Topography strongly affects atmospheric deposition and canopy exchange processes in different types of wet lowland rainforest, Southwest Costa Rica

F. Hofhansl · W. Wanek · S. Drage · W. Huber ·
A. Weissenhofer · A. Richter

Abstract Bulk precipitation and throughfall were collected in a wet lowland rainforest in SW Costa Rica on an event basis to allow modelling the contributions of dry deposition and canopy exchange to nutrient inputs and internal cycling of nutrients. Estimates based on bulk precipitation underestimated total atmospheric deposition to tropical rainforests by up to 10-fold ignoring the contributions of dry deposition. Canopy exchange contributed most of the aboveground inputs to the forest soil of Na^+, about half for K^+, 10% for P and Mg^{2+} and negligible for N, C and other elements. Tree species composition did not account for the differences found in net throughfall between forest sites, and vegetation structure (plant area index) had only a small effect on net throughfall. Forest regrowth affected net throughfall through reduced soil fertility and differences in leaf traits. Topography most significantly affected net throughfall via increased dry deposition at sites of higher elevation and via soil fertility and increased canopy exchange at down slope sites.

Keywords Canopy exchange · Dry deposition · Nutrient cycling · Secondary succession · Topography

F. Hofhansl · W. Wanek (✉) · S. Drage · A. Richter
Department of Chemical Ecology and Ecosystem
Research, University of Vienna, Althanstrasse 14,
1090 Vienna, Austria
e-mail: wolfgang.wanek@univie.ac.at

W. Huber · A. Weissenhofer
Department of Palynology and Structural Botany,
University of Vienna, Rennweg 14, 1030 Vienna, Austria

Introduction

Tropical forests are of global significance to climate because of their ability to alter the global water and carbon cycles through the exchange of energy, water and trace gases (Beringer et al. 2002; Fisch et al. 2004). They contribute significantly to the world's carbon budget (Clark et al. 2001a), accounting for 32–36% of terrestrial net primary production (Field et al. 1998; Melillo et al. 1993), and about 59% of the global carbon pool in forests is stored in tropical regions (Dixon 1994). Net primary production (NPP) of tropical forests is strongly controlled by climate (temperature, precipitation) (Schuur 2003). This general pattern is modified by two other factors, soil fertility and dry season length. Both have been shown to affect tree species composition, aboveground biomass and wood density across regional scales, e.g. across the Amazon basin, while NPP was only related to soil nutrient availability (Baker et al. 2004a, b; Malhi et al. 2004; ter Steege et al. 2006). Moreover, nutrient limitation of forest NPP has been conclusively demonstrated in Hawaii across wide

climatic gradients (precipitation, altitude and/or temperature) but also along substrate age gradients ranging from 100s to millions of years (Harrington et al. 2001; Martinelli 2004; Vitousek 2004). Nutrients are therefore a key determinant of forest productivity and of the functioning of tropical rainforests in the global carbon cycle. To understand current and future responses of tropical rainforests to global changes, external nutrient inputs, losses and internal cycling processes of nutrients have to be better quantified and understood.

In order to sustain high NPP there must be a relatively closed cycling of nutrients, since tropical soils are often highly weathered and thus are poor in nutrients. Continuous losses of nutrients from the system would lead to further nutrient depletion if not replenished by atmospheric deposition, weathering and N fixation (Vitousek 1984). While atmospheric deposition represents the sum of wet and dry deposition (and occult deposition from fog and clouds), most if not all studies in tropical forests have assessed atmospheric nutrient inputs only via bulk precipitation—the inputs by dry deposition being largely unknown. Nutrients are recycled via production and decomposition of dead plant material in litterfall and root turnover and through dissolution of elements in throughfall and stemflow. The contribution of root turnover and decay to internal nutrient cycling is almost unknown in tropical rainforests (Tobón et al. 2004a). In contrast, nutrient fluxes in litterfall and throughfall are relatively easy to measure and studies have produced a good general understanding of the relative roles of litterfall and throughfall. For instance, it was shown that the production of fine (and coarse) litter represents the major source of aboveground input of nutrients (e.g. N, P, Ca^{2+}) in tropical forests, while throughfall can account for up to 50% of the input of K^+ and other elements to the forest floor. Throughfall may therefore potentially comprise an important pathway for the internal recycling of nutrients aboveground (Chuyong et al. 2004; Schroth et al. 2001; Tobón et al. 2004b). It is, however, highly problematic to compare litterfall and throughfall directly in terms of internal nutrient cycling processes since external inputs and internal recycling processes contribute to throughfall fluxes. Elements in throughfall derive from three processes (Chapin et al. 2002; Hansen et al. 1994; Lovett and Lindberg 1984; Lovett et al. 1996; Parker 1983):

