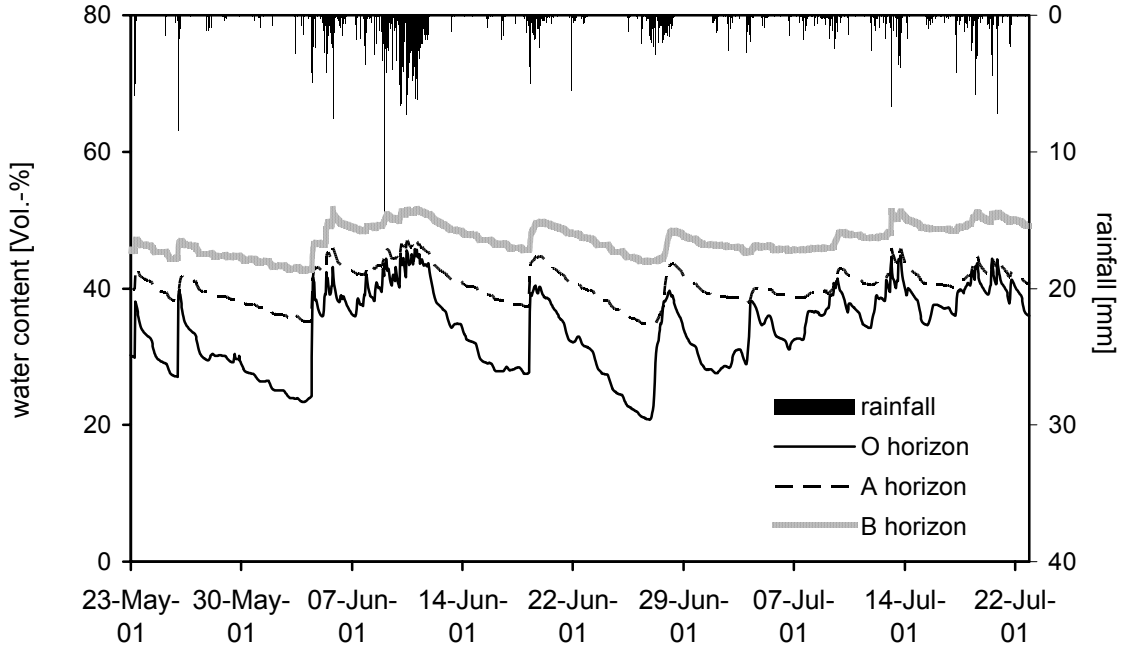

Figure 8: Rainfall volumes and volumetric soil water contents of the O, A, and B horizons on transect MC2.1 during a wetter period between 23 May and 23 July 2001.

To illustrate the soil water dynamics during rainstorm conditions, three single rain events on 4 and 5 June 2001 were selected (Figure 9). The volumetric soil water data indicate an immediate response of the soil water regime to the rainstorm event within one hour. The strongly elevated rain water input caused a rapid increase of the water content in the organic layer and also in the mineral soil horizons.

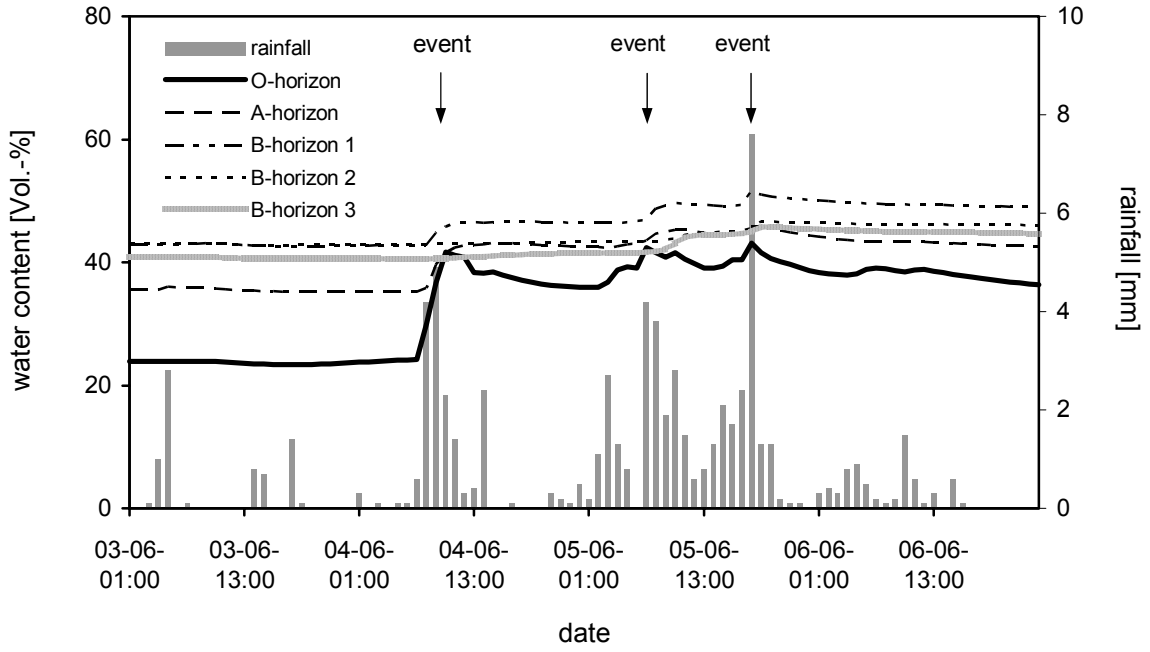

Figure 9: Rainfall volumes and volumetric soil water contents of the O, A, and B horizons on transect MC2.1 during a wetter period between 3 and 7 June 2001.

Notably, the first event on 4 June caused a greater net increase of the soil water content in the O and A horizons than on the following events, though having a smaller peak rain intensity (4.9 mm h^{-1}) than the third event (7.6 mm h^{-1}). Again, this can be explained with a higher presaturation of the soil after the first event on 4 June (see above).

3.1.3 Catchment discharge

Using the hourly discharge values (logged data and with TOPMODEL substituted data gaps from Fleischbein 2004), the three−year means for the monitored period between May 1999 and April 2002 of the catchment discharge were 2.57 (MC1), 3.38 (MC2), and 3.36 (MC3) l s^{-1}, respectively.

The discharge of all three microcatchments quickly responded to the incident rainfall clearly reflecting the drier and the wetter periods of the year (Figure 10). Usually, the courses of the catchment discharges were parallel. However, during periods with high water input and/or heavy rainstorm events, MC3 showed a partly different behaviour from MC1 and 2. This is probably caused by a periodic contribution of water from a higher subcatchment (Figure 2), which supplies an additional water input after high level rain events

combined with presaturated soil moisture conditions in the subcatchment (Yasin 2001). This conclusion is furthermore confirmed by markedly higher DOC concentrations in the stream water of MC3 than of MC1 and 2 associated with high runoff events (data not shown) that might have originated in the peaty soils of the relatively flat subcatchment (own field observation).

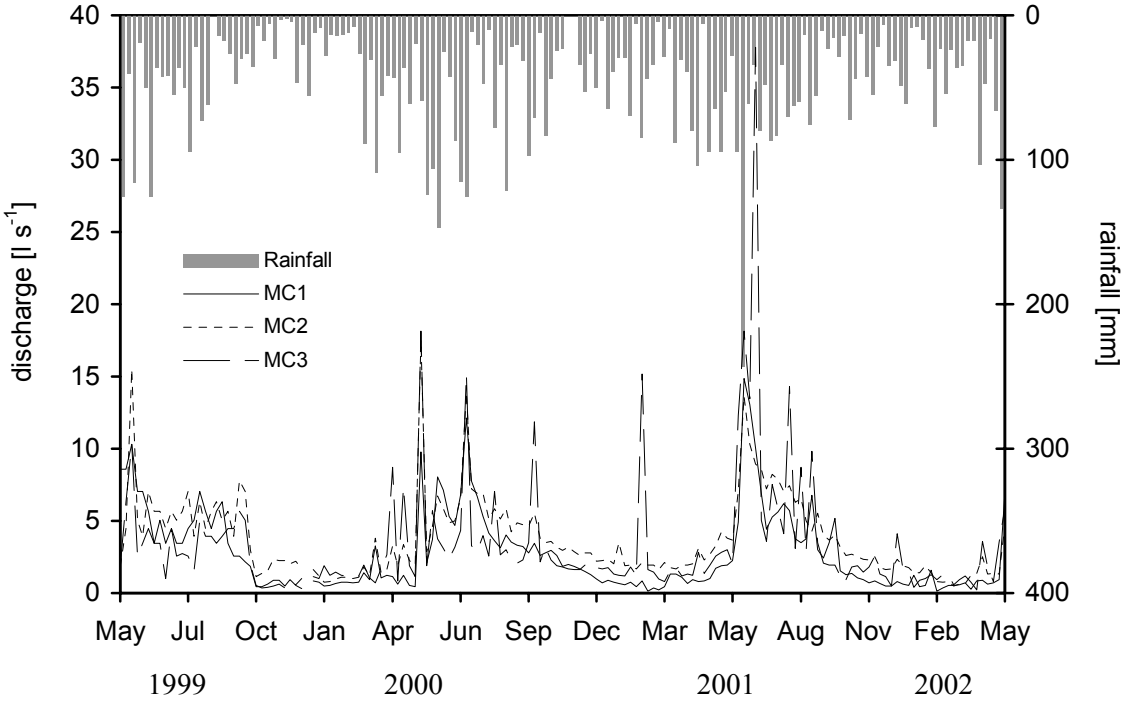

Figure 10: Temporal courses of stream discharge of the three microcatchments (MC1−3) and rainfall volumes between May 1999 and April 2002

3.2 Combined oxygen isotope and hydrometric approach

3.2.1 Isotope signatures of ecosystem fluxes

The rainfall showed considerable variations in $\delta^{18}O$ over the monitored year between 23 August 2000 and 15 August 2001 between -12.6 ‰ (MC1) on 23 May 2001 and +2.1 ‰ (MC1) on 15 August 2001 (Figure 11). The three microcatchments showed similar $\delta^{18}O$ in rainfall over the year (standard deviation: less than 0.9 ‰). The large variation in $\delta^{18}O$ values over the year is due to the alternating influence of air masses from different source regions and is shown by correlation of $\delta^{18}O$ of rainfall with synoptic wind directions. The

comparison of my data with the weighted monthly $\delta^{18}O$ values of Amaluza, the nearest IAEA station 70 km SW, showed a similar trend in $\delta^{18}O$ (Figure 12). The influence of the rainfall amount and temperature on the isotopic composition of rainfall is not seen (r=0.26).

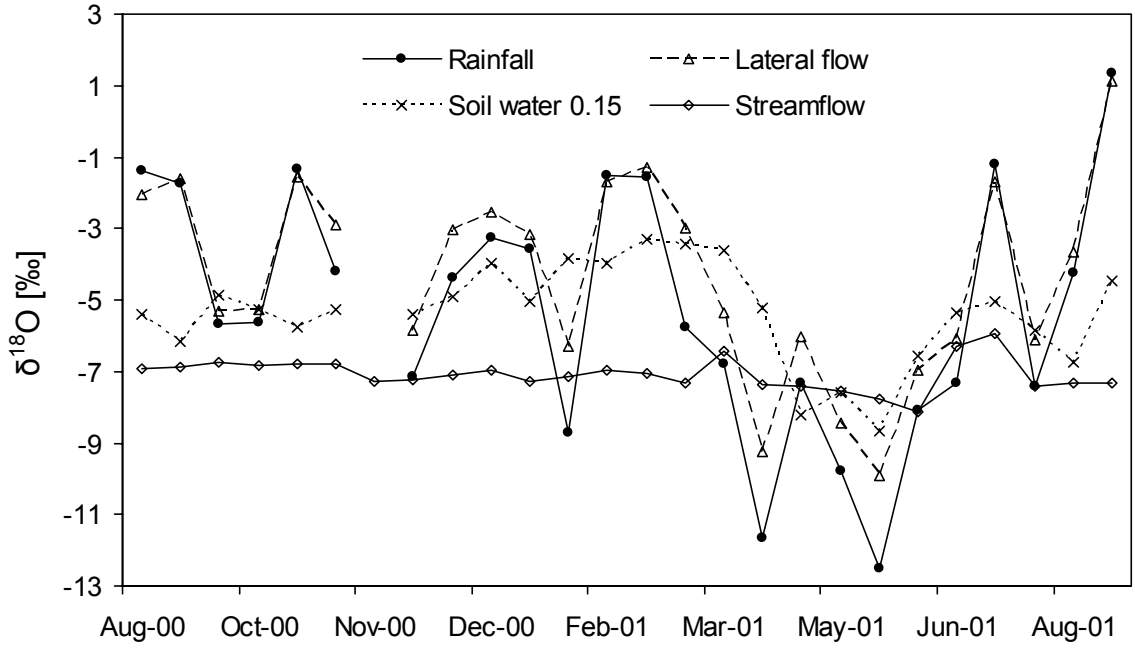

Figure 11: Annual courses of mean $\delta^{18}O$ values of rainfall, lateral (organic layer) flow, soil solution, and stream water between 23 August 2000 and 15 August 2001.

The $\delta^{18}O$ values in throughfall (-12.4 ‰ to +0.6 ‰) were almost identical to those in rainfall, although occasionally, when throughfall and rainfall were slightly (< 1 ‰) higher in $\delta^{18}O$. Thus, evaporation in the canopy seems to be negligible. The local meteoric water line (LMWL) using both rainfall and throughfall (Figure 13) suggests that evaporation of throughfall is insignificant.

The $\delta^{18}O$ values in lateral flow ranged between -10.5 ‰ (MC3) and +2.8 ‰ (MC1) and closely follow $\delta^{18}O$ in rainfall and throughfall indicating that new rain water predominantly controls the O isotope signal in lateral flow (Figure 11). In general, the lateral flow water was slightly enriched in ^{18}O compared with rainfall and throughfall, which is interpreted as a result of evaporation of and plant plant uptake water from the forest floor.

The annual course of the $\delta^{18}O$ values in the soil solution shows a dampening of the more variable O isotope signal in rain water (Figure 11) which is a typical development for

soil waters (Förstel 1996).

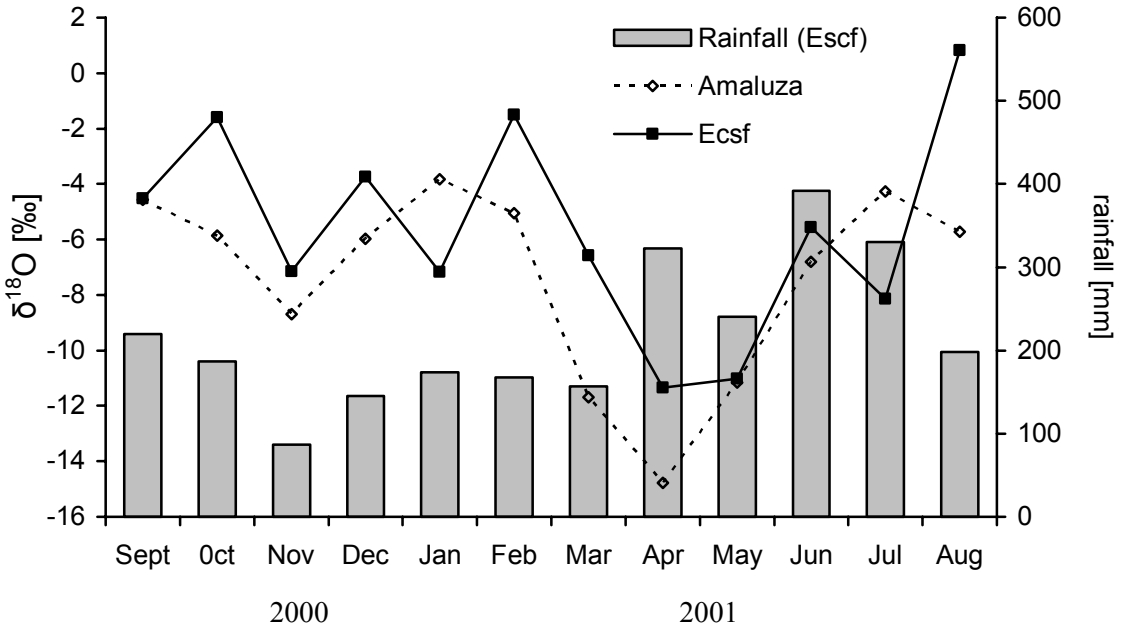

Figure 12: Annual course of weighted monthly means of $\delta^{18}O$ in rainfall from long−term data (Amaluza, south Ecuador) and own data of the monitored year (ECSF, study area), and monthly rainfall in the study area (ECSF) between September 2000 and August 2001.

Variations in $\delta^{18}O$ values of soil solution at two sampling depths are identical and are smaller than in rainfall, throughfall, and lateral flow, ranging between -9.1 ‰ (MC1 and 2) and -3.0 ‰ (MC3). The O isotope variations are similar in the three microcatchments except on 6 September 2000, when $\delta^{18}O$ values in soil solution at 0.15 m (-8.7 ‰) and 0.30 m (-9.0 ‰) in MC3 were significantly different to values in MC1 (-4.9 and -7.0 ‰) and MC2 (-4.9 and -5.4 ‰), which was confirmed by the δD values (-59.2 and -62.8 ‰ for MC3, -29.9 and -48.5 ‰ for MC1, and -30.4 and 35.8 ‰ for MC2). This variation could not be explained by the input of isotopically different rain water, since the isotope signal of rainfall exhibited only small spatial variations between the microcatchments ($\delta^{18}O$ values of -1.9, -1.7, and -1.6 ‰) or an influence by isotopically different rising water from the deeper soil ($\delta^{18}O$ of stream water of -6.8, -6.9, and -6.8 ‰). The $\delta^{18}O$ values in mineral soil solutions from MC3 were lower than those of the lateral flow indicating that the soil solution at that time had a contribution of unknown isotopically lighter water source.

Variations in $\delta^{18}O$ of stream water were small during the year ranging between -5.8 ‰

(MC3) and -8.7 ‰ (MC3) (Figure 11). The mean value of -7.1 ‰ is similar to the long−term $\delta^{18}O$ mean of precipitation at the IAEA station in Amaluza (-7.4 ‰), and probably represents the isotope signal of groundwater in the local area.

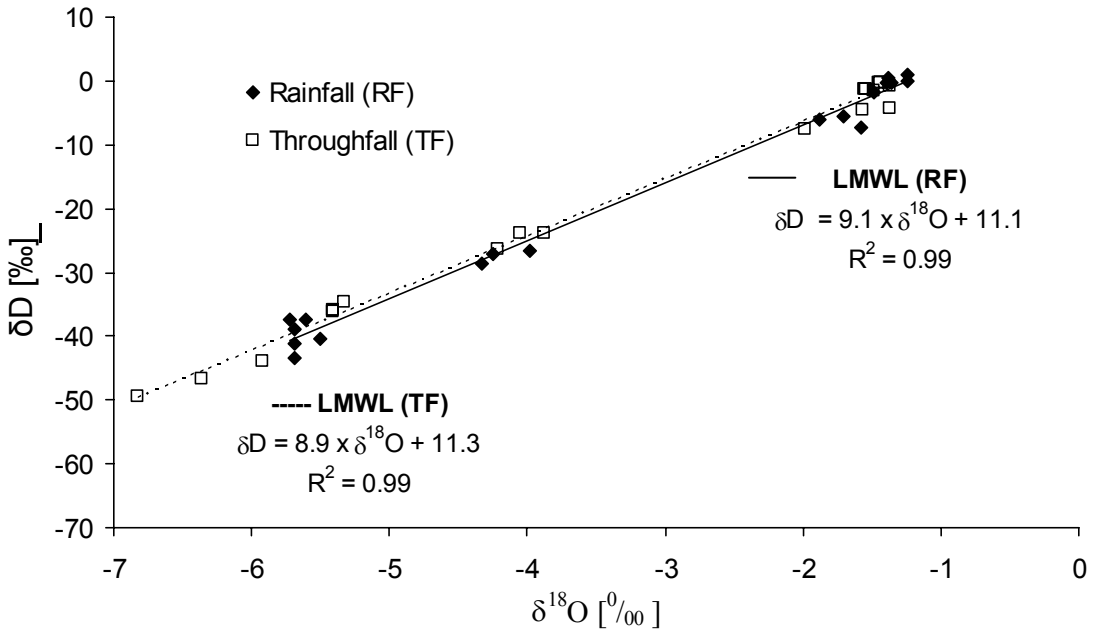

Figure 13: Local meteoric water lines (LMWL) of rainfall and throughfall in the study area.

The greatest variation of the mean $\delta^{18}O$ signal of stream water occurred on 28 March 2001 (-6.5 ‰) and for the period from the late May 2001 to early July 2001, when the mean $\delta^{18}O$ first decreased to a minimum of -8.1 ‰ and then increased to -6.3 ‰, reaching a maximum value of -5.9 ‰ on 4 July 2001 (Figure 11). The peak in stream water on 28 March 2001 may be the result of the preceding five weeks rainfall which had high $\delta^{18}O$ values (Figure 11). The isotope signal of stream water responded to the strong decrease of $\delta^{18}O$ of rainfall after 28 March to a minimum value of -12.5 ‰ on 23 May 2001 (Figure 11) with a continuous decrease to a minimum mean value of -8.1 ‰ reached on 6 June 2001, which was the lowest of the entire monitored year.

The subsequent increase in $\delta^{18}O$ in June 2001 may be attributable to the humid conditions in the preceding weeks, especially an extremely wet week between 6 and 13 June 2001, when weekly rainfall was 227 mm including a strong rainstorm event with a maxi-

mum rainfall intensity of 15.4 mm/h causing soil water saturation. Matric potentials ranged between 0 and -28 kPa on 13 June 2001. Additionally, soil moisture probes showed high volumetric water content in A and B horizon between ca. 42 and 51 vol % between 6 and 13 June 2001 on transect MC2.1. Under these conditions the infiltration capacity of the soils may temporarily have been exceeded resulting in near−surface water flow. The stream water had a $\delta^{18}O$ value that is likely to be a mixture of the local groundwater (not sampled and that must have had a more negative $\delta^{18}O$ than the soil solution at 0.30 m depth) and the lateral flow water within the organic layer. These conditions seem to have prevailed for the following three weeks. On 4 July 2001 the $\delta^{18}O$ in lateral flow and in rain water are identical. Thus, there seem to be changes from mainly vertical to lateral water flow, which is further confirmed by a significant increase of the water content in the organic layer, while the water content of the deeper mineral soil horizons only slightly increased in the A horizon and remained almost stable in the B horizons (Figure 14). To understand these hypothetical changes, I examined a selected rainstorm event in more detail.