(1) Passage of incident precipitation through the canopy (wet or bulk precipitation),

(2) Wash-off of dry deposited materials such as particles and adsorbed gases ("dry deposition"), and

(3) Solute exchange between intercepted rainfall and canopy surfaces like foliage, woody parts, epiphytes and microorganisms ("canopy exchange").

Net throughfall corrects for bulk precipitation, but represents a mixture of dry deposition (2) and canopy exchange (3). It is therefore of great importance to differentiate their contributions to throughfall to allow comparisons between litterfall and canopy exchange as internal recycling processes, to investigate landscape scale controls on canopy exchange and dry deposition and to assess the significance of dry deposition for atmospheric deposition in tropical forests.

There have been several attempts to dissect the contribution of dry deposition and canopy exchange to throughfall chemistry, most thereof based on the canopy budget model (Staelens et al. 2008) and the multiple regression model (Lovett and Lindberg 1984; Lovett et al. 1996). In the canopy budget model dry deposition of base cations is estimated by a 'filtering approach' which is based on the assumption that aerosols containing K^+, Ca^{2+}, and Mg^{2+} are deposited equally onto the forest canopy as particles containing a tracer ion. Generally, Na^+ is used as a tracer ion because it is only deposited by particles and is assumed not to be affected by canopy exchange processes. However, Na^+ has been shown to be leached from mangrove canopies (Wanek et al. 2007) or to be taken up in canopies of tropical lowland rainforests (Tobón et al. 2004b). Moreover, several assumptions with unconstrained parameters are necessary to compute canopy exchange and dry deposition of NH_4^+, NO_3^- and H^+ (Staelens et al. 2008). The multiple regression model is based on the finding that net throughfall fluxes of dissolved nutrients are highly correlated with (i) the amount, duration and intensity of precipitation penetrating the canopy (positively related to canopy exchange) and (ii) the length of antecedent dry period being positively related to dry deposition (Lovett and Lindberg 1984; Lovett et al. 1996). A bias in this multiple regression model may arise as dry deposition can be

underestimated due to incomplete wash-off from canopy surfaces or overestimated through accumulated material in throughfall samplers during dry periods.

For temperate and boreal forests it was shown that throughfall chemistry mainly depends on factors like latitude, elevation, seasonality, proximity to the sea, species composition, forest age and local land use (Levia and Frost 2006; Parker 1983). In tropical rainforests the mechanistic understanding of throughfall hydrochemistry is much less developed, though effects of season, soil fertility, vegetation cover, tree species and vicinity to the sea were reported to affect dry deposition and canopy exchange of elements (Filoso et al. 1999; Schroth et al. 2001; Tobón et al. 2004b; Wanek et al. 2007, 2008).

Therefore this study investigated the following research questions:

(1) What are the major landscape scale controls of nutrient fluxes via net throughfall?

  a. season, topography and stage of succession
  b. plant (leaf) area index and tree species composition

(2) What is the magnitude of internal nutrient cycling via litterfall and canopy exchange?

(3) What is the contribution of dry deposition to external nutrient inputs by atmospheric deposition?