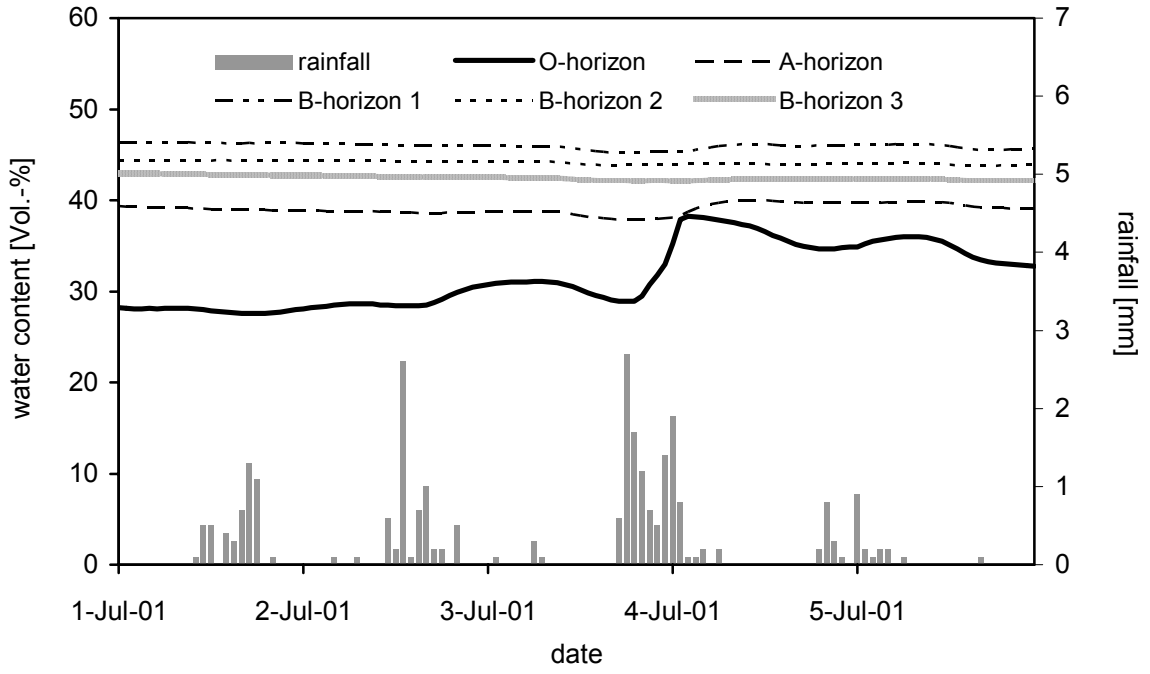

Figure 14: Rainfall volumes and volumetric soil water contents of the O, A, and B horizons under presaturated soil moisture conditions between 1 and 6 July 2001 on transect MC2.1.

3.2.2 Rainstorm event

The rainstorm event on 19 September 2000 had two maxima with throughfall intensities of 6.5 and 7.8 mm/h, respectively (Figure 15). Notably, the discharge of MC2 responded quickly to high rainfall showing only a short peak delay of about two hours compared with the peak of throughfall (Figure 15). During the storm $\delta^{18}O$ values in stream water increased in all three microcatchments to -6.0 ‰ (MC1), -6.4 ‰ (MC2), and -5.9 ‰ (MC3).

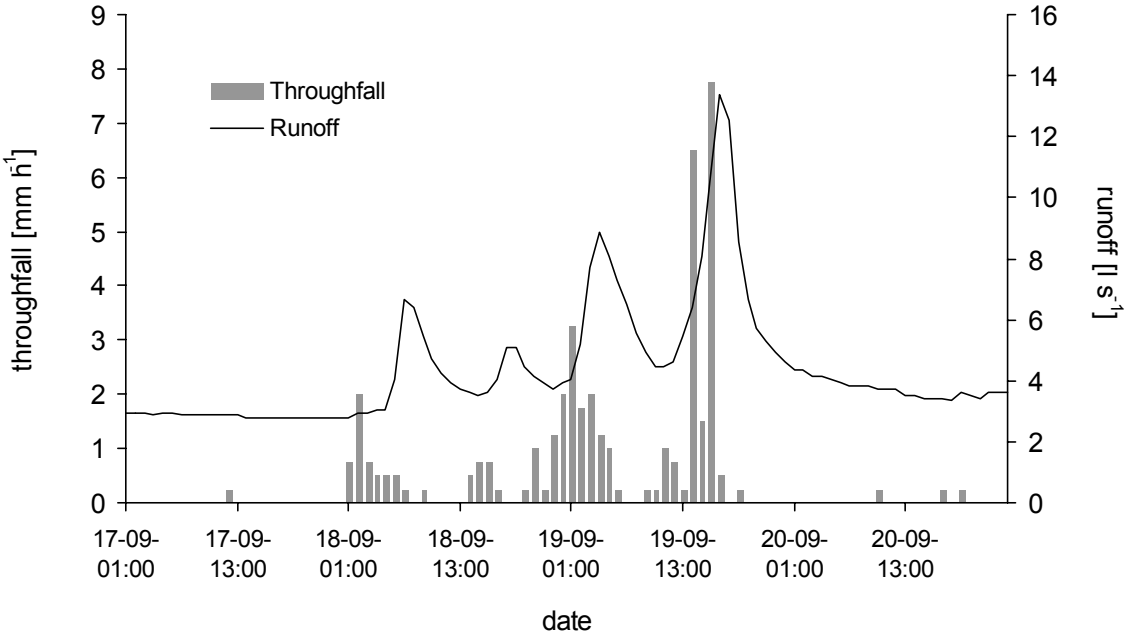

Figure 15: Hourly throughfall and storm hydrograph of runoff in a lower montane rain forest during the rainstorm event on 19 September 2000 on transect MC2.1 (no measured data for MC1 and MC3 available because of logger breakdown).

The following day, $\delta^{18}O$ values of the stream waters had values near -7.0 ‰ (Figure 16).

The isotope signal of the mineral soil solutions showed only a small change in MC1 from -6.6 ‰ to -6.0 ‰ between 19 September (rainstorm event) and 20 September 2000, whereas it remained unchanged in MC2 and 3, which indicates that there was no input of isotopically different water from the soil surface (Figure 17).

On transect MC2.1 soil water content started increasing continuously 6 days before the event, on 13 September 2000, after a period of drier conditions (Figure 18). The hydrograph of the rainstorm event on 19 September shows three smaller rain events prior to the actual rainstorm event between 13.00 and 16.00 hours (Figure 15), which led to a presatu-

ration of the soil documented by the soil water probes (Figure 18). The rise of the water content was markedly stronger in the O horizon compared with the A horizon with a rapid increase of about 12 vol % within 24 hours before the beginning of the rainstorm event (Figure 18).

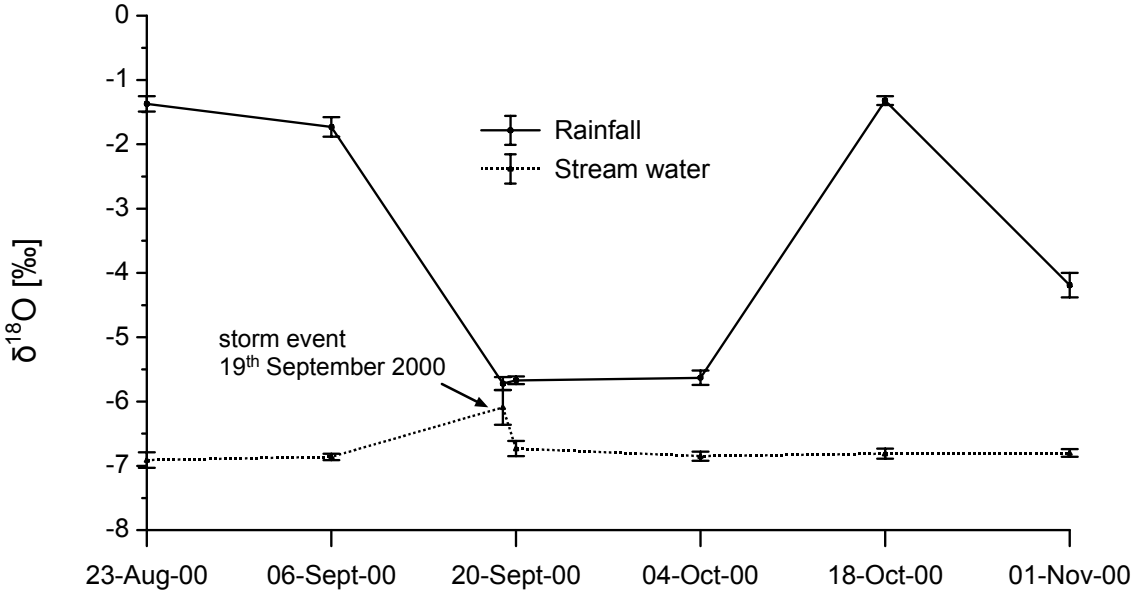

Figure 16: Courses of mean $\delta^{18}O$ in rainfall and stream water in the three microcatchments between 23 August and 1 November 2000 including the rainstorm event on 19 September 2000 (Error bars show standard deviation between the three microcatchments).

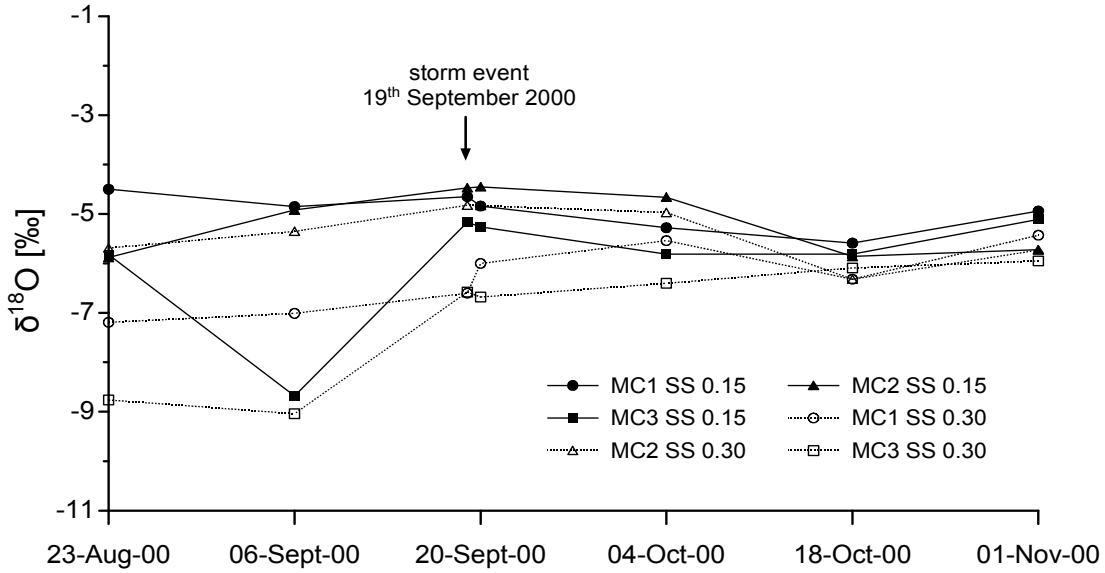

Figure 17: Courses of $\delta^{18}O$ in soil solution at 0.15 m and 0.30 m depth in the three microcatchments between 23 August and 1 November 2000 including the rainstorm event on 19 September 2000.

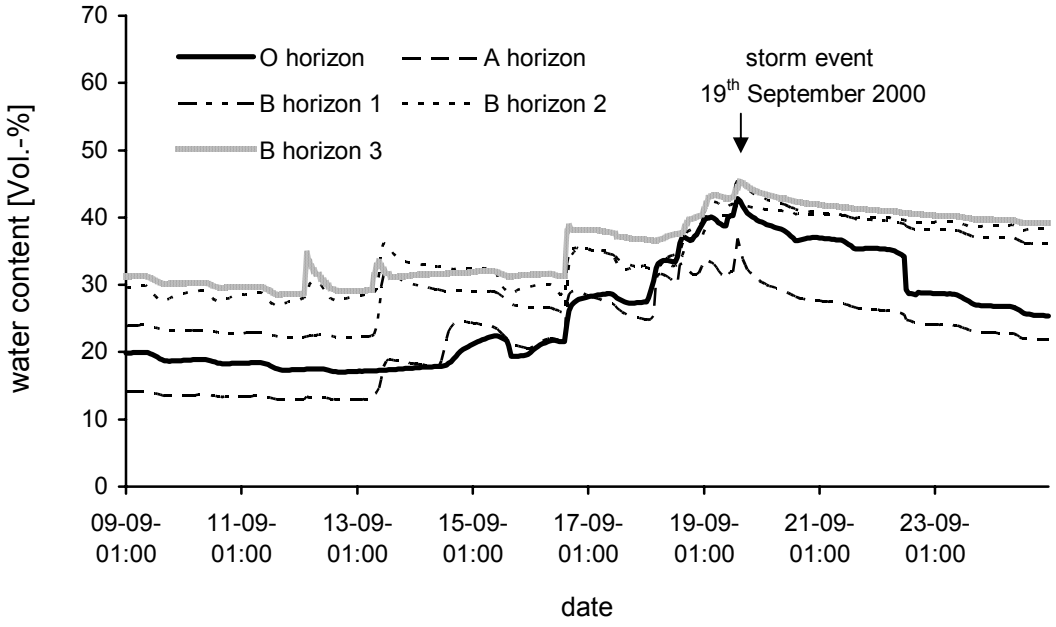

Figure 18: Courses of the volumetric soil water contents in the O, A, and B horizons during the rainstorm event on 19 September 2000 on transect MC2.1.

3.2.3 Isotope hydrograph separation

An isotope two−component hydrograph separation revealed that event water contributed 81, 44, and 78 % to the total stormflow runoff in MC1, 2, and 3, respectively, during the rainstorm event on 19 September 2000.

To evaluate the possible error of non−constant $\delta^{18}O$ values in rainfall (the event water component), an estimation of uncertainty considering two extreme scenarios was made for all three microcatchments: (1) to estimate maximum deviation, the annual mean of the $\delta^{18}O$ in rainfall of the entire monitored year was used instead of the $\delta^{18}O$ in the rainfall during the event and (2) to estimate minimum deviation the $\delta^{18}O$ in the rainfall of the day after the event (20 September) was used. Results showed that the contribution of the event water component to the total stormflow runoff ranged between 54 and 74 % in MC1, 30 and 42 % in MC2, and 58 and 78 % in MC3.

3.3 Dissolved organic nitrogen, phosphorus, and sulfur

3.3.1 Soil properties of the study transects

To characterize the soils on the five study transects some major soil properties were selected (Table 4). According to Wilcke et al. (2001), the soils on transects MC1 and MC3 had significantly higher pH in the organic layer than transects MC2.1, MC2.2, and MC2.3. Notably, the pH were still higher in A and B horizons on transects MC1 and MC3, whereby differences were partly not significant. Furthermore, the higher pH corresponded with distinctly higher base saturations in the A and B horizons.

Detailed discussions of the soil properties on the study transects are given in Wilcke et al. (2001, 2002).

Table 4: 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	BS	pH	C	N	P	S
		($mmol_c\ kg^{-1}$)	(%)	(H_2O)	($g\ kg^{-1}$)			
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

3.3.2 Dissolved organic carbon

The vertical distribution of mean annual DOC concentrations across the ecosystem showed a consistent pattern at all five transects (Table 5). Mean DOC concentrations were low in rainfall and increased in the order throughfall<stemflow<lateral flow<litter leachate. In litter leachate, mean concentrations were highest, except on transect MC2.2, where DOC concentrations of lateral flow were highest. 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. Mean 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 January, (Figure 19a). Similar variations of the DOC/Cl ratios (data not shown) and the lack of correlation between volume and DOC concentrations of rainfall ($r<0.1$) indicated that the variations in DOC concentrations could not be attributed to dilution/concentration effects. Data from a meteorological station on the highest peak of the study area (‘Cerro de Consuelo’, 3180 m a.s.l.) frequently showed a change of the prevailing wind direction from E to W during the drier periods at the end of the monitored years (P. Emck, Friedrich−Alexander−University Erlangen−Nürnberg, Germany, personal communication).

Elevated stream discharge during the moister periods between April to May and July to August and after rainstorms resulted in increased DOC concentrations in stream water of all three microcatchments (Figure 20b). Rainfall volumes and DOC concentrations in stream water seemed to be related. However, weekly rainfall volumes were not correlated with DOC concentrations of the same week in stream water. Therefore, I divided the data set into two subsets, one consisting of samples collected during weeks, in which rainstorms occurred at least three days before sampling, and the other representing non−storm conditions. Since rainfall volumes and DOC concentrations were not normally distributed, data were log−transformed for correlation analysis. There was a weak significant correlation between mean weekly rainfall volume and mean weekly DOC concentrations in stream

water under non−storm conditions (r= 0.40). Dissolved organic C concentrations in stream water during rainstorms were significantly higher than under non−storm conditions (Figure 21a).

Table 5: Annual volume−weighted mean concentrations (VWM; mg l^{-1}) 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 (SS−30) m mineral soil depth (where the flux is not known), flow−weighted mean concentrations in stream water (SW) and ranges of means in parentheses in an Ecuadorian lower montane forest between May 1999 and April 2002 (between May 2000 and April 2002 for RF at MC1 and MC3). Different letters indicate significant differences of the means between transects (Wilcoxon matched−pairs test, $p<0.01$). Literature values are given for reference.

	DOC							
	RF	TF	SF	LF	LL	SS−15	SS−30	SW
MC1	4.0	12c	15b	36b	35b	20b	12b	5.2b
	(4.0−4.1)	(12−13)	(14−17)	(32−43)	(29−41)	(18−22)	(11−13)	(4.1−6.9)
MC2.1	4.5	11d	14c	24c	37b	27a	15a	4.6c
	(3.8−5.9)	(9.9−13)	(13−16)	(20−31)	(35−38)	(27)	(15)	(4.0−5.7)
MC2.2	n.a.[a]	12c	n.a.	37abc	27c	7.2d	6.6c	n.a.
		(11−14)		(28−42)	(27−28)	(7.1−7.4)	(6.5−6.7)	
MC2.3	n.a.	15b	n.a.	40a	40ab	10c	6.3d	n.a.
		(13−17)		(39−44)	(37−50)	(9.5−11)	(6.1−6.8)	
MC3	4.5	17a	19a	28abc	55a	20b	14ab	5.6a
	(4.3−4.6)	(13−25)	(17−21)	(28−37)	(39−63)	(15−20)	(13−15)	(4.0−8.4)
Tropical forests								
	4.3 [7]	6.2 [4]	9.2 [1]	–	30 [2]	5 [6]	–	1.6−3.8 [1]
Temperate forests								
	1.1 [3]	2.7−60 [5]	–	–	20−90 [5]	–	2−35 (B horizon)[5]	–

[a]n.a.: not available. [1] Frangi & Lugo (1985), [2] Hafkenscheid (2000), [3] Likens et al. (1983), [4] McDowell (1998), [5] Michalzik et al. (2001), [6] Möller (2001), [7] Schrumpf (2004).

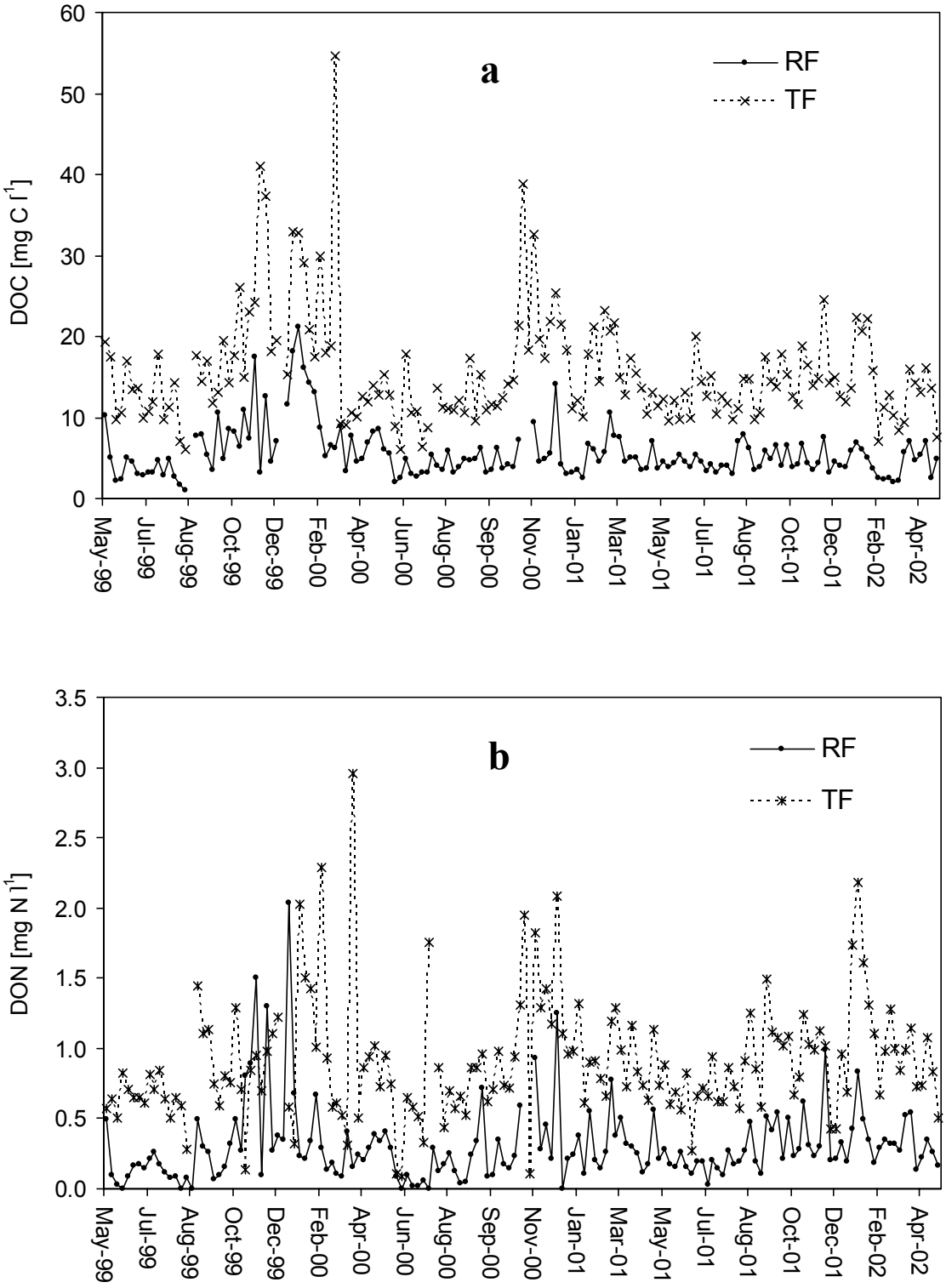

Figure 19: Temporal courses of mean weekly DOC (a) and DON (b) concentrations in rainfall (RF) and throughfall (TF) at three rainfall gauging sites and five study transects between May 1999 and April 2002.

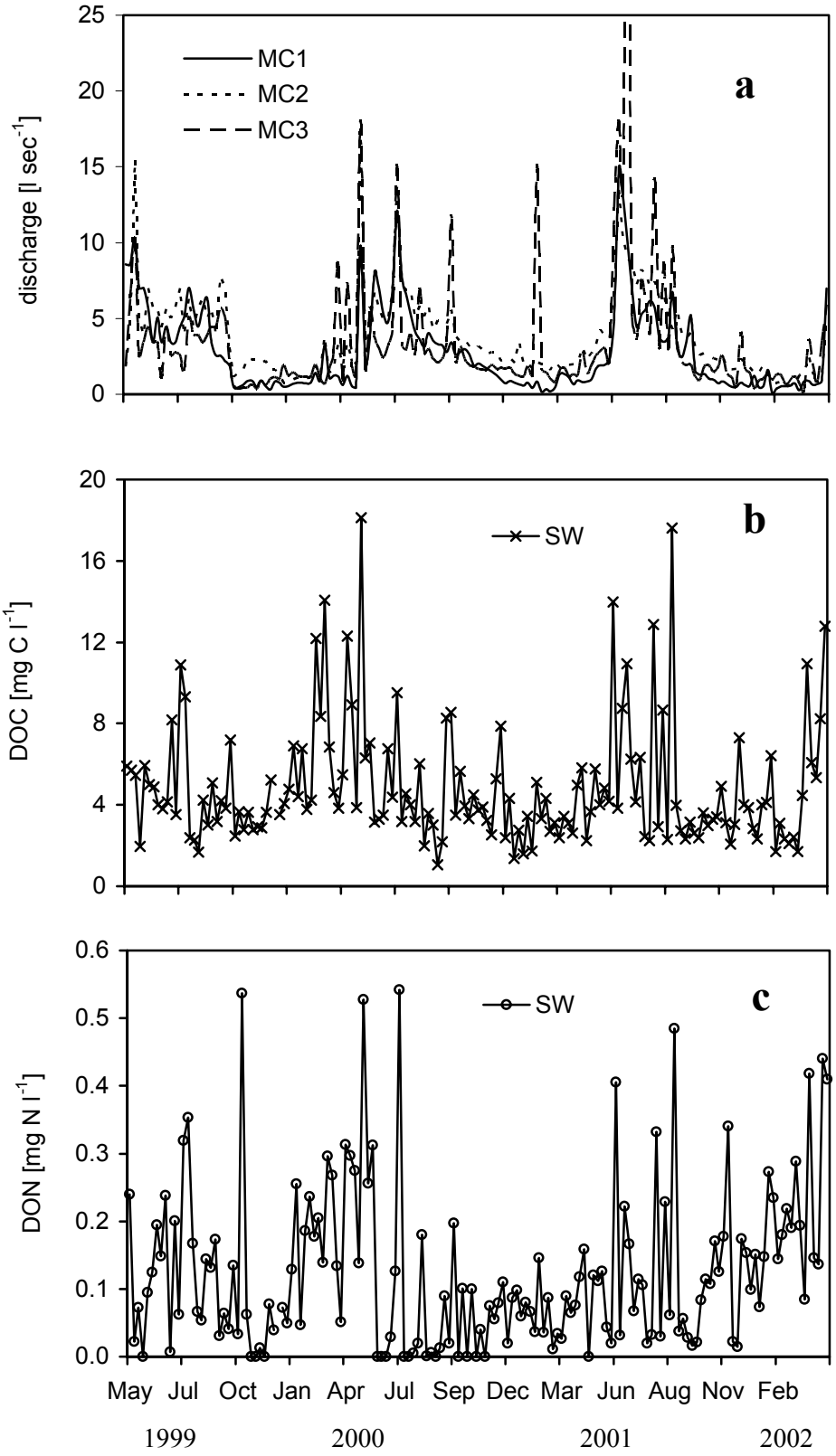

Figure 20a−c: Temporal courses of the discharge of three microcatchments and mean weekly DOC and DON concentrations in stream water between May 1999 and April 2002.

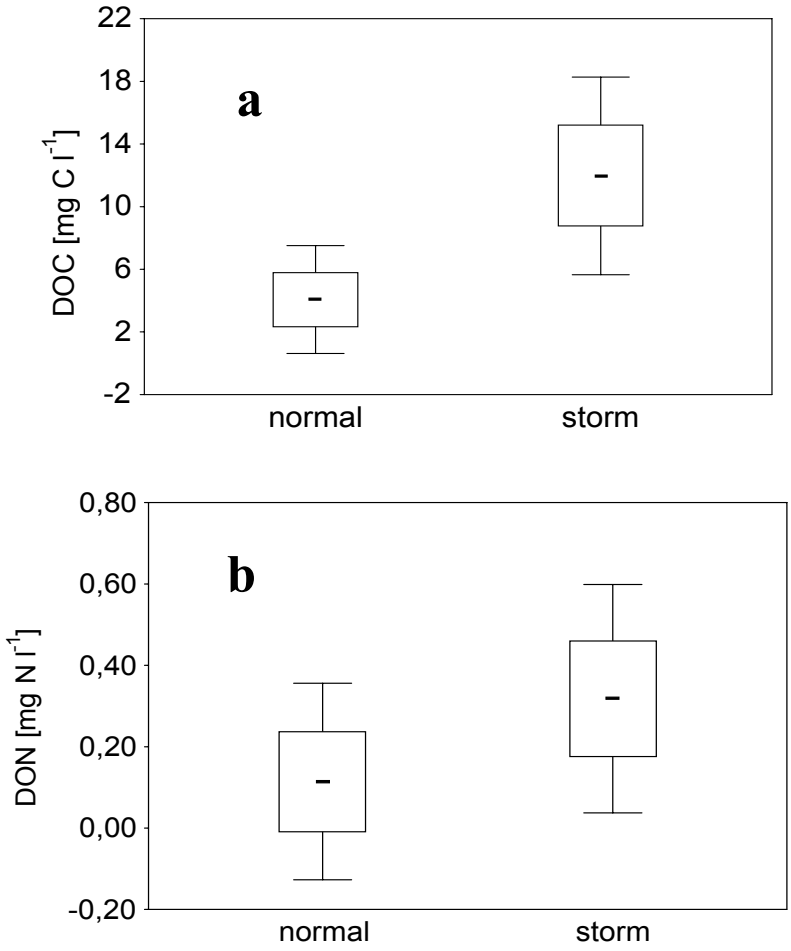

Figure 21: Mean (a) DOC and (b) DON concentrations in stream water of three microcatchments under non−storm ('normal') and storm conditions between May 1999 and April 2002. Whiskers represent ranges of 1.96 x standard deviation (S.D.), boxes ranges of 1 x S.D., and lines inside the boxes arithmetic means. (n_{storm} = 15, $n_{non-strom}$ = 141).

3.3.3 Dissolved organic nitrogen

The vertical distribution of mean annual DON concentrations was similar to that of the DOC concentrations at all five transects (Table 6). 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. Again, DON concentrations were highest in litter leachate except for transect MC2.2, where DON concentrations of lateral flow were highest.

Similar to DOC, the DON concentrations varied seasonally with higher weekly DON concentrations in rainfall and throughfall during the drier period between November and

Table 6: Annual volume−weighted mean concentrations (VWM; mg l^{-1}) 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 (SS−30) m mineral soil depth (where the total volume is not known), flow−weighted mean concentrations in stream water (SW) and ranges of means in parentheses in an Ecuadorian lower montane forest between May 1999 and April 2002 (between May 2000 and April 2002 for RF at MC1 and MC3). Different letters indicate significant differences of the means between transects (Wilcoxon matched−pairs test, $p<0.01$). Literature values are given for reference.

	RF	TF	SF	LF	LL	SS−15	SS−30	SW
				DON				
MC1	0.20a	0.67b	0.85b	1.9ab	2.0b	1.2a	0.80b	0.10b
	(0.16−0.24)	(0.59−0.74)	(0.77−0.90)	(1.8−2.2)	(1.8−2.5)	(1.1−1.4)	(0.79−0.81)	(0.09−0.12)
MC2.1	0.19b	0.57c	0.71c	1.0d	1.4c	0.87b	0.52c	0.14b
	(0.17−0.23)	(0.52−0.64)	(0.67−0.74)	(0.69−1.4)	(1.3−1.4)	(0.86−0.87)	(0.51−0.53)	(0.09−0.19)
MC2.2	n.a.[a]	0.62c	n.a.	1.4c	1.2d	0.39d	0.36d	n.a.
		(0.57−0.69)		(1.2−1.6)	(1.1−1.4)	(0.37−0.39)	(0.34−0.36)	
MC2.3	n.a.	0.70a	n.a.	2.1a	2.2b	0.55c	0.34d	n.a.
		(0.59−0.78)		(1.8−2.4)	(1.8−3.5)	(0.52−0.60)	(0.33−0.34)	
MC3	0.21a	0.89a	1.0a	1.5b	2.9a	1.3a	0.94a	0.21a
	(0.21−0.22)	(0.76−1.1)	(0.97−1.1)	(1.2−1.9)	(2.0−3.4)	(1.1−1.4)	(0.84−1.1)	(0.12−0.28)
Tropical forests								
	0.0−0.4 [1] 0.21 [8]	0.45 [8]	–	–	1.1 [2]	0.25 [7]	–	0.15 [3]
Temperate forests								
	0.17 [6]	0.25−1.1 [5]	–	–	0.4−2.5 [5]	–	0.2−1.1 (B horizon) [5]	0.05 [4]
				TDN				
MC1	0.40	1.5	1.6	2.8	3.1	1.5	1.0	0.36
	(0.33−0.48)	(1.3−1.8)	(1.3−1.9)	(2.4−3.1)	(2.5−3.8)	(1.4−1.8)	(1.0−1.1)	(0.26−0.45)
MC2.1	0.39	1.0	1.2	1.4	2.0	0.99	0.60	0.34
	(0.33−0.46)	(0.94−1.1)	(1.0−1.3)	(1.0−1.9)	(1.9−2.1)	(0.93−1.0)	(0.59−0.63)	(0.21−0.42)
MC2.2	n.a.	1.0	n.a.	2.3	1.9	1.5	1.3	n.a.
		(0.95−1.1)		(2.2−2.4)	(1.7−2.1)	(1.4−2.0)	(1.1−1.7)	
MC2.3	n.a.	1.4	n.a.	3.2	4.5	1.0	1.1	n.a.
		(1.3−1.5)		(2.7−4.6)	(2.6−5.9)	(0.95−1.3)	(0.94−1.2)	
MC3	0.48	1.8	2.0	3.6	5.3	2.3	1.9	0.39
	(0.45−0.50)	(1.6−2.1)	(1.9−2.1)	(3.0−4.4)	(4.6−5.9)	(1.8−3.5)	(1.5−2.8)	(0.28−0.48)

[a]n.a.: not available. [1] Eklund et al. (1997), [2] Hafkenscheid (2000), [3] Hedin et al. (1995), [4] McDowell & Asbury (1994), [5] Michalzik et al. (2001), [6] Michalzik & Matzner (1999), [7] Möller (2001), [8] Schrumpf (2004).

January (Figure 19b). Based on the variations in DON/Cl ratios (data not shown) and the lack of correlation between the volume and DON concentrations of rainfall ($r<0.1$) dilution/concentration effects could again be ruled out. There was no correlation between weekly rainfall volumes and DON concentrations in stream water even if the subsets for storm and non−storm conditions were evaluated separately.

Dissolved organic N concentrations in stream water increased during moister periods and rainstorms paralleling those of DOC (Figure 20). Mean DON concentrations in stream water were significantly different between the storm and non−storm subsets (Figure 21b).

In contrast to DOC, DON concentrations in soil solutions were related to soil moisture. 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 22a). During dry periods weekly DON concentrations in litter leachate and in mineral soil solutions were low (Figure 22b). Periods with strongly decreased DON concentrations in litter leachate were short, normally lasting one week to at most three 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 (Figure 22a). 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 after drier periods, e.g. on 20 September, 22 November, and 27 December 2000, on 23 May, 10 October, 26 December 2001, and on 23 January and 27 February 2002 (Figure 22b).

Although there was no correlation between pH and DON concentrations in the soil solution, the transects with the more acid soils, MC2.1 (median pH 4.21 in mineral soil solution at 0.15 depth), MC2.2 (4.51), MC2.3 (4.96) showed the lowest DON concentrations in mineral soil solution at 0.15 m depth and the transect with the least acid soil, MC3 (6.24) the highest (Table 6). Similar results were found for the litter leachate having lowest DON concentrations on transects MC2.1 (median pH 4.75) and MC2.2 (5.95) and highest on

transect MC3 (6.60, Table 6). Most differences in DON concentrations of the various soil solutions among the transects were significant (Table 6). The annual volume−weighted mean (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.

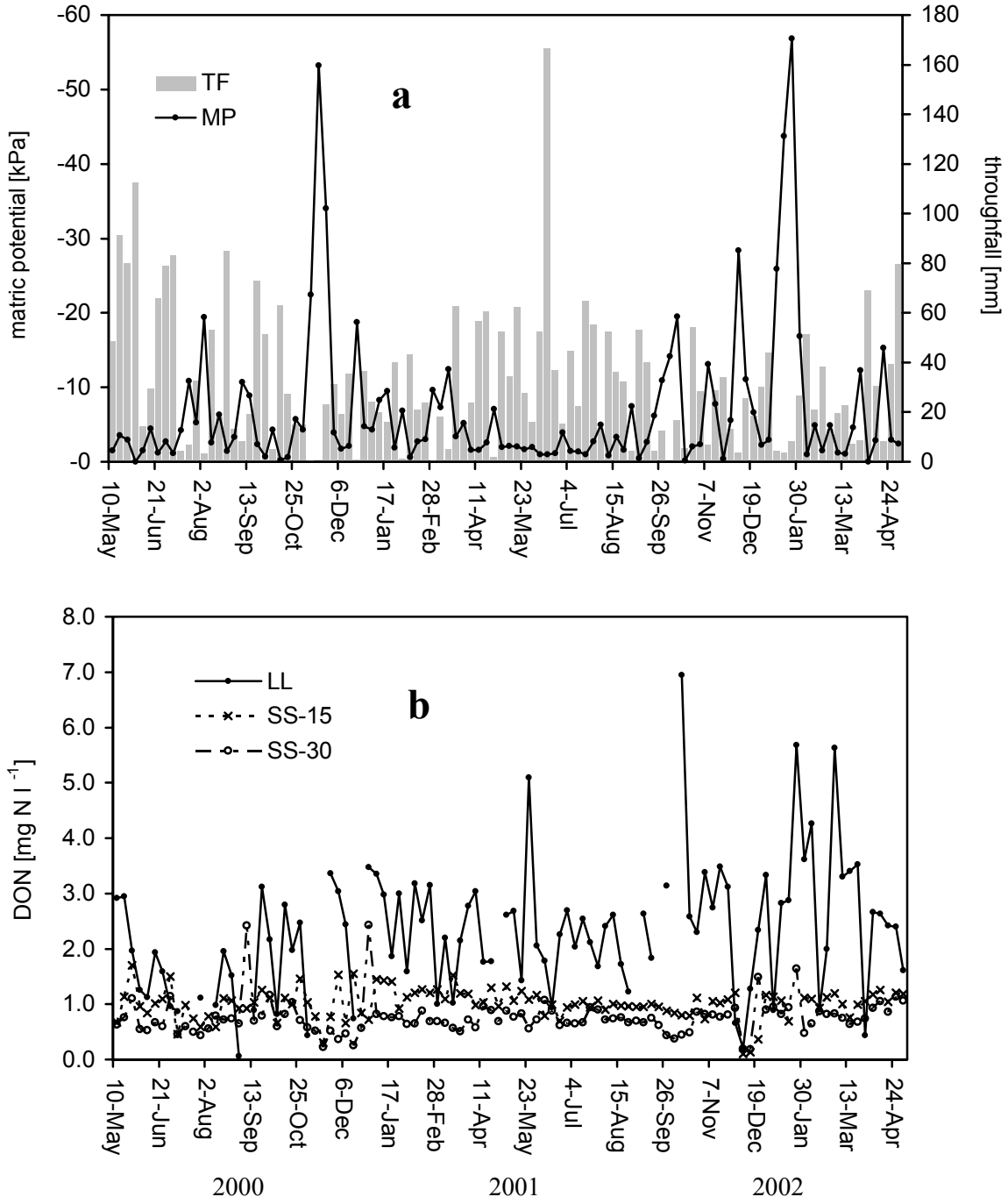

Figure 22: (a) Temporal courses of mean weekly throughfall (TF) and matric potentials (MP) and (b) of mean weekly DON concentrations in litter leachate (LL) and mineral soil solutions at 0.15 (SS−15) and 0.30 (SS−30) m depth at five study transects between May 2000 and April 2002.

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 7).

Table 7: 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 (SS−30) m 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. Values in parentheses indicate ranges of annual mean DON contributions.

	RF	TF	SF	LF	LL	SS−15	SS−30	SW
				DON contribution (%)				
MC1	50	45	52	70	66	82	77	29
	(48−51)	(40−49)	(48−61)	(71−76)	(65−72)	(82)	(75−78)	(23−33)
MC2.1	50	55	60	74	68	88	88	41
	(48−51)	(52−57)	(56−66)	(69−72)	(64−74)	(85−93)	(81−91)	(35−46)
MC2.2	n.a.[a]	59	n.a.	62	61	26	27	n.a.
		(53−64)		(54−66)	(58−69)	(19−28)	(22−30)	
MC2.3	n.a.	49	n.a.	65	50	54	32	n.a.
		(45−53)		(52−67)	(47−71)	(40−63)	(29−35)	
MC3	45	51	52	42	55	57	49	53
	(41−49)	(47−53)	(49−53)	(33−47)	(44−58)	(32−78)	(30−70)	(45−66)
				DOP contribution (%)				
MC1	n.d.[b]	5	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.[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	18	100	n.d.	n.d.	n.d.
				DOS contribution (%)				
MC 1	n.d.	58	59	78	94	39	47	8
MC2.1	n.d.	51	74	76	62	38	30	20
MC2.2	n.a.	91	n.a.	94	83	8	15	n.a.
MC2.3	n.a.	67	n.a.	85	50	37	23	n.a.
MC3	n.d.	61	82	88	100	35	27	26

[a]n.a.: not available, [b]n.d.: not detected.

Temporal variations in DON contributions during the three−year period were small in all ecosystem fluxes at all five transects with coefficients of variance (C.V.) ranging between 1 and 30 %, except for the mineral soil solutions at 0.15 and 0.30 m depth on transect MC3, which showed a greater variation between May 2000 and April 2002 (C.V.: 58 %).

3.3.4 Dissolved organic phosphorus and sulfur

Since dissolved concentrations of P in rainfall, mineral soil solution, and stream water and S in rainfall were often below the detecton limits of the analytical methods (see chapter 2), the concentrations of dissolved organic forms were not calculated in these fluxes. However, annual means of TDP and TDS are presented in spite of their uncertainty to illustrate concentration trends during the passage of water through the ecosystem.

The vertical ecosystem profile of mean annual DOP concentrations was slightly different from that of DON and DOC (Table 8). Litter leachate had the highest DOP concentrations in the superficial water fluxes. Stemflow had higher DOP concentrations than throughfall and litterfall, which had similar DOP concentrations. During the passage through the mineral soil to the stream, TDP concentrations decreased. Mean TDP concentrations were extremely low in rainfall mineral soil solutions (Table 8). Mean annual DOS concentrations paralleled those of DOC and DON (Table 5 and 6, respectively).

There was no correlation between soil moisture and DOP and DOS concentrations. This might be attributable to the small number of samples because DOP and DOS analyses were only performed on the monthly bulked samples of one year.

Similar to DON, mean concentrations of TDP and DOS were lowest in litter leachate of the more acid transects MC2.1, MC2.2, and MC2.3 and highest in litter leachate of the least acid transect MC3 (Table 8 and 9) although for the individual soil solutions there was no correlation between pH and TDP or DOS concentrations. Most differences among the transects were significant. Spatial variations in the concentrations of DOP (C.V.: 108−346 %) and DOS (46−346 %) to their respective total concentrations between the transects were higher than for DON (27−202 %).

Annual means of DOP contributions to TDP increased, on the average of all five transects, in the order throughfall (40 %)<stemflow (41 %)<lateral flow (60 %)<litter leachate

(97 %) with high variations between the five study transects in throughfall (range: 5−84 %) and lateral flow (18−100 %, Table 7). Annual means of DOS contributions to TDS increased, on the average of all five transects, in the order throughfall (66 %)<stemflow (mean 71 %)<litter leachate (mean 78 %)<lateral flow (mean 84 %). In the mineral soil and the stream water, portions of DOS were markedly lower with similar means between the two studied soil depths (31 % at 0.15 and 28 % at 0.30 m) and smallest organic fractions in stream water (mean 18 %, Table 7).

Table 8: Annual mean concentrations (mg l^{-1}) of DOP 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 in stream water (SW) in an Ecuadorian lower montane forest between May 2000 and April 2001. Standard deviation (S.D.) represents the spatial variation between the five study transects. Literature values are given for reference.

	RF	TF	SF	LF	LL	SS−15	SS−30	SW
				DOP				
MC1	n.d.[a]	0.03	0.30	0.10	0.36	n.d.	n.d.	n.d.
MC2.1	n.d.	0.10	0.13	0.15	0.02	n.d.	n.d.	n.d.
MC2.2	n.a.[b]	0.30	n.a.	0.09	0.21	n.d.	n.d.	n.a.
MC2.3	n.a.	0.11	n.a.	0.16	n.d.	n.d.	n.d.	n.a.
MC3	n.d.	0.15	0.57	0.08	2.20	n.d.	n.d.	n.d.
mean	−	0.14	0.33	0.12	0.70	−	−	−
S.D.	−	0.10	0.22	0.04	1.01	−	−	−
Literature					0.06 [1] 0.03−0.20 [2]			
				TDP				
MC 1	0.00	0.58	0.82	0.21	0.41	0.00	0.03	0.00
MC2.1	0.00	0.16	0.28	0.15	0.02	0.07	0.02	0.00
MC2.2	n.a.	0.36	n.a.	0.12	0.21	0.00	0.02	n.a.
MC2.3	n.a.	0.37	n.a.	0.26	n.d.	0.00	0.01	n.a.
MC3	0.02	0.88	1.5	0.43	2.2	0.01	0.06	0.01

[a]n.d.: not detected, [b]n.a.: not available. [1] Hafkenscheid (2000) tropical forest, [2] Kaiser et al. (2000) temperate forest.

Table 9: Annual mean concentrations (mg l^{-1}) of DOS 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. Standard deviation (S.D.) represents the spatial variation between the five study transects. Literature values are given for reference.

	RF	TF	SF	LF	LL	SS−15	SS−30	SW
				DOS				
MC1	n.d.[a]	0.17	0.38	0.52	0.90	0.20	0.16	0.01
MC2.1	n.d.	0.11	0.25	0.31	0.37	0.33	0.12	0.01
MC2.2	n.a.[b]	0.23	n.a.	0.32	0.55	0.03	0.07	n.a.
MC2.3	n.a.	0.18	n.a.	0.80	0.70	0.11	0.07	n.a.
MC3	n.d.	0.28	0.63	0.56	2.0	0.46	0.25	0.01
mean	−	0.19	0.42	0.50	0.90	0.23	0.13	0.01
S.D.	−	0.06	0.19	0.20	0.63	0.17	0.07	0.00
Literature					0.05−1.4 [1]	0.13−0.15 [3]	0.28 (B horizon)[2]	
				TDS				
MC1	0.02	0.30	0.66	0.66	0.96	0.51	0.34	0.15
MC2.1	0.01	0.22	0.34	0.41	0.60	0.87	0.41	0.04
MC2.2	n.a.	0.26	n.a.	0.34	0.66	0.38	0.49	n.a.
MC2.3	n.a.	0.26	n.a.	0.94	1.4	0.30	0.31	n.a.
MC3	0.07	0.45	0.77	0.65	2.0	1.3	0.90	0.05

[a]n.d.: not detected, [b]n.a.: not available. [1] Homann (1990), [2] Houle et al. (2001), [3] Kaiser & Guggenberger (2003).

3.3.5 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 on transects MC1 (r= 0.97, n=6), MC2.1 (r=0.94, n=6), and MC3 (r=0.92, n=8) and litter leachate on 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 (Figure 23a−c).