There is a particular gap in studies of net primary production and nutrient cycling (litterfall and throughfall) in areas of high precipitation and temperature, where forest net primary production was reported to decline (Schuur 2003). Moreover, most studies in high rainfall tropical rainforests were performed on nutrient poor Oxisols not on more fertile soils such as Inceptisols and Ultisols. This study was carried out in the Esquinas forest, Parque National Piedras Blancas, in SW Costa Rica. The study site is of particular interest for investigations on biogeochemistry, because forests are growing on nutrient rich Ultisols and Inceptisols due to ongoing tectonic land lift and moderate erosion (Gardner et al. 1992; Weissenhofer et al. 2008), tree diversity is high (140–210 spp. >10 cm dbh per hectare), mean annual precipitation (MAP) is >5800 mm and mean annual temperature (MAT) is about 28°C, representing a tropical wet lowland rainforest climate.

Material and methods

Study area

The study was conducted at the Tropical Research Station La Gamba (TRSLG; 8°42′03″ N, 83°12′06″ W, 70 m.a.s.l.) situated at the borders of the Piedras Blancas National Park, covering an area of approximately 148 km^2, reaching from the Golfo Dulce's seashore to the village of La Gamba, in the province Puntarenas in the Southwest of Costa Rica. The vegetation is characterized by wet tropical lowland rainforest (Holdridge 1967) extending from sea level up to 580 m altitude. Ultisols and Inceptisols are the major soil types typically found in the region (Vasquez 1989). Ultisols are strongly acidic and weathered soils, appearing especially on ridges and upper slopes, and are replaced by the moderately weathered, younger Inceptisols on lower slopes and ravines (Pamperl 2001).

Mean annual temperature was 28.1°C and ranged from 22.9 to 34.2°C on monthly average (Weber et al. 2001). Mean annual temperature inside the forest was 25.2°C, monthly averages ranging from 22.3 to 28°C, and humidity was high (97.7%) throughout the year (Weissenhofer 1996). Average annual bulk precipitation was 5810 ± 430 mm (1998–2007, Tropical Field Station La Gamba) with a short dry season from January to March (monthly mean precipitation approx. 180 mm), and a pronounced wet season from September to November (monthly mean precipitation about 800 mm).

Study design

Study plots where randomly established in three different forest types: primary ridge (PRi; 8°42′16″ N, 83°12′20″ W, 120 m.a.s.l.), primary ravine (PRa; 8°42′16″ N, 83°12′15″ W, 80 m.a.s.l.) and secondary ravine (SRa; 8°42′01″ N, 83°12′09″ W, 80 m.a.s.l.) forest. Secondary stands were formerly used as cacao plantations and for tree logging but have remained undisturbed for over 20 years. Plots were set up in triplicate either as squares of 20 × 20 m, separated by a distance of >10 m and divided into subplots of 10 × 10 m each, or as rectangles of 10 × 40 m subdivided into subplots of 10 × 10 m and separated by 10–30 m due to spatial restriction at the ridge site. Distance

between sites was approximately 1.5 km and each forest type was covered by 0.12 ha of survey area. Inside these subplots all trees above 10 cm diameter at breast height (dbh) were labelled and determined to species level. In one of the four subplots trees between 2.5 and 10 cm in dbh were labelled and determined to species level. Herbarium specimens were deposited in the National Herbarium at the Museo Nacional (San Jose, Costa Rica) and at the Biologiezentrum Linz (Upper Austria, Austria). A photo-herbarium is available at the TRSLG.

The plant (leaf) area index (PAI) was estimated by two techniques. (1) PAI within ±30° zenith angle (total 60°) above each throughfall collector was estimated by taking hemispherical photographs on days of uniform overcast skies. A digital camera (Nikon Coolpix 8100 with FC-E9 fisheye adaptor lens 183°) was balanced horizontally and directed to the geographic north. For evaluation of PAI we employed the software Hemiview (Delta-T-Devices 1999) and Sidelook (Nobis 2005) using the following parameters: solar transmission coefficients: transmissivity 0.4, diffuse proportion 0.45, external solar flux 1370 W/m^2; diffuse distribution: standard overcast sky; picture settings: threshold 182, radiant 911, rotation 0.0 (north) and magnetic declination 0.5 east. (2) PAI was estimated by light absorbance through the canopy using a SunScan probe v1.05 and the Sunshine Sensor BF3 (Delta-T Ltd, U.K.).