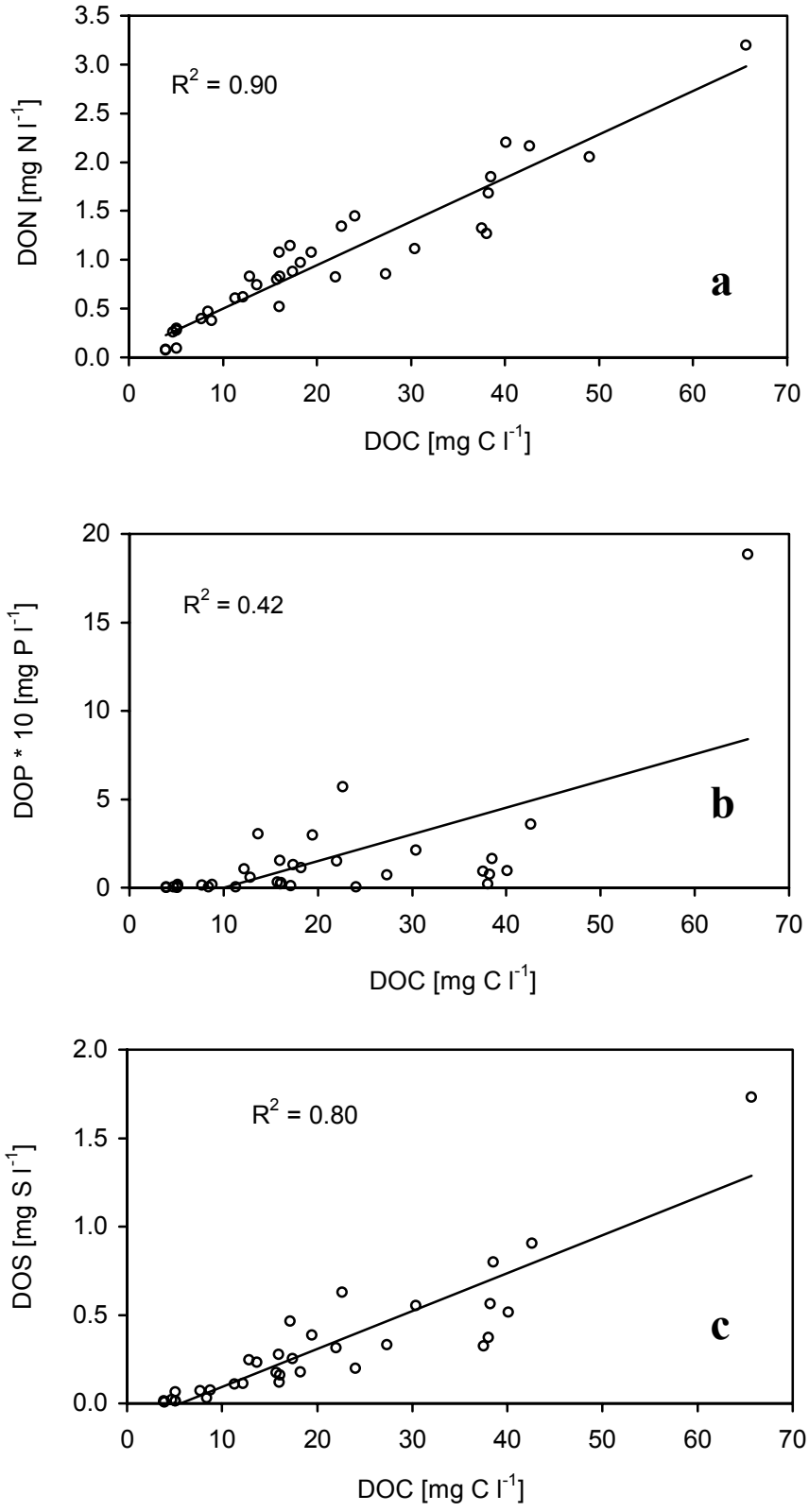

Figure 23: Relations between annual mean concentrations of DOC and of (a) DON, (b) DOP, and (c) DOS in the ecosystem fluxes of all transects between May 1999 and April 2002 (n = 34 for DOC and 33 for each of DON, DOP, and DOS).

3.4 Dissolved inorganic nitrogen, phosphorus, and sulfur

3.4.1 Dissolved inorganic nitrogen concentrations

The annual volume−weighted mean (VWM) NH_4−N and NO_3−N concentrations at the five study transects showed a similar vertical distribution across the study forest during the three hydrological years. Annual VWM NH_4−N and NO_3−N concentrations were low in rainfall, mineral soil solutions, except for NO_3−N, and stream water and distinctly higher in the aboveground fluxes (throughfall, stemflow, lateral flow, and litter leachate) with highest concentrations in the organic layer (Table 10).

Spatial variations of annual VWM NH_4−N concentrations between the transects were small in all ecosystem fluxes (coefficients of variation (C.V.): 4−40 %). In contrast, annual VWM NO_3−N concentrations showed considerable variations in the aboveground fluxes (C.V.: 43 % in throughfall, 48 % in stemflow, 73 % in lateral flow, and 76 % in litter leachate) and particularly in the mineral soil solutions (C.V.: 98 % at 0.15 and 84 % at 0.30 m depth).

Although the weekly NO_3−N concentrations in lateral flow and litter leachate were not correlated with the pH, the transects with the more acid organic layer solutions, MC2.1 (median pH 5.39 in lateral flow and 4.75 in litter leachate) and MC2.2 (median pH 5.13 in lateral flow and 5.95 in litter leachate) had the lowest annual VWM NO_3−N concentrations and the transect with the least acid organic layer solutions, MC3 (6.72 and 6.60) the highest (Table 10). The mineral soil solutions also had lowest VWM NO_3−N concentrations at the most acid transect MC2.1 (median pH 4.21 at 0.15 and 4.42 at 0.30 m depth), but highest VWM NO_3−N concentrations on transect MC2.2 (4.51 at 0.15 and 4.61 at 0.30 m depth). Most differences in VWM NO_3−N concentrations among the transects were significant. The VWM NH_4−N did not differ significantly among the transects. Annual VWM NH_4−N concentrations in all ecosystem fluxes varied less among the three monitored years than those of NO_3−N (see ranges in Table 10).

During the three monitored years, the mean weekly NO_3−N concentrations in rainfall and throughfall were considerably higher in the drier period between November and Janu-

ary (Figures 24a−b). The mean weekly NO_3−N concentrations in rainfall and throughfall increased by about 10 times from low values during the wetter to strongly elevated values during the drier periods. The findings that there was no correlation between weekly rainfall volume and NO_3−N concentrations in rainfall and that the NO_3−N /Cl ratios in rainfall were not constant (data not shown) indicated that concentration/dilution effects because of reduced rainfall were not responsible for the detected NO_3−N variations in rainfall.

Table 10: Three−year means of annual volume−weighted mean concentrations (VWM; mg l^{-1}) of NH_4−N and NO_3−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 (SS−30) m mineral soil depth (where the total volume is not known), flow−weighted mean concentrations in stream water (SW) and ranges (of annual means) in parentheses in an Ecuadorian lower montane forest between May 1999 and April 2002 (except for SS and partly RF, between May 2000 and April 2002). S.D. is the standard deviation of the arithmetric mean of five transects or three microcatchments, respectively. 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.

	NH_4−N							
	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
	(0.10−0.12)	(0.21−0.26)	(0.23−0.33)	(0.16−0.26)	(0.15−0.26)	(0.06−0.08)	(0.05−0.07)	(0.09−0.16)
MC2.1	0.11	0.23	0.26	0.13	0.12	0.05	0.05	0.15
	(0.10−0.11)	(0.17−0.29)	(0.20−0.29)	(0.09−0.15)	(0.11−0.18)	(0.05−0.06)	(0.04−0.05)	(0.11−0.21)
MC2.2	n.a.[a]	0.21	n.a.	0.18	0.14	0.05	0.05	n.a.
		(0.18−0.23)		(0.15−0.30)	(0.13−0.16)	(0.05)	(0.04−0.06)	
MC2.3	n.a.	0.24	n.a.	0.22	0.33	0.05	0.05	n.a.
		(0.21−0.27)		(0.15−0.33)	(0.21−0.36)	(0.05−0.06)	(0.05−0.06)	
MC3	0.11	0.32	0.33	0.36	0.27	0.08	0.07	0.13
	(0.10−0.12)	(0.22−0.46)	(0.32−0.34)	(0.26−0.47)	(0.18−0.30)	(0.06−0.11)	(0.06−0.07)	(0.08−0.18)
mean	0.11	0.25	0.29	0.22	0.22	0.06	0.05	0.13
S.D.	0.00	0.04	0.04	0.08	0.09	0.01	0.01	0.02
Tropical montane forests								
	0.05[1] – 0.86[2]	0.07[1] – 1.16[2]			0.1−0.2[3]	0.03−0.04[6]	0.02−0.04[6]	0.01[5]
					0.27[6]		0.82[5] (40 cm)	0.05−0.06[6]

	NO_3−N							
	RF	TF	SF	LF	LL	SS−15	SS−30	SW
MC1	0.10a	0.61a	0.50b	0.42b	0.45bc	0.06c	0.10c	0.16a
	(0.08−0.12)	(0.47−0.84)	(0.27−0.66)	(0.28−0.60)	(0.41−0.73)	(0.05−0.10)	(0.05−0.15)	(0.11−0.19)
MC2.1	0.10b	0.24b	0.21c	0.10c	0.31d	0.00d	0.00d	0.08b
	(0.08−0.11)	(0.23−0.25)	(0.15−0.27)	(0.04−0.13)	(0.26−0.38)	(0.00−0.07)	(0.00−0.03)	(0.05−0.09)
MC2.2	n.a.	0.22b	n.a.	0.35b	0.41cd	1.0a	0.88a	n.a.
		(0.18−0.28)		(0.19−0.54)	(0.27−0.56)	(0.89−1.4)	(0.68−1.3)	
MC2.3	n.a.	0.48a	n.a.	0.55a	1.0b	0.41b	0.64b	n.a.
		(0.44−0.53)		(0.33−1.1)	(0.32−2.3)	(0.28−0.50)	(0.54−0.71)	
MC3	0.16a	0.54a	0.63a	1.1a	1.7a	0.70a	0.82ab	0.09b
	(0.13−0.19)	(0.51−0.60)	(0.57−0.68)	(0.80−1.9)	(1.6−1.8)	(0.26−2.3)	(0.28−1.8)	(0.07−0.11)
mean	0.12	0.42	0.45	0.50	0.78	0.44	0.49	0.11
S.D.	0.03	0.18	0.22	0.36	0.59	0.43	0.41	0.04
Tropical montane forests								
	0.05[1] – 0.11[4]	0.02[3] – 0.20[4]			0.0−0.2[3]	1.5[6]	1.4[6]	0.06[5]
					0.92[6]		0.02[5] (40 cm)	0.56−0.60[6]

[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 & Asbury (1994), Ultisol; [6]Schrumpf (2004), Andisol.

Mean weekly NH_4−N concentrations in rainfall and throughfall showed a slighty different course with increased concentrations during the drier, but also during the wettest periods of the three monitored years in May 2000 and June 2001 (Figures 24a−b).

The mean weekly NH_4−N and NO_3−N concentrations in litter leachate responded negatively to rainfall and positively to soil matric potential. 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 NH_4−N concentrations (Figures 25a−c).

The responses of the weekly NH_4−N and NO_3−N concentrations in the mineral soil solutions to moisture conditions were similar as in litter leachate. However, temporal variations were smaller than in the litter leachate (data not shown).

In stream water, the mean weekly NH_4−N concentrations increased from relatively constant values of about 0.1 mg l^{-1} during most part of the entire monitored period up to

0.8−1.5 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, NH_4−N concentration peaks were related to heavy rainstorm events (Figure 26c). The weekly NO_3−N concentrations in stream water were positively related to elevated catchment discharge during the wetter periods of the monitored years.

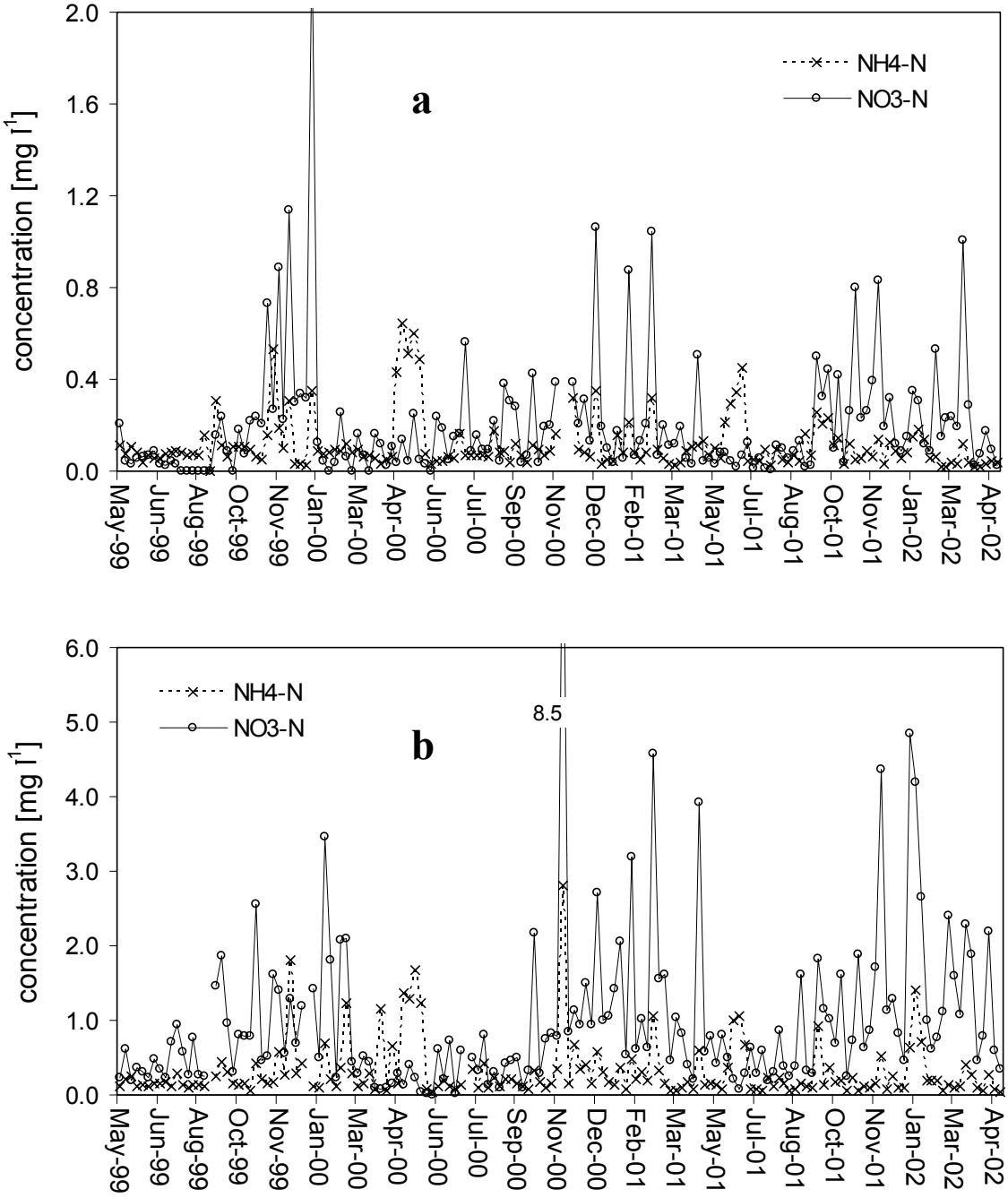

Figure 24a−b: Temporal courses of mean weekly NH_4−N and NO_3−N concentrations in (a) rainfall at three gauging sites and (b) throughfall at five study transects between May 1999 and April 2002.

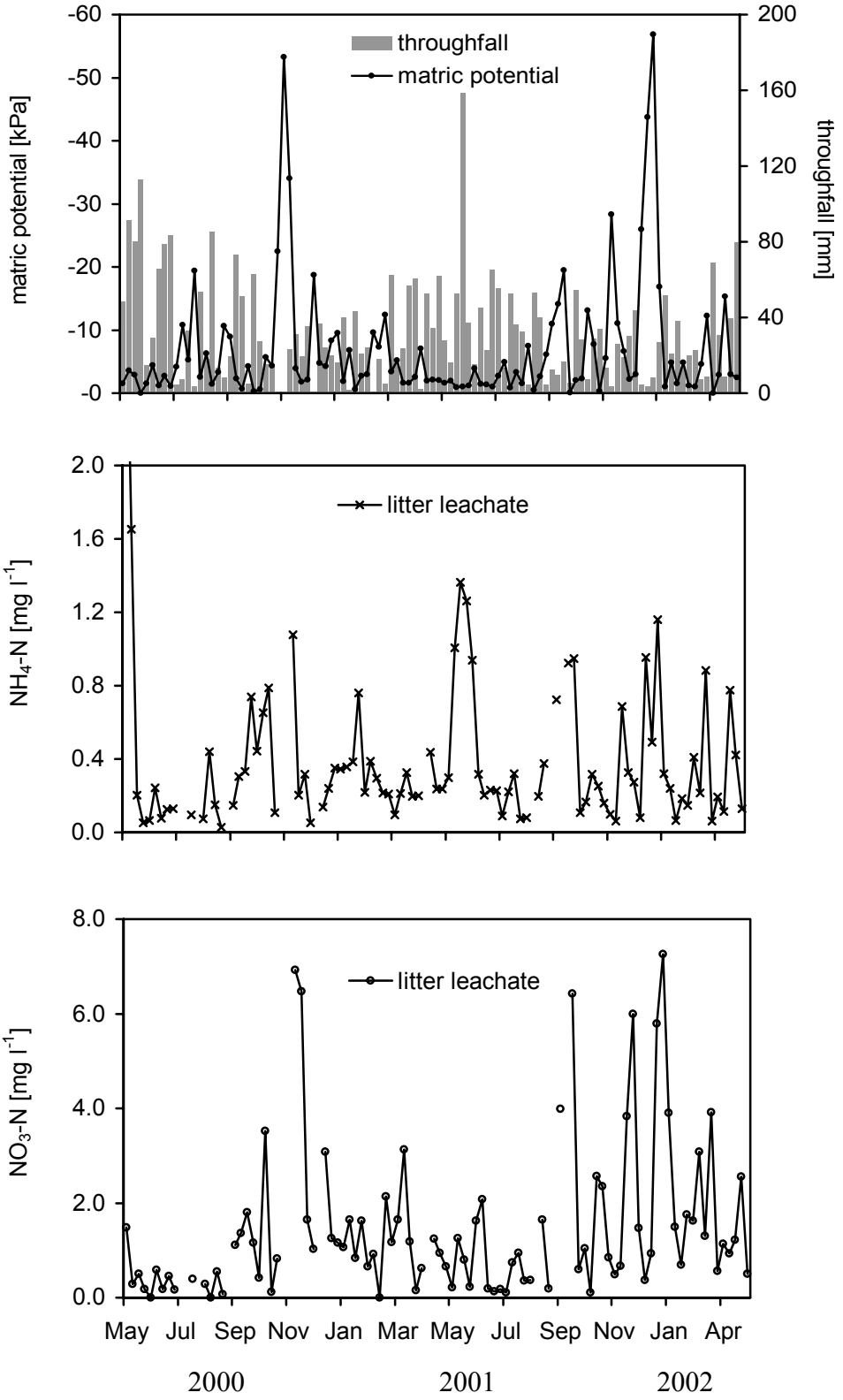

Figure 25a−c: (a) Temporal courses of mean weekly throughfall and matric potentials, (b) of mean weekly NH_4−N and (c) NO_3−N concentrations in litter leachate at five study transects between May 2000 and April 2002.

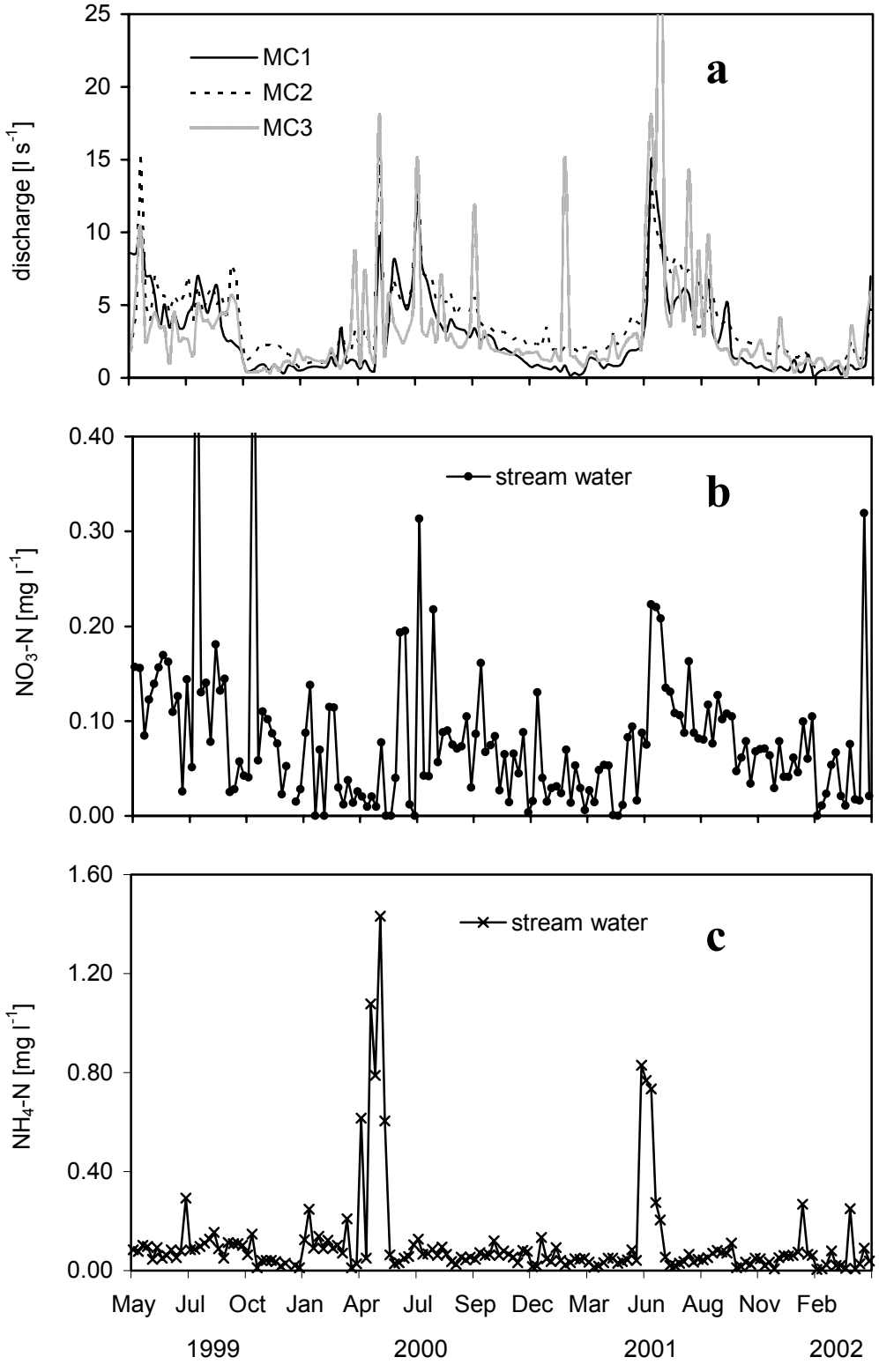

Figure 26a−c: (a) Temporal courses of the discharges of three microcatchments and mean weekly (b) NO_3−N and (c) NH_4−N concentrations in stream water between May 1999 and April 2002.

Although peakflow events following rainstorms were partly associated with increased NO_3−N 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 26b), no correlation existed between rainstorm events and increased NO_3−N concentrations. Furthermore, the three−year flow−weighted mean NO_3−N concentrations in stream water during baseflow were not significantly different from those during stormflow.

3.4.2 Dissolved inorganic phosphorus and sulphur concentrations

The patterns of mean annual DIP and DIS concentrations in an ecosystem profile through the study forest were different from those of DIN and totally contrasting between DIP and DIS. Mean annual DIP concentrations were extremely low in rainfall, mineral soil solutions, and stream water and distinctly higher in the aboveground fluxes with highest concentrations in throughfall and stemflow (Table 11). In contrast, mean annual DIS 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 DIS concentrations in stream water were similar to those of the aboveground ecosystem fluxes, the rainfall showed the lowest DIS concentrations of all ecosystem fluxes (Table 11).

During the monitored period, both mean monthly DIP and DIS concentrations in throughfall, stemflow, lateral flow, and litter leachate were highest in November 2000, the driest month of the monitored year (Figures 27 and 28). Monthly DIS concentrations in mineral soil solutions showed a continuous decline from high values during the wetter period between May and August 2000 to relatively constant values for the other part of the monitored period, whereas monthly DIS concentrations in stream water remained relatively stable during the entire monitored period (Figure 29). Furthermore, the mean monthly DIP and DIS concentrations in throughfall and stemflow showed a negative correlation with the respective water fluxes (Figure 30).

The mean monthly DIS concentrations in the mineral soil solutions of both studied soil depths were significantly positively correlated with monthly rainfall volume (0.15 m: r=0.77, 0.30 m: r=0.62). I could not determine, whether there is a relation between water fluxes and monthly DIP concentrations in the mineral soil solutions, because DIP concen-

trations were mostly near the detection limit of the analytical method. Similar to NO_3−N, mean annual DIP concentrations in throughfall, stemflow, lateral flow, and litter leachate were lowest at the most acid transects MC2.1 and MC2.2 and highest at the least acid transect MC3 (Table 11). However, I could not test, if differences between means were significant, since the number of valid data pairs was often not sufficient for statistical analysis. For DIS, a relationship between concentration and solution acidity was not found.

Table 11: Annual mean concentrations (mg l^{-1}) of DIP (PO_4−P) and DIS (SO_4−S) in rainfall (RF), throughfall (TF), stemflow (SF), and stream water (SW), median concentrations in lateral flow (LF), litter leachate (LL), and soil solutions at 0.15 (SS−15) and 0.30 (SS−30) m mineral soil depth (where the total volume is not known) in an Ecuadorian lower montane forest between May 2000 and April 2001. S.D. is the standard deviation of the arithmetric mean of five transects or three microcatchments, respectively. Literature values representing ranges of data summarized by Hafkenscheid (2000) are given for reference.

	PO_4−P							
	RF	TF	SF	LF	LL	SS−15	SS−30	SW
MC1	0.00	0.60	0.56	0.11	0.05	0.01	0.00	0.00
MC2.1	0.00	0.07	0.15	0.00	0.02	0.00	0.00	0.00
MC2.2	n.a.[a]	0.06	n.a.	0.03	0.01	0.01	0.00	n.a.
MC2.3	n.a	0.28	n.a.	0.20	n.a.	0.00	0.00	n.a.
MC3	0.04	0.73	0.97	0.47	0.32	0.00	0.00	0.03
mean	0.01	0.35	0.56	0.16	0.10	0.00	0.00	0.01
S.D.	0.02	0.30	0.41	0.19	0.15	0.01	0.00	0.02
Tropical montane forests								
	0.002[1] – 0.034[2]	0.004[4] – 0.090[2]						0.002[6] (TDP)
	SO_4−S							
	RF	TF	SF	LF	LL	SS−15	SS−30	SW
MC1	0.00	0.14	0.29	0.14	0.05	0.32	0.20	0.24
MC2.1	0.00	0.11	0.10	0.17	0.23	0.54	0.32	0.14
MC2.2	n.a.	0.02	n.a.	0.02	0.11	0.45	0.52	n.a.
MC2.3	n.a.	0.09	n.a.	0.26	n.a.	0.21	0.29	n.a.
MC3	0.08	0.18	0.16	0.08	0.42	0.88	0.77	0.18
mean	0.03	0.11	0.18	0.13	0.20	0.48	0.42	0.19
S.D.	0.05	0.06	0.09	0.09	0.16	0.26	0.23	0.05
Tropical montane forests								
	0.14[3] – 1.51[4]	0.28[5] – 2.67[2]						0.78[6]

[a] n.a.: not available; [1] Clark et al. (1998), [2] Veneklaas (1990), [3] Hafkenscheid (2000), [4] Asbury et al. (1994), [5] Cavelier et al. (1997), [6] McDowell & Asbury (1994).

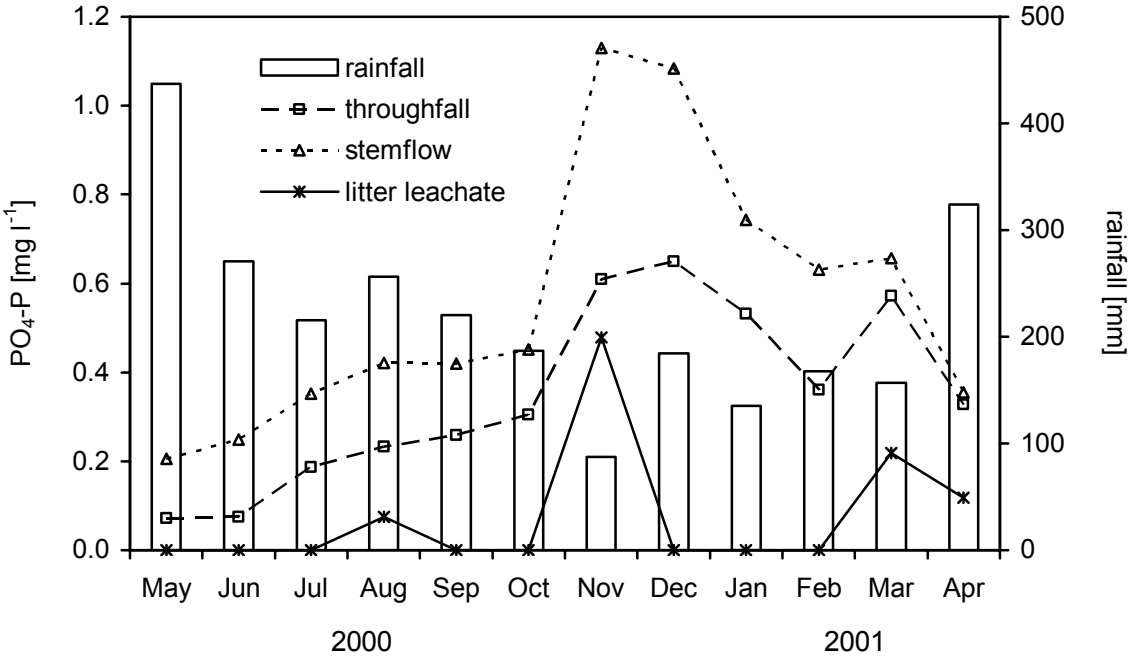

Figure 27: Monthly rainfall volumes at three gauging sites and courses of mean monthly PO_4−P concentrations in throughfall, stemflow, and litter leachate at five study transects between May 2000 and April 2001.

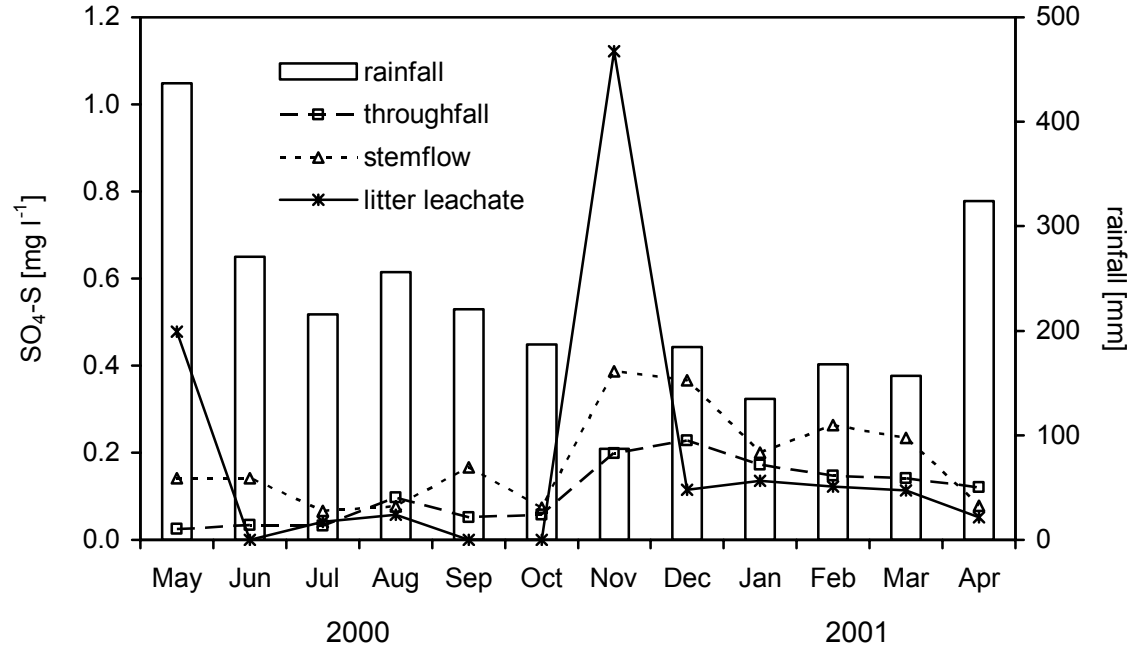

Figure 28: Monthly rainfall volumes at three gauging sites and courses of mean monthly SO_4−S concentrations in throughfall, stemflow, and litter leachate at five study transects, and stream water of three microcatchments between May 2000 and April 2001.

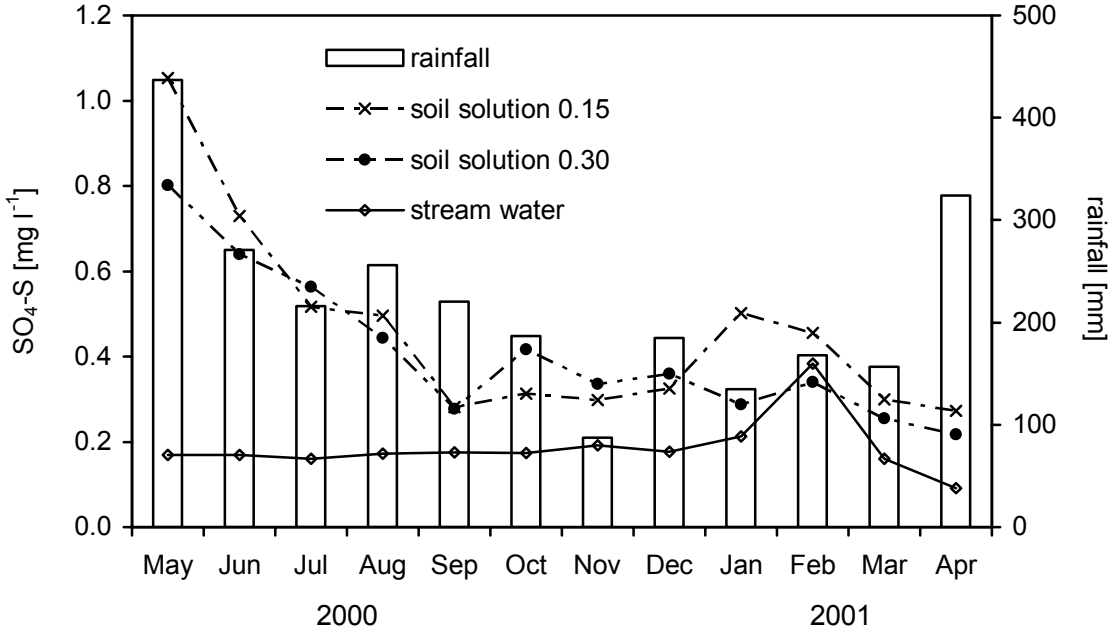

Figure 29: Monthly rainfall volumes at three gauging sites and courses of mean monthly SO_4−S concentrations in mineral soil solutions at 0.15 and 0.30 m depth at five study transects, and stream water of three microcatchments between May 2000 and April 2001.

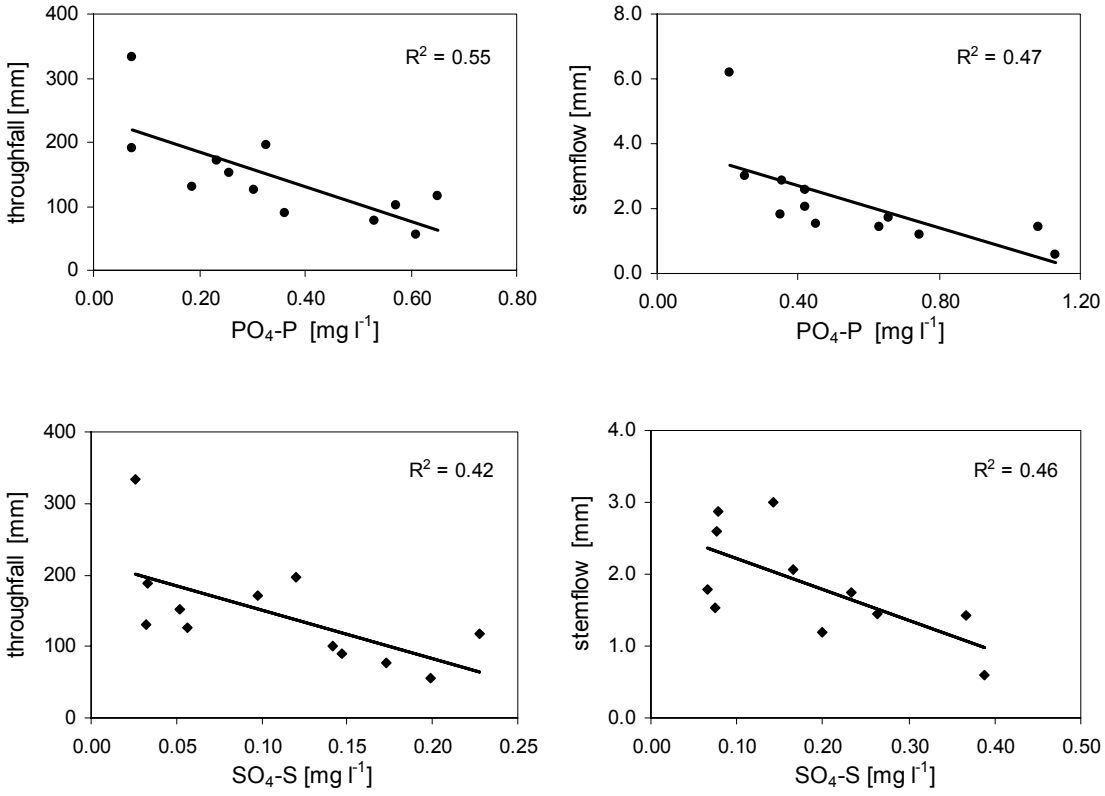

Figure 30: Relationships between monthly throughfall and stemflow volumes and monthly PO_4−P and SO_4−S concentrations in throughfall and stemflow between May 2000 and April 2001.

3.4.3 Dissolved inorganic nitrogen, phosphorus, and sulphur fluxes

The throughfall deposition of DIN, DIP, and DIS was always higher than the rainfall deposition. Hence, the net throughfall deposition, i.e. throughfall + stemflow - rainfall deposition, was positive and deposition ratios, i.e. (throughfall + stemflow)/rainfall deposition, greater than 1 (Tables 12 and 13). The throughfall showed the highest annual N, P, and S fluxes of all studied ecosystem fluxes, except that the highest DIS fluxes occurred in the streams of MC1 and MC2. Although N, P, and S concentrations were high in stemflow, especially for P, the total nutrient flux was small compared to the nutrient fluxes in throughfall (Tables 12 and 13) owing to the low water flux via stemflow, which comprised 1.0 % of the rainfall in the study forest.

I correlated the weekly and monthly rainfall amounts with the weekly and monthly net deposition rates, respectively, in order to evaluate the relative importance of element leaching from the canopy for throughfall enhancement but did not detect any significant correlation.

The output fluxes of DIN and DIP and of DIS in microcatchment MC3 were at least by a factor of 2 lower than the element input via wet deposition. The annual DIS exports from microcatchments MC1 and MC2 were higher than the throughfall + stemflow deposition, i.e. the total nutrient input to the forest floor (Table 12 and 13).

Table 12. Three−year means and ranges of annual means in parentheses of DIN fluxes in rainfall (RF), throughfall (TF), stemflow (SF), and stream water (SW), net throughfall deposition ([TF+SF]-RF deposition), and deposition ratios ([TF+SF]/RF deposition) in an Ecuadorian lower montane rain forest between May 1999 and April 2002. Values are kg ha^{-1} a^{-1}. S.D. is the standard deviation of the arithmetic mean of five transects or three microcatchments, respectively. Literature values representing ranges of data of tropical montane forests summarized by Hafkenscheid (2000) are given for reference.

	RF	TF	SF	SW	Net throughfall deposition	Deposition ratio
			NH_4−N			
MC1	2.9	3.1	0.1	1.1	0.3	1.1
	(2.7−3.1)	(2.3−3.8)	(0.1)	(0.9−1.2)		
MC2.1	2.5	3.4	0.1	1.9	1.0	1.4
	(2.3−2.7)	(2.8−4.2)	(0.1)	(1.2−2.8)		
MC2.2	2.5	3.3	0.1	n.a[a]	0.8	1.3
		(2.8−3.7)				
MC2.3	2.5	3.9	0.1	n.a	1.5	1.6
		(3.2−4.8)				
MC3	3.1	5.2	0.1	1.0	2.2	1.7
	(2.7−3.4)	(4.3−6.6)	(0.1)	(1.0−2.4)		
mean	2.8	3.8	0.1	1.4	1.2	1.4
S.D.	0.3	0.9	0.0	0.5	1.0	0.3
Tropical montane forests	<3.9[3]−18.1[2]	1.3[1]−21.5[2]		1[6]−1.7[3]	−3.5[4]−3.2[2]	0.6[4]−1.2[3]
			NO_3−N			
MC1	2.7	8.4	0.1	1.5	5.9	3.2
	(2.2−3.1)	(5.1−12)	(0.1−0.2)	(1.1−1.8)		
MC2.1	2.2	3.6	0.1	0.9	1.4	1.6
	(2.1−2.4)	(3.3−4.0)	(0−0.2)	(0.6−1.2)		
MC2.2	2.2	3.5	0.1	n.a	1.3	1.6
		(2.3−4.6)				
MC2.3	2.2	7.9	0.1	n.a	5.7	3.5
		(6.2−9.5)				
MC3	4.2	9.2	0.1	0.7	5.1	2.2
	(3.3−5.1)	(7.5−10)	(0.1−0.2)	(0.6−0.9)		
mean	3.0	6.5	0.1	1.1	4.1	2.4
S.D.	1.0	2.7	0.0	0.4	2.4	0.8
Tropical montane forests	1.7[1]−5.3[4]	0.6[1]		3.0[3]−14[6]	−1.4[3]−5.8[4]	0.3[3]−1.6[4]

[a] n.a.: not available; [1] Clark et al. (1998), [2] Veneklaas (1990), [3] Hafkenscheid (2000), [4] Asbury et al. (1994), [5] Cavelier et al. (1997), [6] Bruijnzeel et al. (1993).

Table 13: Annual fluxes of DIP (PO_4−P) and DIS (SO_4−S) in rainfall (RF), throughfall (TF), stemflow (SF), and stream water (SW), net throughfall deposition ([TF+SF]-RF deposition), and deposition ratios ([TF+SF]/RF deposition) in an Ecuadorian lower montane rain forest between May 2000 and April 2001. Values are kg ha^{-1} a^{-1}. S.D. is the standard deviation of the arithmetic mean of five transects or three microcatchments, respectively. Literature values representing ranges of data of tropical montane forests summarized by Hafkenscheid (2000), except for SO_4−S in SW, are given for reference.

	RF	TF	SF	SW	Net throughfall deposition	Deposition ratio
			PO_4−P			
MC1	0.00	7.0	0.10	0.00	7.1	n.c.[b]
MC2.1	0.00	0.67	0.03	0.00	0.70	n.c.
MC2.2	0.00	0.81	0.03	n.a.[a]	0.84	n.c.
MC2.3	0.00	3.6	0.03	n.a.	3.7	n.c.
MC3	0.91	12	0.16	0.15	11	13
mean	0.30	4.8	0.10	0.05	4.7	−
S.D.	0.52	4.7	0.07	0.09	4.4	−
Tropical montane forests	0.05[1]–0.70[5]	0.40[2] –2.15[5]		0.07[3]–0.10[7]	−0.1[2]–1.45[5]	0.8[2]–9.6[1]
			SO_4−S			
MC1	0.57	1.7	0.06	2.4	1.2	3.1
MC2.1	0.28	1.3	0.02	1.5	1.1	4.8
MC2.2	0.28	0.32	0.02	n.a.	0.06	1.2
MC2.3	0.28	0.98	0.02	n.a.	0.73	3.7
MC3	1.8	3.2	0.03	1.3	1.4	1.8
mean	0.88	1.5	0.04	1.8	0.89	2.9
S.D.	0.80	1.1	0.02	0.62	0.53	1.4
Tropical montane forests	<4.4[3]–38[4]	6.1[5]–40.9[2]		13.7[6]	−7.1[5]–14.7[2]	0.5[5]–3.6[4]

[a] n.a.: not available; [b] n.c.: not calculable; [1] Clark et al. (1998), [2] Veneklaas (1990), [3] Hafkenscheid (2000), [4]Asbury et al. (1994), [5] Cavelier et al. (1997), [6] McDowell & Asbury (1994), [7] Bruijnzeel et al. (1993).

4 Discussion

4.1 Hydrological conditions of the study site

The study area is characterized by an unimodal annual rainfall distribution with a wetter period between April and September and a drier period between October and March, which coincides with the regional climate conditions described in 2.1.5.

Results show that the catchment soils and discharge are highly responsive to precipitation with hydrometric results suggesting that shallow subsurface stormflow may be the dominant hydrological pathways during storm events. Owing to the high hydraulic conductivity of the organic layer, Fleischbein (2004) excluded the occurrence of Horton flow (infiltration excess flow; Buttle 1998) in the study area. Furthermore, since monthly temperature variations were relatively low during the year, ranging between 14.5 °C in July, the coldest month of the entire period, and 16.6 °C in November, the warmest month (P. Emck personal communication), the rainfall has to be considered as the dominant climatic factor of the study area.

4.2 Tracing water paths through small catchments by an oxygen isotope approach

To assess the consequences of the increasing human pressure on montane forests for the water cycle, knowledge of the flow paths is required and it has to be demonstrated how these flow paths are linked to the rainfall regime. It is particularly important to determine the flow direction (vertical vs. lateral) and the percolation depth of rainfall water because the destruction of montane forest can result in the loss of the organic layer and possibly also part of the mineral topsoil. If this part of the soil with its higher water conductivity than in the denser subsoil played a major role in the transformation of rainfall water to stream flow, the loss of the forest would markedly change runoff conditions.