Sampling design

Soil samples were taken in triplicate from 5 × 5 m subplots situated in each plot. Samples were taken with a soil corer (8 cm diameter) to a depth of 5 cm after removal of the litter layer. Soils were sieved through a 2 mm sieve. Soil water content was measured by oven drying 5 g fresh weight of each sample at 80°C for 48 h. Nutrients were extracted from soil (2 g fresh weight) by adding 15 ml 10 mM $CaCl_2$, shaking for 1 h and filtering through ash-free filter paper (Whatman ashless, Grade 40: 8 µm pore size, Whatman International Ltd. Maidstone, England). Extracts were stabilized against microbial transformations by addition of phenyl mercuric acetate to 50 µM, and kept frozen until transported to our laboratory in Vienna. Soil bulk density was determined by measuring the dry weights of three replicates of 10 × 10 × 10 cm soil cubes from each plot.

Plots were equipped with collectors for litterfall (10 per forest type), throughfall (15 per forest type), stemflow (12 per forest type) and soil water (6 per forest type). Litterfall samplers were made from fine-mesh nylon (1 mm mesh size) mounted on 0.5 × 0.5 m PVC frames at 1 m height aboveground and placed in ten of twelve subplots per forest site to reduce sampling effort. Sampling of litterfall was done every 2 weeks throughout the study period. Litter samples were divided into two fractions: fine leaf litter and residual litter (consisting of twigs, reproductive material and fine unidentifiable material). Sampling for hydrochemistry was performed on an event basis ($n = 30$) from February to April and August to October 2005 after every rainstorm. Precipitation events below 5 mm were discarded in consideration of minimum canopy interception storage. Of the total 30 precipitation events collected, 12 were studied for solute concentrations and analyzed by multiple regression model and canopy budget model, and six were statistically investigated for hydrochemical differences between rainy and dry season. In this study we individually analyzed single collector samples to assess the heterogeneity of throughfall fluxes and its controls, and therefore did not combine them to compound samples for each event and plot. Bulk deposition samplers ($n = 2$) were placed in an open area surrounding the TRSLG to quantify the amount and chemistry of open precipitation. They consisted of plastic (PVC) tubes of 20.5 cm diameter and 100 cm length that were fixed to two steel posts using cable ties. Polyethylene bags (80 l, thickness 0.2 mm) were inserted and fixed with rubber straps, the opening being at 1.5 m height aboveground. The bags allowed rainwater collection of up to 300 mm per event. Polyethylene bags were displaced every month or when leaky or contaminated, and the first sampling event after renewal was discarded. Generally bulk deposition includes a small fraction of dry deposition. In this study the closure of bulk precipitation samplers between sampling periods reduced this small contribution of dry deposition to bulk deposition samplers and bulk deposition therefore largely represents wet deposition. To avoid contamination during and between sampling intervals collectors for throughfall were covered with a wire net (mesh width 10 mm) to keep litter and other material off the traps. Between each sampling period the collectors were kept closed with polyethylene