In a south Ecuadorian lower montane forest there was a considerable increase in Al, Cu, Mn, Zn and total organic C (TOC) concentrations and a decrease in pH in surface water during high discharge after rainstorm events (Wilcke et al. 2001). Associated with the find-

ing that concentrations of these elements, except for Al, are highest in the organic layers (Wilcke et al. 2002), this suggested that in the studied microcatchments a large portion of water flow in soil during rainstorms occurs laterally, whereas during baseflow conditions most of the stream water comes from the deeper mineral subsoil. It is likely that the water flow during storm conditions is restricted to the organic layer and only slightly infiltrates the mineral soil. Thus, if the organic layer and the topsoil, slowing down the near−surface water flow, were lost, storm event water might become heavily erosive and contribute to flashfloods. The runoff water would probably contain less solutes but more sediment.

The occurrence of rapid interflow is a frequent phenomenon on steep forested hillslopes (Mulholland et al. 1990; Bonell et al. 1998), and mainly attributable to the high significance of macropores (Buttle & McDonald 2000). While intensive hillslope catchment research has been conducted in temperate environments, studies investigating water Dunne (1978) found that 'subsurface stormflow' accounts for the major proportion of total stormflow on evenly steep hillslopes with a high topsoil conductivity, which means a rapid runoff component in shallow soil depths (Buttle 1998). There has been disagreement among catchment researchers concerning the question whether stormflow runoff consists of pre−event or of event water. The majority of small hillslope catchment studies has found that total stormflow runoff caused by rainstorm events is dominated by pre−event ('older') water as summarized by Genereux & Hooper (1998) while fewer studies found that it was dominated by event water (Bonell et al. 1998; Schellekens et al. 2004).

To determine the relationship between the rainfall regime and the dominating water flow direction, the natural abundance of $^{18}O/^{16}O$ and D/H ratios (expressed as $\delta^{18}O$ and dD values) may be used. The application of O and H isotopes as conservative tracers in the investigation of hydrological processes of water catchments has become a common tool in the last two decades (Kendall & Caldwell 1998). The rationale for using $\delta^{18}O$ and/or δD values in tracing water paths is their temporal variability in precipitation (Genereux & Hooper 1998; Rhode 1998) related to isotope fractionation in the atmosphere as a result of evaporation/condensation cycles (Kendall et al. 1999). However, to better elucidate the flow paths of the water passing through an ecosystem the isotope data should be combined with more traditional data from both hydrochemical and hydrological studies (Kennedy et al.

1986; Bonell et al. 1998; Kendall et al. 1999). Therefore, we used high−resolution measurement of the soil water content in different soil horizons to provide further evidence of soil water dynamics during rainstorm events. Where multi−proxy data is used information can be gained on the influence of rainstorm events and on the mobilisation of ecosystem−relevant nutrients and their subsequent loss with catchment runoff (e.g. Wilson et al. 1991; Wilcke et al. 2001).

4.2.1 Isotope signatures of ecosystem fluxes under different moisture conditions

Non−storm conditions

The use of environmental isotopes in characterizing different water sources in catchments requires the knowledge of the temporal variability of the isotope signals in the various water types within the studied ecosystem throughout the year. Therefore, the temporal trends of $\delta^{18}O$ in the ecosystem fluxes were examined.

The finding that $\delta^{18}O$ values in rainfall, throughfall, and lateral flow were highly variable during the monitored year, while soil water and particularly stream water showed considerably less variation in $\delta^{18}O$ and consistently lower values, allowes to distinguish different water sources of the stream.

The dampening of the $\delta^{18}O$ values of the various ecosystem fluxes representing the passage of the water passing through the forest from rainfall to stream water indicated that during normal wet conditions vertical water flow dominated resulting in a systematic decrease in the mean $\delta^{18}O$ (Figure 11).

Storm conditions

The finding that $\delta^{18}O$ values changed significantly in the stream waters of all three microcatchments during the rainstorm event and subsequently again had values near -7 ‰ the following day demonstrated that during the rainstorm event a proportion of water from a different source reached the stream water. There are three possible sources for isotopically enriched water in the study area: the throughfall, which had a mean $\delta^{18}O$ value of -5.5 ‰, the lateral flow with a mean $\delta^{18}O$ value of -5.4 ‰, and the soil solution with mean $\delta^{18}O$ values of -4.8 ‰ at 0.15 m and -6.0 ‰ at 0.30 m mineral soil depth during the

values of -4.8 ‰ at 0.15 m and -6.0 ‰ at 0.30 m mineral soil depth during the event. In water catchment research three major models of stormflow generation are suggested (Fritsch & Katzenmaier 2001): (i) water flow in preferential pathways (macropores and flow in highly permeable layers/pipes), which mainly consists of event water, (ii) 'translatory or piston flow' (dischargement of soil water by hydraulic pressure transmission) and (iii) 'groundwater ridging' (Sklash & Farvolden 1979), whereby the last two mechanisms contribute older pre−event water to the stream.

The observation that there was no change in the isotope signal of mineral soil solutions directly after the rainstorm event indicated that the major part of water transport must have occurred in the upper soil layer. Since the portion of water reaching the stream by direct channel precipitation is negligible (Buttle 1998), I conclude that the observed increase in the $\delta^{18}O$ values of the stream water was caused by a relatively high contribution of the ^{18}O−enriched rain water, which has quickly run through near−surface soil regions to the stream channels. This conclusion was further confirmed by the course of the soil water content during the rainstorm event, since the rise of the water content was markedly stronger in the O horizon compared with the A horizon with a rapid increase of about 12 vol % within 24 h before the beginning of the rainstorm event (Figure 18). This indicates the occurrence of 'organic horizon flow' (Kendall et al. 1999) in the uppermost part of the soil. Since the soil water content of the A horizon was considerably lower (by ca. 7 vol %) around the rainstorm event, I assume that there was a domination of lateral flow in the organic layer. This interpretation is further confirmed by considerably higher saturated hydraulic conductivity in the organic layer (geometric mean 4.5×10^{-4} m s^{-1}), compared with the upper (1.8×10^{-6} m s^{-1}) and lower (1.4×10^{-7} m s^{-1}) mineral soil in MC2 (Fleischbein 2004). The distinct decrease of the hydrologic conductivity of the soil with depth is commonly considered as a further prerequisite for the occurrence of interflow (Casper 2002).

4.2.2 Pre−event versus event water

The finding that the contribution of the event water component to the total stormflow runoff was markedly greater than the contribution of the pre−event component in two microcatchments, in addition to the rapid response of the stream water levels to the onset of rain-

fall (Figure 15), strongly suggest that in two of the three studied microcatchments stream waters during peak discharge were dominated by event water that has quickly reached the stream channels by using near−surface flow paths. This is further confirmed by the rapid change of the $\delta^{18}O$ signal of the stream water directly after the rainstorm event in all three microcatchments. As mentioned in 4.2, this result partly contrasts the findings of numerous small catchment studies, which reported a dominance of pre−event water in stormflow runoff and supports fewer studies that found the event water component to be predominant.

The strong variation in the event water contributions between MC2 and the two other catchments during the monitored storm event illustrates how variable adjacent small water catchments may respond to a rainstorm event. To explain this variation, a more detailed study of the linkage between catchment hydrology and physical soil properties (especially the hydraulic conductivity) is necessary (Elsenbeer 2001). The comparatively lower event water fraction in MC2 (44 %) indicates a more pronounced contribution of a pre−event water mobilizing runoff mechanism. According to Sklash et al. (1986), the displacement of older (pre−event) water can occur because of groundwater ridging particularly in pre-saturated lower parts of the slope (Ward 1984). I assume that this mechanism may be important in the lower part of MC2, where temporarily water−saturated Aquic Dystrudepts (Yasin 2001) are the dominating soil type near the stream channel. Additionally, following the conclusions of Bonell et al. (1998), who emphasized rainfall intensity as a major factor for the response of small water catchments in high−rainfall areas, the old water contribution by the ground water ridging mechanisms was further promoted by less rainfall intensity in MC2 during the monitored storm event because of its less exposed topographic position in a depression.

4.3 Dissolved organic nitrogen, phosphorus, and sulfur in the nutrient cycle

The ecological significance of organic N, P, and S forms has often been considered to be low compared with inorganic forms (Buffam et al. 2001; Stevenson & Cole 1999; Van Breemen 2002) because, until recently, organically bound nutrients were supposed to be unavailable for the direct uptake by plants (Currie et al. 1996; Qualls et al. 2002). How-

ever, Van Breemen (2002) and Neff et al. (2003) challenged this view. It has been shown in a number of mycorrhizal studies that the direct uptake of organically bound macronutrients plays a more prominent role than realized so far (Aerts & Chapin 2000), particularly because 80−90 % of terrestrial plants are associated with fungi (Aerts 2002). Moreover, dissolved organic nutrients can be converted to readily available inorganic forms, especially through mycorrhizal fungi, which play a dominant role in P uptake (Stevenson & Cole 1999), particularly in tropical rain forests (Grubb 1995). Microbial release of inorganic S from organic S forms is the major source of plant−available S in soils (Stevenson & Cole 1999).

In a temperate forest in south Germany, the contribution of DOC to total C ranged between 8 % in throughfall and 75 % in litter leachate (Zech et al. 1996). Dissolved organic N can account for about 50 % of the total N concentrations in throughfall (Qualls et al. 1991), litter leachate (Currie et al. 1996; Qualls et al. 1991), soil solution (Cortina et al. 1995; Kaiser et al. 2000), and stream water (Campbell et al. 2000; Hagedorn et al. 2000) of temperate forests. The reports on the contribution of DOP to total P in forest in litter leachates and soil solutions are inconsistent. Whereas Kaiser et al. (2000) found that DOP was the dominant P form in litter leachates (79−81 %) and in soil solution (>95 %) under beech and pine forests in south Germany, DOP portions were lower (25 %) in the O horizon and upper mineral soil of a boreal aspen stand in Canada (Huang & Schoenau 1998). According to Homann (1990), organic S contributed up to 54 % of total S in ecosystem fluxes of 8 water cachments under temperate forest in the USA.

In temperate forests, the soil organic layer generally is the main source and the mineral soil is the main sink of DOM (Kaiser et al. 2000; Kalbitz et al. 2000; Michalzik et al. 2001). Few studies have found that the forest canopy can release similar amounts of DOM as the soil organic layer (Qualls et al. 1991). Information on DOM sources in tropical forests is limited and contradictory. For tropical montane forests, Wilcke et al. (2001) in Ecuador and Schrumpf (2004) in Tanzania showed highest total organic carbon (TOC) concentrations in the litter leachate. In contrast, McDowell (1998) found that the DOC production in the soil organic layer of a montane forest in Puerto Rico was small. The latter might be explained by the thin organic layer of the studied forest and the indirect measurement of

DOC leaching from the forest floor by soil sorption experiments.

Dissolved organic matter dynamics in forests is controlled by biotic (microbial and fungal activity, Guggenberger & Zech 1994; Møller et al. 1999) and abiotic factors (e.g. temperature, soil moisture, ionic strength, water flux, and pH, Buffam et al. 2001; Kalbitz et al. 2000; Savric 2001; Solinger et al. 2001). The evaluation of the contribution of each factor is difficult (Kalbitz et al. 2000). The effect of pH on DOM release in soils is not completely understood partly owing to the inconsistency among results from laboratory and field experiments (Michalzik et al. 2001). The water flux in soils is a major control of the dynamics of DOC and DON (Solinger et al. 2001) and DOP and DOS (Kaiser et al. 2000) in forested water catchments, especially after rainstorms. Fewer studies illustrated the correlation between high−discharge events following rainstorms and elevated DON concentrations in stream water of small water catchments (Buffam et al. 2001; Hagedorn et al. 2000). Kaiser et al. (2000) reported that rainstorms induced a nearly conservative transfer of DOC, DON, DOP, and DOS in seepage water through the soil column of strongly structured soils under a forest in south Germany. As discussed in chapter 4.2, results from the study forest in Ecuador showed that during rainstorms a large portion of the incoming water drains quickly in lateral direction through the near−surface soil to the stream. This resulted in elevated DOC concentrations in stream water (Wilcke et al. 2001).

4.3.1 DOC, DON, DOP, and DOS concentrations in ecosystem fluxes

The DOC and DON concentrations in rainfall of the study forest were similar to those at other tropical forest sites (Tables 5 and 6; Eklund et al. 1997; Schrumpf 2004). Compared to temperate forests, DOC concentrations in rainfall of the study site were high and DON concentrations were similar (Likens et al. 1983; Michalzik & Matzner 1999). Elevated DOC concentrations of rainfall at the study site compared to many temperate forests may be attributable to the release of organic compounds from the extended forest area in the Amazon basin and transport with the mainly easterly winds (Forti & Neal 1992).

In most solutions except stream water, DOC and DON concentrations were higher than at other tropical forest sites (Frangi & Lugo 1985; Hafkenscheid 2000; McDowell 1998; Möller 2001; Schrumpf 2004) but comparable to those in temperate forests (Michalzik et

al. 2001; Tables 5 and 6). This may be related with the comparatively high litterfall and organic matter storage of the Ecuadorian forest (Wilcke et al. 2002). The DOC and DON concentrations in stream water were similar to those in other forested catchments in Puerto Rico and Chile (Hedin et al. 1995; McDowell & Asbury 1994; Tables 5 and 6).

The considerable increase (three– to fivefold) of DOC and DON concentrations in throughfall and stemflow at all transects indicates that the canopy was a DOC and DON source. This is the result of the leaching of plant tissue and of humic material accumulated by epiphytes in the forest canopy (Vance & Nadkarni 1990).

The further marked increase in DOC and DON concentrations in lateral flow and litter leachate relative to throughfall and stemflow demonstrates that the organic layer was the major source of DOC and DON in the studied forest. This corroborates results of Qualls & Haines (1992) that the organic layer of a temperate forest in North Carolina was a much larger DON source than the canopy. The elevated DOC and DON concentrations in litter leachate can be attributed to microbial decomposition of the soil organic matter and the leaching of C– and N–containing humic substances from fresh litter (Kalbitz et al. 2000).

The decrease in DOC and DON 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 (McDowell 2003; Stevenson & Cole 1999). This is similar to findings of Qualls & Haines (1992) that more than 95 % of the DOC and DON input were retained during the passage through a temperate forest ecosystem. The main reason is the adsorption of DOC and DON to Al and Fe oxides and hydroxides (Kaiser et al. 1996; Qualls et al. 2002). Guggenberger & 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).

In stream water, mean DOC and DON concentrations were similar to those in rainfall (Tables 5 and 6). The mean 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 (1.6-3.8 mg l^{-1}), whereas the mean 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 & Lugo

1985).

From the similarity of the vertical profiles of DOP and DOS in ecosystem solutions I conclude that the organic layer and to smaller degree the canopy were DOP and DOS sources, which is analogous to findings for DOC and DON. Qualls et al. (1991) found that 65 % of the DOP input to the A horizon in a temperate forest in North Carolina originated from throughfall and stemflow indicating that the canopy was a substantial DOP source. However, Kaiser et al. (2000) and Kaiser & Guggenberger (2003) reported highest DOP and DOS concentrations in litter leachate of two forests in south Germany, pointing at the organic layer as the major DOP and DOS source (Tables 8 and 9). Most organic S in soil originates from litterfall and accumulates in the organic layer, which is therefore the major source for DOS (Houle et al. 2001).

The mean DOP 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). This indicates strong P leaching from the canopy. The DOS concentrations in throughfall and stemflow were lower than in a temperate coniferous forest in Quebec (Houle et al. 2001; Table 9). The fact that mean DOS concentrations decreased markedly between litter leachate and mineral soil solution in two of the studied microcatchments may be explained by adsorption and mineralization (Stevenson & Cole 1999).

The mean DOP concentration was by far highest in litter leachate (Table 8). This was about 12 times higher than reported by Hafkenscheid (2000) for a tropical montane forest in Jamaica. The DOP concentrations in litter leachate were much higher than in temperate forests (Kaiser et al. 2000; Qualls et al. 1991; Table 8). The mean DOS concentration in litter leachate of the studied forest was in the range of those in 8 temperate forested water catchments in North America (Homann et al. 1990). In mineral soil solutions, the mean DOS concentrations were slightly lower than in temperate forest soils in south Germany (Kaiser & Guggenberger 2003) and in Quebec (Houle et al. 2001; Table 9).

4.3.2 Controls on dissolved organic nutrient concentrations

Increased DON concentrations during drier periods were frequently related to westerly wind directions carrying a solute load that probably originated in the inner Andean valley.

I suggest that vegetation fires in and dust from the much drier Loja basin were sources for the elevated DON concentrations in rainfall of the study site during dry periods.

The decreasing DON concentration in the soil solution during dry periods 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 & Zech 1993, Tipping et al. 1999; Zsolnay et al. 1999).

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).

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 (Guggenberger et al. 1994; Vance & David 1989). 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 DOM concentrations in the litter leachate. The finding that the mean annual DOC/DON ratios in soil solutions at 0.15 m and 0.30 m mineral soil depth were higher on transects MC2.1 and MC2.2 (data not shown) than at the other transects indicating a slower turnover of organic matter supports this assumption.

4.3.3 The role of rainstorm events

The DOC concentrations in stream water were positively related to the rainfall under non–storm 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 20). 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). As shown in chapter 4.2, flow paths of water in the soil switched rapidly from mainly vertical to mainly near–surface lateral flow during rainstorms, 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. Brown et al. 1999; Hagedorn et al. 2000; Jardine et al. 1990).

However, the increase in DOC and DON concentrations was not quantitatively 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. Similar results were reported by Bushaw et al. (2001), who found that stormflow contributed more than 50 % to the total DOC and DON export from a forested water catchment in Virginia.

I was not able to evaluate the relation between rainstorms and DOP and DOS concentrations in stream water because of the monthly resolution of my measurements. However, from the correlation between DOC and DOP and DOS concentrations (Figure 23b and c), I infer a similar response of organic P and S to rainstorms as found for DOC.

4.3.4 Contribution of organic forms to total nutrient fluxes

Dissolved organic N contributed <50 % to TDN in almost all ecosystem fluxes. 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 on 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; K. Kalbitz, University of Bayreuth, personal communication).

The DON contributions in litter leachate at the study site were similar to those reported by Currie et al. (1996) of 56–67 % but lower than those reported by Qualls & Haines (1992) of 95 % for North American temperate forests. The DON contribution to TDN 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 & Swanson 1996) and 97 % (Perakis & 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. 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 (5–100 %). 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 contributions to TDS (59 %) demonstrates that DOS plays a major role in the S dynamics of the studied forest. Dissolved organic S was the most abundant S form in all ecosystem fluxes above the mineral soil (Table 7). This coincides with the conclu-

sions of Stevenson & Cole (1999) that most of the aboveground S cycling occurs in the organic form. The DOS contributions in throughfall, stemflow, and litter leachate (Table 7) were higher than DOS portions in 8 temperate forests in the 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 contributions of DON to their total concentrations. The shift from DOS to sulphate in the mineral soil solution is attributable to the efficient exchange of sulphate by DOM (Kaiser et al. 1998). Strong adsorption of DOS is further supported by the low DOS contribution to TDS in stream water, which were similar to DOS portions of 12−21 % in Canadian catchments (Mitchell et al. 1986).

4.4 Dissolved inorganic nitrogen, phosphorus, and sulfur in the nutrient cycle

Anthropogenic activity has changed nutrient cycles of forests. The use of mineral fertilizers and N emissions to the atmosphere in densely populated areas seem to have shifted the composition of the N output of forested watersheds from mainly organic at remote locations to mainly inorganic N forms (Perakis & Hedin 2002; Van Breemen 2002). It is reasonable to assume a similar effect of human activity on P and S cycles.

Forest ecosystems receive N via deposition from the atmosphere and biological N fixation. Losses of N include leaching and runoff, denitrification, and erosion. In temperate forests with high ambient N input, the N export via stream water mainly occurs as nitrate (Tamm 1991). The canopy of tropical forests can act as a sink for DIN because of N uptake by plants (Bentley 1987). However, DIN can also be released by mineralization of dead organic matter accumulated in the canopy (Bentley & Carpenter 1980). Coxson (1990) reported an annual N release of 11 kg ha^{-1} from the mineralization of dead biomass of upper canopy bryophytes in a montane forest on Guadeloupe. In contrast, Schrumpf (2004) found a net uptake of nitrate in the canopy of a montane forest in Tanzania. In the soil organic layer of temperate forests, N forms are shifted from inorganic to organic (Yavitt & Fahey 1986; Qualls et al. 1991). Nevertheless, DIN concentrations in litter leachate are in some tropical montane forests higher than in throughfall indicating a DIN leaching from the organic layer (Hafkenscheid 2000; Wilcke et al. 2001; Schrumpf 2004).

Weathering of phosphate minerals is the primary P source in terrestrial ecosystems (Hedin et al. 2003). In acid soils, P is strongly sorbed to Fe and Al oxides (Sanchez 1976; Sollins et al. 1988). Therefore, the greatest portion of plant−available P in forests on acid soils cycles between the canopy and the organic layer. Parker (1983) estimated that leaching of the canopy contributes 70−90 % to throughfall phosphate. The mineral soil of forest ecosystems is the major sink for inorganic P because of the strong sorption. The soil organic layer may also act as a sink for inorganic P because of microbial immobilisation (Qualls et al. 1991) and P conservation by roots and mycorrhizae (Stark & Jordan 1978; Cuevas & Medina 1986).

In forests, inorganic S exists as sulphate derived from mineralized organic S compounds, oxidation of airborne SO_2, and weathering of S minerals (Likens et al. 2002; Stevenson & Cole 1999). In the north Andes, volcanic exhalations contribute additional S (Veneklaas 1990). The microbial release of inorganic S is the major source of plant−available S in soils (Stevenson & Cole 1999). However, the organic S pool in forest soils can also be a sink for inorganic S (Alewell et al. 1999). Similar to phosphate, sulphate adsorption to Al and Fe minerals can immobilize DIS in the mineral soil (Likens et al. 2002).

The release of DIN, DIP, and DIS in the soil is governed by a variety of biotic and abiotic processes. The former include microbial turnover and uptake by plants, the latter physico−chemical soil properties (e.g. pH, water content, redox conditions, and soil temperature). The contribution of each factor varies with climatic and topographic conditions, soil and vegetation types (Stevenson & Cole 1999).

In an old−growth temperate forest in southern Chile, losses of inorganic N were strongly influenced by microbial turnover, whereas export of organically bound N was mainly controlled by hydrological factors (Perakis & Hedin 2001). Contrasting results have been reported concerning the influence of the water flux on the mobilization of DIN. While Lovett et al. (2000) showed that DIN losses are not significantly affected by hydrological flushing, Mitchell (2001) found a clear linkage of nitrate losses in water catchments to hydrological processes. For P, Frangi & Lugo (1985) attributed a 7−fold increase in total dissolved P concentrations in river water relative to the average monthly P concentrations to

river discharge peaks in a subtropical forest in Puerto Rico. In bulk precipitation and stream water of the temperate forest of Hubbard Brook, USA, sulphate fluxes were strongly positively correlated with water volumes (Likens et al. 2002).

The pH is a major controlling factor for the P and S dynamics in the soil (Stevenson & Cole 1999). The role of soil pH in the biogeochemical N cycle is more complex. Contrasting results have 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 activity of the autotroph nitrifiers (Kilham 1990) others did not detect a significant relationship between pH and nitrification rates in temperate forests (Robertson 1982).

In pristine forests with steady−state conditions, nutrient cycles are generally tight except if there is a release of some elements by weathering of the subsoil (McDowell & Asbury 1994; Ulrich 1981). Thus, setting up an input−output budget of forested catchments helps in detecting whether the studied forest is in equilibrium and whether there is a loss of nutrients by the weathering of the subsoil.

4.4.1 Concentrations of dissolved inorganic nitrogen, phosphorus, and sulphur

The low DIN concentrations in the input and output fluxes accompanied by high DIN concentrations in the organic layer solutions indicated a tight N cycling between the canopy and the soil in the study forest. Such a tight nutrient cycle has frequently been observed in tropical forests on nutrient−poor soils (e.g. Brinkmann 1985; Herrera et al. 1978; Jordan 1989). However, I did not determine gaseous N fluxes (dry deposition, N_2 fixation, denitrification). Therefore, my N budget is incomplete. Denitrification might play an important role because of the frequently low redox potentials and high N mineralization rates (own unpublished data and Wilcke et al. 2002). Furthermore, I observed a high interannual variation in NO_3−N fluxes. A reliable budget may therefore also require a longer monitoring period.

The cycling of DIP, which was mainly restricted to the canopy and the organic layer, indicated by extremely low DIP concentrations in rainfall, mineral soil solutions and stream water, was tight. The low DIP concentrations in the mineral soil solution and the

stream water can be explained by a strong sorption to clay minerals and Fe and Al oxides. The finding that DIP concentrations were highest in throughfall and stemflow indicated leaching of inorganic P from the canopy, i.e. plant tissue, phyllosphere organisms, and canopy litter (Figure 27). This confirmed conclusions of Wilcke et al. (2001) that P is taken up by the plants from the organic layer and recycled by leaching from the canopy in the study forest. High enrichment factors for DIP in throughfall were also reported by Cavelier et al. (3.07, 1997) for a tropical montane cloud forest in Panama.

The cycling of DIS was clearly different from that of DIN and DIP. The concentrations of DIS varied little in stream water during the monitored year indicating a continuous DIS release from the soils of the studied catchments (Figure 29). The concentrations of DIS in the stream water of microcatchments MC1 and MC2 were consistently higher than in rainfall indicating DIS sources in the mineral soil. The assumption of DIS sources in the mineral soil is further supported by the fact that the mean annual DIS concentrations in the litter leachate were less than half of that in the mineral soil solutions. Given the high density of roots in the organic layer (Wilcke et al. 2002) and the marked decrease in N and P concentrations between the organic layer and the mineral soil, it seems unlikely that the higher DIS 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 DIS 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 less crystalized reduced S forms that are released during drier periods.

4.4.2 Controls of the DIN, DIP, and DIS dynamics

Periods with increased NO_3−N concentrations in rainfall coincided with dry periods (Figures 24a−b) 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). I 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) were sources for the increased NO_3−N concentrations in rainfall of my study site during drier periods. A similar relationship for NH_4−N concentrations in rainfall and throughfall was not evident, since NH_4−N concentrations were not only elevated in drier but also in the wettest periods.

The assumed transport of air masses from the Loja basin during drier periods seemed to play a minor role as source of inorganic P and S in wet deposition to the study forest, since concentrations in rainfall were consistently low throughout the monitored period. Furthermore, local vegetation fires and the eruptions of the Tungurahua volcano, which is located at a distance of c. 200 km and had several eruptions during the monitored year, did not substantially contribute to DIS deposition.

The NH_4−N and NO_3−N concentrations in litter leachate and mineral soil solutions also increased during dry periods. Furthermore, NH_4−N concentrations appeared to be affected by heavy rainstorms occurring in wet periods with near waterlogged soil conditions (Figure 25a−c). Soil drying and rewetting is known as a DIN generating process. The inorganic N results from the bursting of dead cells during drying, 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 & Cole 1999).

The course of the mean weekly NO_3−N concentrations in stream water paralleled the hydrographs of the three microcatchments indicating that the export of NO_3−N from the study forest was mainly governed by the hydrological runoff conditions (Figure 26). The rapid increase in NO_3−N concentrations in stream water at the beginning of the wetter periods indicated an elevated NO_3−N input from the catchment soils. I suggest that this was induced by two processes: (i) a direct NO_3−N input from the organic layer via shallow interflow during stormflow conditions, which was found to be an important runoff mechanism in the study catchments (chapter 4.2) and was also reported for NO_3−N by Hagedorn et al. (2001) in a temperate montane forest in Switzerland and (ii) the leaching of NO_3−N from the upper mineral soil and transfer through preferential flow paths, which are abundant in the stone−rich catchment mineral soils (J. Zeilinger, University of Bayreuth, personal communication) directly to the streams. Although mean NO_3−N concentrations in

stream water were not significantly higher during stormflow conditions, the strong increases in NO_3−N concentrations in response to discharge peaks, particularly at the beginning of the wetter season (May 2000 and June 2001, Figure 26), suggested that stormflow plays an appreciable role in NO_3−N export. The consistent decrease in NO_3−N concentrations in stream water following the beginning of wetter periods indicated reduced nitrification and enhanced denitrification because of (near−)waterlogged conditions (Figure 25a).

Similar to DIN, DIP and DIS concentrations in throughfall, stemflow, lateral flow, and litter leachate seemed to be negatively related to humidity. However, this might be partly explained by concentration/dilution effects because of reduced water fluxes during drier periods particularly in the canopy, since DIP and DIS concentrations in throughfall and stemflow were negatively related to the respective water fluxes (Figure 30). However, DIP and DIS concentrations were also strongly elevated in the organic layer solutions in November 2000, which was the driest month of the monitored year (87 mm rainfall) without rainfall during the first three weeks (own field observation). Since evaporation from the forest floor of tropical rain forests is known to be small (Jordan & Heuveldop 1981), the elevated DIP and DIS concentrations in litter leachate cannot be attributed to a concentration/dilution effect. I suggest that the dry weather conditions were responsible for the dying of microbes in the canopy and the organic layer. Subsequently, the rapid decay of the dead biomass led to a release of labile organic compounds, which were quickly mineralized and oxidized to phosphate and sulphate (Stevenson & Cole 1999). At the same time, P and S uptake by the vegetation might be reduced because of enhanced litterfall in the study forest during the drier period at the end of the year (Wilcke et al. 2002).

In the mineral soil, the positive relationship between rainfall and DIS concentrations showed that inorganic S dynamics were mainly controlled by hydrologic conditions. Furthermore, the sulphate release in the soil is promoted by alternating soil drying and rewetting because of the stimulation of the microbial activity (Stevenson & Cole 1999).

The NO_3−N concentration in litter leachate and mineral soil solutions were significantly lower ($p<0.01$, Table 10) at the most acid transect MC2.1 than at all other transects indicating reduced microbial activity. This confirms findings of Wilcke et al. (2002) in the study forest, who reported a reduced nutrient turnover in the organic layer on transect MC2.1

compared with the transects MC1 and MC3. However, NO_3−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 NO_3−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: 20 and 18, respectively) and at 0.30 m depth (DOC/DON: 19 and 19, respectively) on transect MC2.2 than on transect MC2.1 (0.15 m: 31 and 31 and 0.30 m: 29 and 27, respectively − own unpublished data, methods explained in Wilcke et al. 2001). This is likely to be related with a higher NO_3−N release. In contrast, the NH_4−N concentration in the soil solutions at the five transects seemed to be independent of the pH.

4.4.3 Fluxes of inorganic nitrogen, phosphorus, and sulphur

The mean annual NH_4−N input with rainfall was at the lower end, mean NO_3−N and PO_4−P well within, and mean SO_4−S distinctly below the ranges given by Hafkenscheid (Tables 12 and 13). The higher SO_4−S concentrations in rainfall of the studies summarized by Hafkenscheid (2000) than at the study site may be attributed to sea water spray and exhalations and ashes of active volcanoes. Net throughfall deposition of NH_4−N was well within and NO_3−N at the upper end of the range in Hafkenscheid (2000), indicating a considerable NO_3−N flux to the forest floor at the study site. This contrasts the results from several other tropical montane forests (Hafkenscheid 2000; McDowell & Asbury 1994; Schrumpf 2004) where a net retention of NH_4−N and NO_3−N in the canopy has been observed. The absorption of inorganic N in the canopy is common in N−deficient ecosystems (Lindberg et al. 1986). This supports the conclusions of Wilcke et al. (2002) that the study forest is not N−limited.

The ‘throughfall enhancement’, i.e. the increase in DIN, DIP, and DIS concentrations in throughfall and stemflow compared to rainfall, is attributable to the washoff of the canopy surface and leaching of plant tissue (Parker 1983). The contribution of particulate and gaseous dry deposition to net throughfall can be significant for N and S in industrialized regions (Parker et al. 1983). For the study forest, the overall contribution of dry deposition

was likely to be smaller than in many temperate forests because of the remote location of the study area. Lin et al. (2000) found that the contribution of dry deposition to total deposition in a subtropical rain forest in northeast Taiwan was generally small relative to many temperate forests and might have resulted from the lack of longer dry periods which is also the case at the study site. However, as indicated by elevated concentrations in the throughfall, the dry deposition probably increased during the drier periods at the end of the year.

The lack of correlation between rainfall volumes and net throughfall deposition, which was also observed by Hafkenscheid (2000) in a tropical montane forest in Jamaica, indicated that the leaching of DIN, DIP, and DIS from plant tissue played a minor role. Thus, dry deposition (particulate and gaseous), N fixation and microbial nutrient release in the phyllosphere are likely sources of DIN, DIP, and DIS for throughfall and stemflow. A similar microbial biomass in canopy organic matter as in the organic layer was reported by Vance and Nadkarni (1990) for a tropical montane forest in Costa Rica.

The nutrient export of both NH_4−N and NO_3−N via stream water was low (Table 12) and within the range of other tropical montane forests in Hafkenscheid (2000) for NH_4−N, but distinctly lower for NO_3−N, again indicating a tight nutrient cycle for inorganic N in the study forest.

Exports of DIP and DIS were at the lower end of the range in Hafkenscheid (2000) for PO_4−P and much lower than values reported by McDowell & Asbury (1994) for SO_4−S from a small water catchment under a subtropical rain forest in Puerto Rico. The latter might be explained by the geologically young bedrock in Puerto Rico. However, results indicated that DIS was lost from MC1 and MC2, since the output via stream water exceeded the net precipitation in throughfall plus stemflow fluxes. A higher sulphate export has often been reported for forested catchments of regions receiving high ambient SO_2 input (Likens et al. 2002; Prechtel et al. 2001). Suggested reasons for this mass imbalance are S additions by dry deposition, mineral weathering, ‘excess mineralisation’, and oxidation of reduced S species (Mitchell 2001; Prechtel et al. 2001). I assume that the reasons for the observed DIS loss from microcatchments MC1 and MC2 were SO_4−S mobilisation through mineral weathering and partly re−oxidation of reduced S during drier periods.

5 General conclusions

The first part of my work addressed the flow paths of water in the studied tropical montane forest. The $\delta^{18}O$ in rainfall on the Cordillera Real was highly variable during the monitored year. This was also true for throughfall and lateral flow in which the $\delta^{18}O$ paralleled that of the rainfall. Soil water and particularly stream water showed considerably less variation in $\delta^{18}O$ and consistently lower values. This allowed to distinguish between event input water and pre–event soil and groundwater. The $\delta^{18}O$ values of the various ecosystem fluxes indicated that during normal wet conditions vertical water flow dominated resulting in a systematic decrease in the mean $\delta^{18}O$ when the water passed through the forest from rainfall to stream water. This decrease is attributed to higher $\delta^{18}O$ values of the input water during almost the whole year when compared to the long–term $\delta^{18}O$ value in rainfall at the nearest IAEA station. During rainstorm events transport conditions switch to rapid lateral flow which occurs near–surface and results in rapid changes of the $\delta^{18}O$ signal in the stream water and becomes more similar to the $\delta^{18}O$ of rain water and near–surface soil solution. Results from a two–component hydrograph separation of three adjacent microcatchments show a high contribution of event water to stormflow runoff in two microcatchments. The distinctly lower event water contribution in MC2 indicates that the significance of stormflow generating processes may vary even in catchments with comparable climatic and edaphic conditions. I conclude that the loss of the organic layer and the topsoil as a consequence of forest destruction would markedly change the runoff generation processes.

In the second part of my work, I investigated the sources and fate of dissolved organic C, N, P, and S with particular attention to the influence of hydrological conditions on their fate. In the studied forest, the organic layer was the major source for DOC, DON, DOP, and DOS followed by the forest canopy, whereas the mineral soil acted as a sink for all compounds, which is similar to findings in temperate forests. The mean annual DOC and DON concentrations in a vertical ecosystem profile at five study transects paralleled each other during the three−year study period confirming that C and N cycles were closely linked. I observed a comparable vertical distribution for DOS and in a slightly modified

manner for DOP indicating a similar fate of all organically bound nutrients during the passage through the forest. The concentrations of organically bound nutrients in soil solutions tended to be positively related to pH. Hydrological conditions controlled DON transport and transformation through the ecosystem. Dissolved organic N concentrations in soil solutions were reduced during dry periods 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 DOC and DON 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. My findings demonstrate that DOM was the major vector for the cycling of N, P, and S in the studied forest except for S in the mineral soil. Although the concentrations of DON, DOP, and DOS 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 the soil.

In the third part of my work, I focussed on the sources and fate of inorganic N, P, and S as related to the dynamics of their organic forms and to hydrological conditions. Similar to DOM, the organic layer was the major source for DIN followed by the canopy, whereas the mineral soil acted as a sink, especially for NH_4−N. Most DIP originated from the canopy, which was almost completely retained in the mineral soil. In contrast, the mineral soil was the major source for DIS. Thus, the dynamics of DIN, DIP, and DIS were independent of each other. Hydrological conditions were the main factor controlling the dynamics of DIN, DIP, and DIS. Drying and rewetting cycles played a key role in the release of inorganic N from the organic layer. Furthermore, NO_3−N concentrations in the ecosystem output were mainly governed by runoff conditions. Strong rainstorms were responsible for NO_3−N and partly NH_4−N pulses to the stream water. Soil acidity appeared as a further control of the DIN and DIP dynamics in the organic layer, since DIN and DIP concentrations were positively related to the pH in the organic layer. In the studied tropical montane forest, nutrient cycles were tight for DIN and DIP with low ecosystem input and output, except for a short period at the end of the year, when concentrations in stream water in-

creased. In contrast, the export of DIS partly exceeded the input by wet deposition because of mineral weathering in the subsoil.

Summarizing, the findings of my study show that the hydrologic conditions of the studied tropical montane forest have a major impact on the dynamics of C, N, P, and S within the ecosystem. My results further indicate a tight nutrient cycle for C, N, and P with relatively low input and output fluxes under non−storm conditions, whereby the gaseous N fluxes were not considered. This balance is short−time interrupted during rainstorm events with associated strongly elevated water fluxes (stormflow), which cause an increased output of DON, DOC, NO_3−N and eventually NH_4−N. However, since other studies showed that the flushing of elements only occurs in the first phase of storm events and lasts only for a very short time period (hours), one might assume that the associated total nutrient loss is low. To quantify the nutrient loss during storm events, a short−interval sampling during storm events is required.

6 References

Aerts R (2002) The role of various types of mycorrhizal fungi in the nutrient cycling and plant competition. In: Van der Heijden MGA & Sanders IR (Eds.) Mycorrhizal Ecology (pp 345−372). Ecol. Stud. 157. Springer−Verlag, New York

Aerts R & Chapin FS (2000) The mineral nutrition of wild plants revisited: a re−evaluation of processes and patterns. Adv. Ecol. Res. 30: 1−67

AG Boden (1994) Bodenkundliche Kartieranleitung. 4. Aufl., Hannover, Schweizerbart´sche Verlagsbuchhandlung

Aldridge MC, Billington M, Edwards M & Laidlaw R (1997) Tropical Montane Cloud Forests: An urgent priority of conservation. WCMC Biodiversity Bulletin no. 2, World Conservation Monitoring Centre, Cambridge, UK

Alewell C, Mitchell M, Likens GE & Krouse R (1999) Sources of stream sulfate at the Hubbard Brook Experimental Forest: long−term analysis using stable isotopes. Biogeochem. 44: 281–299

Asbury CE, McDowell WH, Trinidad−Pizarro R & Berrios S (1994) Solute deposition from cloud water to the canopy of a Puerto Rican montane forest. Atmos. Environ. 28: 1773– 1780

Balslev H & Øllgaard B (2002) Mapa de vegetación del sur de Ecuador. In: Aguirre MZ, Madsen JE, Cotton E & Balslev H (Eds.) Botánica Austroecuatoriana. Estudios sobre los recursos vegetales en las provincias de El Oro, Loja y Zamora−Chinchipe (pp 51–64). Ediciones Abya−Yala, Quito, Ecuador

Barthlott W, Lauer W & Placke A (1996) Global distribution of species diversity in vascular plants: Towards a world map of phytodiversity. Erdkunde 50: 317–327

Bendix J & Lauer W (1992) Die Niederschlagsjahreszeiten in Ecuador und ihre klimadynamische Interpretation: Erdkunde 46: 118−134

Bentley B (1987) Nitrogen fixation by epiphylls in a tropical rainforest. Annals of the Missouri Botanical Garden 74: 234–241

Bentley B & Carpenter E (1980) Effects of desiccation and rehydration on nitrogen fixation by epiphylls in a tropical rainforest. Microb. Ecol. 6: 109–113

Beven KJ, Lamb R, Quinn PF, Romanowicz R & Freer J (1995) TOPMODEL. In: Singh VP (Ed.) Computer Models of Watershed Hydrology. Water Resour. Publ.: 627−668

Bonell M, Barnes CJ, Grant CR, Howard A & Burns J (1998) Oxygen and Hydrogen Isotopes in Rainfall−Runoff Studies. In: Kendall C & McDonnell JJ (Eds.). Isotope Tracers in Catchment Hydrology (pp 347−390). Elsevier, Amsterdam

Bormann FH, Likens GE, Johnson NM & Pierce RS (1963) Hydrologic−mineral cycle interaction in a small forested watershed. Bull. Ecol. Soc. Amer. 44(3): 86

Bremer H (1999) Die Tropen. Geographische Synthese einer fremden Welt im Umbruch. Borntraeger, Berlin, Stuttgart

Brinkmann (1985) Studies on hydrobiogeochemistry of a tropical lowland forest system. Geojournal 11: 89–101

Brown VA, McDonnell JJ, Burns DA & Kendall C (1999) The role of event water, a rapid shallow flow component, and catchment size in summer stormflow. J. Hydrol. 217: 171−190

Bruijnzeel LA (1990) Hydrology of Moist Tropical Forests and Effects of Conversion: A State of Knowledge Review. Unesco, Division of Water Sciences, International Hydrological Programme, Paris, France

Bruijnzeel LA (2001) Hydrology of tropical montane cloud forests: A Reassessment: Land Use and Water Resources Research 1: 1−18

Bruijnzeel LA & Hamilton LS (2000) Decision time for cloud forests. IHP Humid Tropics Programme Series no. 13, IHP−UNESCO, Paris, Amsterdam and WWF International, Gland, 44 pp

Bruijnzeel LA & Proctor J (1995) Hydrology and biogeochemistry of tropical montane cloud forests: What do we really know? In: Juvik JO & Scatena FN (Eds.) Tropical Montane Cloud Forests (pp 38–78). Ecol. Stud. 110. Springer−Verlag, New York

Bruijnzeel LA, Waterloo MJ, Proctor J, Kuiters AT & Kotterink B (1993) Hydrological observations in montane rain forests on Gnung Silam, Sabah, Malaysia, with special reference to the 'Massenerhebung' effect. J. Ecol. 81: 145–167

Bubb P, May I, Miles L, Sayer J (2004) Cloud Forest Agenda. UNEP–WCMC, Cambridge, UK

Buffam I, Galloway JN, Blum LK & McGlathery KJ (2001) A stromflow/baseflow comparison of dissolved organic matter concentrations and bioavailability in an Appalachian stream. Biogeochem. 53: 269–306

Burt TP (1986) Runoff processes and solutional denudation on humid temperate hillslopes. In S.T. Trudgill (ed.). Solute Processes and Landforms. Wiley, Chichester, pp. 193−249

Bushaw KL, Zepp RG, Tarr MA, Schulz−Jander D, Bourbonniere RA, Hodson E, Miller WL, Bronk DA & Moran MA (1996) Photochemical release of biologically available nitrogen from aquatic dissolved organic matter. Nature 381: 404–407

Buttle JM (1998) Fundamentals of small catchment hydrology. In: Kendall C & McDonnell JJ (Eds). Isotope Tracers in Catchment Hydrology (pp 1−50). Elsevier, Amsterdam

Buttle JM & McDonald DJ (2000) Soil macroporosity and infiltration characteristics of a forest podzol. Hydrol. Process. 14: 831−848

Campbell JL, Hornbeck JW, McDowell WH, Buso DC, Shanley JB & Likens GE (2000) Dissolved organic nitrogen budgets for upland, forested ecosystems in New England. Biogeochem. 49: 123– 142

Campling P, Gobi A, Beven K & Feyen J (2002) Rainfall–runoff modelling of a humid tropical catchment: the TOPMODEL approach. Hydrol. Process. 16: 231−253

Casper M (2002) Die Identifikation hydrologischer Prozesse im Einzugsgebiet des Dürreychbaches (Nordschwarzwald). Mitteilungen Inst. f. Wasserwirtschaft u. Kulturtechnik, Univ. Karlsruhe, Heft 210

Cavelier J & Goldstein G (1989) Mist and fog interception in elfin cloud forests in Colombia and Venezuela. J. Trop. Ecol. 5: 309−322

Cavelier J, Jaramillo M, Solis D & León D (1997) Water balance and nutrient inputs in bulk precipitation in tropical montane cloud forests in Panama. J. Hydrol. 193: 83–96

Chappell NA, Franks SW & Larenus J (1998) Multi−scale permeability estimation for a tropical catchment. Hydrol. Process. 12: 1507−1523

Clark KL, Nadkarni NM, Schaefer D & Gholz HL (1998) Atmospheric deposition and net retention of ions by the canopy in a tropical montane forest, Monteverde, Costa Rica. J. Trop. Ecol. 14: 27–45

Coleman ML, Shepherd TJ, Durham JJ, Rouse JE & Moore GR (1982) Reduction of water with zinc for hydrogen isotope analysis. Anal. Chem. 54: 993−995

Cortina J, Romanyá J & Vallejo VR (1995) Nitrogen and phosphorus leaching from the forest floor of a mature Pinus radiata stand. Geoderma 66: 321−330

Coxson DS (1990) Nutrient release from epiphytic bryophytes in tropical montane rain forest (Guadaloupe). Can. J. Bot. 69: 2122–2129

Cuevas E & Medina E (1986) Nutrient dynamics within Amazonian forests. 2. Growth, nutrient availability and leaf litter decomposition. Oecologia 76: 222–235

Currie WS, Aber JD, McDowell WH, Boone RD & Magill AH (1996) Vertical Transport of dissolved organic C and N under long−term amendments in pine and hardwood forests. Biogeochem. 35: 471−505

Daugherty HE (1973) The Montecristo cloud−forest of El Salvador − A chance for protection. Biological Conservation 5(1): 227−230

Douglas I (1977) Humid landforms. The Massachusetts Institute of Technology Press, Cambridge, Massachusetts, 288 pp.