caps to avoid unintended collection of rainwater, accumulation of dry deposits and any contamination when no samples were taken. Collectors were opened every 3–7 days until a rainfall event occurred and was collected. Otherwise the collectors were kept closed. Throughfall collectors ($n = 45$) were set up according to the design described for bulk deposition collectors. Throughfall was sampled by placing the collectors in the middle of every subplot and also in the middle of each plot, so that every plot was equipped with five traps. After each rainfall event the total amount of water per collector was determined volumetrically using measuring cylinders. Two types of stemflow collectors ($n = 36$) were used for trees with diameter at breast height (dbh) greater and smaller than 10 cm. For trees <10 cm dbh 0.5 l polyethylene bottles were longitudinally cut on one side and mounted upside down around the stems. Bottles were sealed to the stem by sanitary silicone and connected to collection bottles (1–5 l, PE) using silicone tubing. Trees with a diameter >10 cm dbh were equipped with a flexible tubing (garden hose) cut in half longitudinally and fixed tightly around the tree trunks in a steeply sloped upward spiral in order to avoid overflow. The tubing was stapled to the tree trunk and silicone sealant was applied sealing the collar to the trunk to avoid stemflow losses. Collection vessels (allowing up to 25 l of stemflow sampling from large trees above 30 cm dbh) were connected to the flexible tubes when sampling was performed or disconnected between sampling events. The first event of stemflow collection was discarded to avoid contamination from injured bark and sanitary silicone. After each rainfall event total amount of water per collector was determined volumetrically using measuring cylinders. Soil water samples ($n = 9$) were taken on an event basis using ceramic soil suction tubes (USM tensiometers SKP-100) positioned to 10 cm soil depth. Suction tubes were connected to collector bottles that where evacuated with a hand operated vacuum pump to a pressure of 40 kPa.

Directly after sample collection the pH was measured in all water fractions at TRSLG using a Sentron ArgusX pH meter (Sentron, Roden, Netherlands). Due to technical problems only four rainfall events were measured for pH. From each collector two sample aliquots (15 ml) were then transferred into 20 ml HDPE vials and stabilized against microbial transformation by addition of $HgCl_2$ (30 μM end concentration, for TOC/TN analysis) or Hg-Phenyl acetate (30 μM end concentration, for ion chromatography) and stored at −20°C immediately after collection.

Chemical analyses

The following chemical analyses were performed at the Department of Chemical Ecology and Ecosystem Research, University of Vienna, Austria: Inorganic anions (Cl^-, NO_3^-, SO_4^{2-}, HPO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}) were analysed by HPLC (high pressure liquid chromatography, DX 500, Dionex, Vienna, Austria) and conductivity detection. Anions were separated on an anion exchange column (AS11, 4×250 mm, Dionex) using a linear KOH gradient (2–30 mM in 6 min, total run time 10 min). Cations were separated on a cation exchange column (CS16, 5×250 mm, Dionex) by an isocratic method with methanesulfonic acid as eluent (30 mM methanesulfonic acid for 26 min and 40°C). Data analysis was conducted with Chromeleon Version 6.70 Build 1820. NPOC (non-purgeable organic carbon) and TDN (total dissolved nitrogen) content of samples were determined using a TOC-V$_{CPH/CPN}$/TNM-1 analyzer (Shimadzu, Japan). DON was calculated by subtracting DIN (dissolved nitrate and ammonium) from measured TDN. The respective details on analytical performance (e.g. linearity, limit of quantification, precision) are presented in Supplementary Table 1.

Dried soil and litter samples were homogenized in a ball mill (Retsch MM2000) and aliquots (1.5–2.0 mg) were weighed into tin capsules for analysis of total carbon and nitrogen content by elemental analysis (EA 1110, CE Instruments). For phosphorus and cation analysis litter samples were first acid digested. Approximately 100 mg dried samples were wet digested with 5 ml nitric acid-perchloric acid mixture (HNO_3:$HClO_3$ 4:1) (Kolmer et al. 1951) in 25 ml glass flasks on a heating plate where the temperature was increased stepwise to 250°C and the final temperature held until a small residual volume was left in the glass flask. Samples were cooled to room temperature, and filled to 25 ml with high purity water. The digests were filtered and total phosphorus measured by colorimetric analysis using the phosphomolybdate blue method (Schinner

et al. 1996) and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) by atomic absorption spectrometry.