Dunne T (1978) Field studies of hillslope flow processes. In: Kirby MJ (Ed). Hillslope hydrology (pp 227−293). New York

Eklund TJ, McDowell WH & Pringle CM (1997) Seasonal variation of tropical precipitation chemistry: La Selva, Costa Rica. Atmos. Environ. 31: 3903–3910

Elsenbeer H. (2001) Hydrologic flowpaths in tropical rainforest soilscapes—a review. Hydrol. Process. 15: 1751–1759

Fleischbein K (2004) Wasserhaushalt eines Bergwaldes in Ecuador: experimenteller und modellhafter Ansatz auf Einzugsgebietsebene. Ph.D. thesis, Justus–Liebig–University Gießen, Germany

Förstel H (1996) Hydrogen and oxygen isotopes in soil water: use of ^{18}O and D in soil water to study the soil−plant−water system. In: Boutton TW (Ed). Mass spectrometry of soils (pp 285−310). Dekker, New York

Foley JA, Botta A, Coe MT, Costa MH (2002) El Nino−southern oscillation and the climate, ecosystems and rivers of Amazonia. Glob. Biogeochem. Cyc. 16(4): 1−20.

Forti MC & Neal C (1992) Hydrochemical cycles in tropical rainforests: an overview with emphasis on central Amazonia. J. Hydrol. 134: 103−115

Frangi JL & Lugo AE (1985) Ecosystem dynamics of a subtropical floodplain forest. Ecol. Monogr. 55: 351–369

Fritsch U & Katzenmaier D (2001) Bericht Umweltbundesamt, http://www.umweltbundesamt.de/wasser/veroeffentlich/download/29724508/

Gaskin GJ & Miller JD (1996) Measurement of soil water content using a simplified impedance measuring technique. J.Agric. Res. 63: 153−160

Genereux DP & Hooper RP (1998) Oxygen and Hydrogen Isotopes in Rainfall−Runoff Studies. In: Kendall C & McDonnell JJ (Eds). Isotope Tracers in Catchment Hydrology (pp 319−346). Elsevier, Amsterdam

Grubb PJ (1995) Mineral nutrition and soil fertility in tropical rain forests. In: Lugo AE & Lowe C (Eds.) Tropical Forests: Management and Ecology (pp 308–330). Ecol. Stud. 112. Springer−Verlag, New York

Guehl JM (1983) La dynamique de l'eau dans le sol mesuree in situ dans un systeme mixte en for−et primaire. pp. 53−71 in C. Bailly (ed.). Le Projet ECEREK. Centre Technique Forestier Tropical, Nogent−sur−Marne, France

Guggenberger G & Kaiser K (2003) Dissolved organic matter in soils: challenging the paradigm of sorptive preservation. Geoderma 113: 293– 310

Guggenberger G & Zech W (1993) Dissolved organic carbon control in acid forest soils of the Fichtelgebirge (Germany) as revealed by distribution patterns and structural composition analyses. Geoderma 59: 109–129

Guggenberger G & Zech W (1994) Composition and dynamics of dissolved organic carbohydrates and lignindegradation products in two coniferous forests, N.E. Bavaria, Germany. Soil Biol. Biochem. 26: 19–27

Guggenberger G, Glaser B & Zech W (1994) Heavy metal binding by hydrophobic and hydrophilic dissolved organic carbon fractions in a spodosol A and B horizon. Water Air Soil Pollut. 72: 111–127

Hafkenscheid R (2000) Hydrology and Biogeochemistry of tropical montane rain forests of contrasting stature in the Blue Mountains, Jamaica. Ph. D. thesis, Free University of Amsterdam

Hagedorn F, Schleppi P, Bucher J & Flühler H (2001) Retention and leaching of elevated N Deposition in a forest ecosystem with Gleysols. Water Air Soil Pollut. 129: 119–142

Hagedorn F, Schleppi P, Waldner P & Flühler H (2000) Export of dissolved organic carbon and nitrogen from Gleysol dominated catchments – the significance of water flow paths. Biogeochem. 50: 137–161

Hamilton LS, Juvik JO & Scatena FN (1995) The Puerto Rico tropical cloud forest symposium: introduction and workshop synthesis. In: Hamilton LS, Juvik JO & Scatena FN (Eds). Tropical montane cloud forests (pp 1−23). Ecol. Stud. 110. Springer−Verlag, New York

Heaton THE & Chenery CA (1990) Use of zinc turnings in the reduction of water to hydrogen for isotopic analysis. Nerc Isotope Geoscience Laboratory Report 24.

Hedin LO, Amesto JJ & Johnson AH (1995) Patterns of nutrient loss from unpolluted, old−growth temperate forests: evaluation of biochemical theory. Ecol. 76: 493–509

Hedin LO, Vitousek PM & Matson PA (2003) Nutrient losses over four million years of tropical forest development. Ecol. 84(9): 2231–2255

Herrera R, Jordan CF, Klinge H & Medina E (1978) Amazon ecosystems: their structure and functioning with particular emphasis on nutrients. Interciencia 3: 223–232

Herwitz SR (1986) Episodic stemflow inputs of magnesium and potassium to a tropical forest floor during heavy rainfall events. Oecologia 70: 423 − 425

Homann PS, Mitchell MJ, van Miegroet H & Cole DW (1990) Organic sulfur in throughfall, stem flow, and soil solutions from temperate forests. Can. J. For. Res. 20: 1535–1539

Homeier J, Dalitz H & Breckle S−W (2002) Waldstruktur und Baumartendiversität im montanen Regenwald der Estación Cientifica San Francisco in Südecuador. Berichte der Reinhold−Tüxen−Gesellschaft 14: 109−118

Houle D, Carignan R & Ouimet R (2001) Soil organic sulfur dynamics in a coniferous forest. Biogeochem. 53: 105−124

Huang WZ & Schoenau JJ (1998) Fluxes of water−soluble nitrogen and phosphorus in the forest floor and surface mineral soil of a boreal aspen stand. Geoderma 81: 251−264

IAEA (2001) GNIP Maps and Animations, International Atomic Energy Agency, Vienna. Accessible at (http://isohis.iaea.org).

Jardine PM, Wilson GV, McCarthy JF, Luxmoore RJ, Tayler DL & Zelazny LW (1990) Hydrogeochemical processes controlling transport of dissolved organic carbon through a forested hillslope. J. Contam. Hydrol. 6: 3–19

Jemison JM & Fox RH (1992) Estimation of zero−tension pan lysimeter collection efficiency. Soil Sci. 154: 85–94

Jordan CF (1989) An Amazonian Rain Forest. UNESCO, Paris; and Parthenon, Carnforth, UK

Jordan CF & Heuveldop J (1981) The water budget of an Amazonian rainforest. Acta Amazonica 11: 87–92

Kaiser K & Guggenberger G (2003) Biogeochemie gelösten organischen Schwefels in zwei Waldökosystemen. Mitteilgn. Dtsch. Bodenk. Gesellsch 91(1): 506−509

Kaiser K & Zech W (1998) Soil DOM sorption as influenced by organic and sesquioxide coatings and sorbed sulfate. Soil Sci. Soc. Am. J. 62: 129–136

Kaiser K, Guggenberger G & Haumaier L (2003) Organic phosphorus in soil water under a European beech (Fagus sylvatica L.) stand in northeastern Bavaria, Germany: seasonal variability and changes with soil depth. Biogeochem. 66 (3): 287−310

Kaiser K, Guggenberger G & Zech W (1996) Sorption of DOM and DOM fractions to forest soils. Geoderma 74: 281−303

Kaiser K, Guggenberger G & Zech W (2000) Organically bound nutrients in dissolved organic matter fractions in seepage and pore water of weakly developed forest soils Acta Hydrochim. Hydrobiol. 28: 411−419

Kalbitz K, Solinger S, Park J−H, Michalzik B & Matzner E (2000) Controls on the dynamics of dissolved organic matter in soils: a review. Soil Sci. 165: 277– 304

Kendall C & Caldwell EA (1998) Fundamentals of isotope geochemistry. In: Kendall C & McDonnell JJ (Eds). Isotope Tracers in Catchment Hydrology (pp 51−86). Elsevier, Amsterdam

Kendall C, Shanley JB & McDonnell JJ (1999) A hydrometric and geochemical approach to test the transmissivity feedback hypothesis during snowmelt. J. Hydrol. 219: 188−205

Kennedy VC, Kendall C, Zellweger GW, Wyerman TA & Avanzino RJ (1986) Determination of the components of stormflow using water chemistry and environmental isotopes, Mattole River basin, California. J. Hydrol. 84(1−2): 107−140

Kilham K (1990) Nitrification in forest soils. Plant Soil 128: 31–44

Kinner DA & Stallard RF (2004) Identifying storm flow paths in a rainforest catchment using hydrological and geochemical modelling. Hydrol. Process. (in press)

Kirby MJ & Chorley RJ (1967) Throughflow, overland flow and erosion. Bulletin of the International Association of Scientific Hydrology 12: 5−21

Lewis WM, Melack JM, McDowell WH, McClain M & Richey JE (1999) Nitrogen yields from undisturbed watersheds in the Americas. Biogeochem. 46: 149–162

Likens GE & Bormann FH (1995) Biogeochemistry of a Forested Ecosystem, 2nd edn. Springer−Verlag, New York

Likens GE & Eaton JS (1970) A polyurethane stemflow collector for trees and shrubs. Ecol. 51: 938–939

Likens GE, Driscoll CT, Buso DC, Mitchell MJ, Lovett GM, Bailey SW, Siccama TG, Reiners WA & Alewell C (2002) The biogeochemistry of sulfur at Hubbard Brook. Biogeochem. 60: 235–316

Likens GE, Edgerton ES & Galloway JN (1983) The composition and deposition of organic carbon in precipitation. Tellus 35B: 16−24

Lin T−C, Hamburg SP, King HB & Hsia Y−J (2000) Throughfall patterns in a subtropical rain forest of Northeastern Taiwan. J. Environ. Qual. 29(4): 1186– 1193

Lindberg SE, Lovett GM, Richter DD & Johnson DW (1986) Atmospheric deposition and canopy interactions of major ions in a forest. Science 231: 141–145

Litherland M, Aspden JA & Jemielita RA (1994) The metamorphic belts of Ecuador: Overseas Memoir of the British Geological Survey 11

Lloyd CR & Marques−Filho ADO (1988) Spatial variability of throughfall and stemflow measurements in Amazonian rain forest. Agricult. For. Meteorol. 42: 63−73

Lodge DJ, McDowell WH & McSwiney CP (1994) The importance of nutrient pulses in tropical forests. Trends Ecol. Evol. 9(10): 384−387

Lovett GM & Lindberg SE (1984) Dry deposition and canopy exchange in a mixed oak forest as determined by analysis of throughfall. J. Appl. Ecol. 21: 1013−1027

Lovett GM, Weathers KC & Sobczak WV (2000) Nitrogen saturation and retention in forested watersheds of the Catskill Mountains, New York. Ecol. Appl. 10: 73–84

Malhi Y & Grace J (2000) Tropical forests and atmospheric carbon dioxide. Trends in Ecology and Evolution 15: 332–337

Matzner E (2004) Biogeochemistry of forested catchments in a changing environment: a German case study. Ecological Studies 172. Springer, in press

Matzner E & Ulrich B (1981) Bilanzierung jährlicher Elementflüsse in Waldökosystemen im Solling. Z. Pflanzenernähr. Bodenk. 144: 660 681

McDowell WH (1998) Internal nutrient fluxes in a Puerto Rican rain forest. J. Trop. Ecol. 14: 521−536

McDowell WH (2003) Dissolved organic matter in soils — future directions and unanswered questions. Geoderma 113: 179− 186

McDowell WH & Asbury CE (1994) Export of carbon, nitrogen, and major ions from three tropical montane watersheds. Limnol. Oceanogr. 39: 111–125

Michalzik B & Matzner E (1999) Dynamics of dissolved organic nitrogen and carbon in a Central European Norway spruce ecosystem. Eur. J. Soil Sci. 50: 579−590

Michalzik B, Kalbitz K, Park J−H, Solinger S & Matzner E (2001) Fluxes and concentrations of dissolved organic carbon and nitrogen − a synthesis for temperate forests. Biogeochem. 52: 173−205

Michalzik B, Küsel K, Solinger S & Matzner E (1998) Dynamics of DOC and DON in forest soils. Mitteilgn. Dtsch. Bodenk. Gesellsch. 87: 225−236

Mitchell MJ (2001) Linkages of nitrate losses in watersheds to hydrological processes. Hydrol. Process. 15: 3305–3307

Mitchell MJ, David MD, Maynard DG & Telang SA (1986) Sulfur constituents in soils and streams of a watershed in the Rocky Mountains of Alberta. Can. J. For. Res. 16:315−320

Möller A (2001) Soil organic matter and organic nutrient transformation in soils of the highlands of northern Thailand. Ph. D. thesis, University of Bayreuth

Møller J, Miller M & Kjøller A (1999) Fungal–bacterial interaction on beech leaves: influence on decomposition and dissolved organic carbon quality. Soil Biol. Biochem. 31: 367–374

Molicová H, Grimaldi M, Bonell M & Hubert P (1997) Using TOPMODEL towards identifying and modelling the hydrological patterns within a headwater, humid, tropical catchment. Hydrol. Process. 11: 1169−1196

Mulholland PJ, Wilson GV & Jardine PM (1990) Hydrogeochemical response of a forested watershed to storms: effects of preferential flow along shallow and deep pathways. Water Resour. Res. 26: 3021−3036

Neff JC, Chapin FS & Vitousek PM (2003) Breaks in the cycle: dissolved organic nitrogen in terrestrial ecosystems. Front. Ecol. Environ. 1(4): 205−211

Parker GG (1983) Throughfall and stemflow in the forest nutrient cycle. Adv. Ecol. Res. 13: 57−133

Paulsch A (2002) Development and Application of a Classification System for Undisturbed and Disturbed Tropical Montane Forests based on Vegetation Structure. Ph. D. thesis, University of Bayreuth

Paulsch A, Schneider R & Hartig K (2001) Land−use induced vegetation structure in a montane region of Southern Ecuador. Die Erde 132 (1): 93−102

Perakis SS & Hedin LO (2001) Fluxes and fate of inorganic nitrogen in an unpolluted old−growth rainforest in southern Chile. Ecol. 82: 2245–2260

Perakis SS & Hedin LO (2002) Nitrogen loss from unpolluted South American forests mainly via dissolved organic compounds. Nature 415: 416–419

Prechtel A, Alewell C, Armbruster M, Bittersohl J, Cullen JM, Evans CD, Helliwell R, Kopácek J, Marchetto A, Matzner E, Meesenburg H, Moldan F, Moritz K, Veselý J & Wright RF (2001) Response of sulphur dynamics in European catchments to decreasing sulphate deposition. Hydrology and Earth System Sciences 5(3): 311–325

Proctor J (1987) Nutrient cycling in primary and old secondary rainforests. Appl. Geogr. 7, 135−152

Qualls RG & Haines BL (1992) Biodegradability of dissolved organic matter in forest throughfall, soil solution, and stream water. Soil Sci. Soc. Am. J. 56: 578–586

Qualls RG, Haines BL & Swank WT (1991) Fluxes of dissolved organic nutrients and humic substances in a deciduous forest. Ecol. 72: 254–266

Qualls RG, Haines BL, Swank WT & Tyler SW (2002) Retention of soluble organic nutrients by a forested ecosystem. Biogeochem. 61: 135–171

Rhode A (1998) Snowmelt−dominated systems. In: Kendall C & McDonnell JJ (Eds). Isotope Tracers in Catchment Hydrology (pp 391–434). Elsevier, Amsterdam

Robertson GP (1982) Nitrification in forested ecosystems. Philisophical transactions of the Royal Society London Series B296, 445– 457

Sanchez PA (1976) Properties and management of soils in the tropics. J. Wiley, New York, 618 pp.

Savric I (2001) Einflussfaktoren auf die Bindung und Mobilität organischer und anorganischer Stoffe in kontaminierten Rieselfeldböden. Ph. D. thesis, Berlin University of Technology

Scatena FN (1990) Watershed scale rainfall interception on two forested watersheds in the Luquillo mountains of Puerto Rico. J. Hydrol. 113: 89–102

Schellekens J, Scatena FN, Bruijnzeel LA, van Dijk AIJM, Groen MMA & van Hogezand RJP (2004) Stormflow generation in a small rainforest catchment in the Luquillo Experimental Forest, Puerto Rico. Hydrol. Proc. 18(3): 505–530

Schindler DW, Bayley SE, Curtis PJ, Parker BR, Stainton MP & Kelly CA (1992) Natural and man−caused factors affecting the abundance and cycling of dissolved organic substances in precambrian shield lakes. Hydrobiologia 229: 1−21

Schrumpf M (2004) Biogeochemical investigations in old growth and disturbed forest sites at Mount Kilimanjaro. Ph. D. thesis, University of Bayreuth

Sklash MG & Farvolden RN (1979) The role of groundwater in storm runoff. J. Hydrol. 43: 45−65

Sklash MG, Stewart MK & Pearce AJ (1986) Storm runoff generation in humid headwater catchments. 2. A case study of hillslope and low−order stream response. Water Resour. Res. 22: 1273–1282

Solinger S, Kalbitz K & Matzner E (2001) Controls on the dynamics of dissolved organic carbon and nitrogen in a Central European deciduous forest. Biogeochem. 55: 327–349

Sollins P, Robertson GP & Uehara G (1988) Nutrient mobility in variable− and permanent−charge soils. Biogeochem. 6: 181–199

Stadtmüller T (1987) Cloud Forests in the Humid Tropics. A Bibliographic Review. The United Nations University, Tokyo and Centro Agronomico Tropical de Investigacion y Ensenanza, Turrialba, Costa Rica, 81 pp.

Stark NM & Jordan CF (1978) Nutrient retention by root mat of an Amazonian rain forest. Ecol. 59: 434–437

StatSoft Inc. (2000) STATISTICA für Windows. Tulsa, OK

Steinhardt U (1979) Untersuchungen über den Wasser− und Nährstoffhaushalt eines andinen Wolkenwaldes in Venezuela. Göttinger Bodenkundl. Ber. 56

Stevenson FJ & Cole MA (1999) Cycles of Soil. Carbon, Nitrogen, Phosphorus, Sulfur, Micronutrients. 2nd edn. J. Wiley & Sons Inc., New York, 427 pp

Tamm CO (1991) Nitrogen in terrestrial ecosystems. Springer−Verlag, Berlin, Germany

Tanner EVJ, Vitousek PM & Cuevas E (1998) Experimental investigations of nutrient limitations of forest growth on wet tropical mountains. Ecol. 79: 10−22

Thurman EM (1985) Organic geochemistry of natural waters. W. Junk, Boston

Tipping E, Woof C, Rigg E, Harrison AF, Ineson P, Taylor K, Benham D, Poskitt J, Rowland AP, Bol R & Harkness DD (1999) Climatic influences on the leaching of dissolved organic matter from upland UK moorland soils, investigated by a field manipulation experiment. Environ. Internat. 25: 83–95

Ulrich B (1981) Theoretische Betrachtungen des Ionenkreislaufs in Waldökosystemen. Z. Pflanzenernähr. Bodenk. 144: 647−659

USDA−NRCS (United States Department of Agriculture – National Resource Conservation Service) (1998) Keys to Soil Taxonomy 8th edition Pocahontas Press, Washington DC

Van Breemen N (2002) Natural organic tendency. Nature 415: 381–382

Vance GF & David MB (1989) Effect of acid treatment on dissolved organic carbon retention by a spodic horizon. Soil Sci. Soc. Am. J. 53: 1242–1247

Vance ED & Nadkarni NM (1990) Microbial biomass and activity in canopy organic matter and the forest floor of a tropical cloud forest. Soil Biol. Biochem. 22: 677–684

Veldkamp E & O'Brien JJ (2000) Calibration of a Frequency Domain Reflectometry Sensor for Humid Tropical Soils of Volcanic Origin. Soil Sci. Soc. Am. J. 64(5): 1549−1553

Veneklaas EJ (1990) Nutrient fluxes in bulk precipitation and throughfall in two montane tropical rain forests, Colombia. J. Ecol. 78: 974–992

Vitousek PM & Sanford RL (1986) Nutrient cycling in moist tropical forest. Ann. Rev. Ecol. System. 17: 137−167

Ward RC (1984) On the response to precipitation of headwater streams in humid areas. J. Hydrol. 74: 171−189

Whitehead HL & Feth JH (1964) Chemical composition of rain, dry fallout and bulk precipitation at Menlo Park, California, 1957−1959. J. Geophys. Res. 69: 3319–3333

Wilcke W, Valladarez H, Stoyan R, Yasin S, Valarezo C & Zech W (2003) Soil properties on a chronosequence of landslides in montane rain forest, Ecuador. Catena 53: 79−95

Wilcke W, Yasin S, Abramowski U, Valarezo C & Zech W (2002) Nutrient storage and turnover in organic layers under tropical montane rain forest in Ecuador. Eur. J. Soil Sci. 53: 15–27

Wilcke W, Yasin S, Valarezo C & Zech W (2001) Change in water quality during the passage through a tropical montane rain forest in Ecuador. Biogeochem. 55: 45–72

Wilson GV, Jardine PM, Luxmoore RJ, Zelasny LW, Todd DE & Lietzke DA (1991) Hydrochemical processes controlling subsurface transport from an upper subcatchment of Walker Branch Watershed during storm events. 2. Solute transport processes. J. Hydrol. 123: 317−336

Wondzell SM & Swanson FJ (1996) Seasonal and storm dynamics of the hyporheic zone of a 4th−order mountain stream II: Nitrogen cycling. J. North Am. Benth. Soc. 15(1): 20–34

Wuethrich B (1993) Forests in the clouds face stormy future. Science News 144(2): 23

Yasin S (2001) Water and Nutrient Dynamics in Microcatchments under Montane Rain Forest in the South Ecuadorian Andes. Ph. D. thesis, University of Bayreuth

Yavitt JB & Fahey TJ (1986) Litter decay and leaching from the forest floor in Pinus contorta (lodgepole pine) ecosystems. J. Ecol. 74: 525–545

Zadroga F (1981) The hydrological importance of a montane cloud forest area of Costa Rica. In: Lal R & Russell EW (Eds.) Tropical Agricultural Hydrology. J. Wiley, New York, pp. 59−73

Zech W, Guggenberger G, Haumaier L, Pöhhacker R, Schäfer D, Amelung W, Miltner A, Kaiser K & Ziegler F (1996) Organic matter dynamics in forest soils of temperate and tropical ecosystems. In: Piccolo A (Ed.) Humic substances in terrestrial ecosystems (pp 101–170). Elsevier Science BV, Amsterdam

Zöttl HW (1987) Stoffumsätze in Ökosystemen des Schwarzwaldes. Forstw. Cbl 106: 105−114

Zsolnay A, Baigar E, Jimenez M, Steinweg B & Saccomandi F (1999) Differentiating with fluorescence spectroscopy the sources of dissolved organic matter in soils subjected to drying. Chemosphere 38: 45–50

Erklärung

Hiermit erkläre ich, dass ich die vorliegende Arbeit selbständig verfasst und keine anderen als die von mir angegebenen Quellen und Hilfsmittel benutzt habe.

Ferner erkläre ich, dass ich weder an der Universität Bayreuth noch anderweitig versucht habe, mit oder ohne Erfolg eine Dissertation einzureichen oder mich der Doktorprüfung zu unterziehen.

Bayreuth, 18. August 2004

Rainer Goller