Calculations

Volume-weighted mean concentrations (VWM, Eq. 1) of each sampling collector were used to express solute concentration of throughfall and rainfall during the study period and were calculated as follows:

$$VWM = \frac{\sum_{i=1}^{n} (C_i * V_i)}{\sum_{i=1}^{n} V_i} \qquad (1)$$

Annual nutrient fluxes were calculated by multiplication of volume weighted mean values per trap with the ratio of throughfall volume: bulk precipitation volume of the respective trap during the sampling period times annual precipitation volume. Throughfall (Eq. 2) is the amount of open bulk precipitation (BP) that is not retained by the vegetation but passes the canopy layer and thus is altered in hydrochemistry due to canopy exchange (CE) and dry deposition (DD):

$$TF = BP + CE + DD \qquad (2)$$

Net throughfall flux (Eq. 3) is defined as the difference between the solute flux in throughfall and in bulk precipitation:

$$NTF = TF - BP = CE + DD \qquad (3)$$

To calculate the contribution of canopy exchange and dry deposition to annual net throughfall fluxes we computed and compared two different approaches i.e. the multiple regression model (Lovett and Lindberg 1984) and the canopy budget model (Ulrich 1983).

Multiple regression model

The multiple regression model was proposed by (Lovett and Lindberg 1984) for the separation of canopy exchange and dry deposition components of net throughfall based on event sampling (Eq. 4):

$$NTF_x = a + b1 * A + b2 * P \qquad (4)$$

In this regression equation factors b1 (dry period constant) and b2 (bulk precipitation constant) represent coefficients of the calculated linear model for A (antecedent dry period; in days) and P (magnitude of precipitation; in mm) and a is the intercept term. A negative canopy exchange coefficient (b2) indicates uptake of the solute during a rain event, while a positive coefficient points to canopy leaching of the solute. For a given precipitation event DD is the product of the dry deposition coefficient (b1) and the antecedent dry period (A), while CE is the product of the canopy exchange coefficient (b2) times the amount of precipitation (P). Multiple regression model calculations were performed with the mean net throughfall fluxes of all collectors of a forest type per event. With this model it is possible to investigate whether a certain element rather derives from dry deposition or canopy exchange processes and therefore originates from external or internal sources in terms of nutrient cycling (Filoso et al. 1999; Lovett et al. 1996; Veneklaas 1990). By multiplying the values for b1 by annual number of dry days (80 days during the study year) and b2 by the annual amount of precipitation (5720 mm during the study year) it is possible to estimate the annual fluxes of dry deposition and canopy retention or leaching.

Moreover, the calculation of annual dry deposition allows studying the uncertainty of atmospheric deposition estimates based on bulk deposition only or based on combined bulk plus dry deposition (total deposition), by calculating the relative contribution of dry deposition to total atmospheric deposition (Eq. 5):

$$relDD(\%) = DD/(DD + BP) * 100 \qquad (5)$$

Canopy budget model

The canopy budget model simulates the interaction of substances within forest canopies based on measurements of throughfall and precipitation and therefore is applicable to distinguish the relative importance of dry deposition and canopy exchange to net throughfall fluxes. The model has been used to estimate dry deposition and canopy exchange fluxes in a wide range of forest ecosystems, and different approaches have been reported (Staelens et al. 2008). Canopy budget model calculations are commonly based on mean (semi)annual fluxes in throughfall per forest site. We here compare three different approaches considering the application of a tracer ion only (filtering approach), the reference approach and the weak acid approach on an annual time step basis:

Filtering approach The filtering approach (Ulrich 1983) is used to estimate dry deposition of base cations (K^+, Ca^{2+}, and Mg^{2+}). In this approach aerosols containing base cations are assumed to be deposited with equal efficiency onto the forest canopy as particles containing an inert tracer ion. Sodium is often used as a tracer ion because it is assumed not to be influenced by canopy exchange processes (Staelens et al. 2008). Dry deposition of a certain element X (DD_X) is calculated as the product of the dry deposition factor (DDF) of the tracer ion (here: Na^+), which is the NTF to BP ratio of Na^+, times the bulk precipitation of element X (Eq. 6):

$$DD_x = \frac{(TF - BP)_{Na}}{BP_{Na}} * BP_X \qquad (6)$$

Canopy exchange viz. canopy leaching (CL) of base cations is then determined by subtracting dry deposition from NTF (Eq. 3). This approach has also been applied to solutes other than base cations (Kopacek et al. 2009).

Reference approach Considering ion exchange processes within a tree canopy, it is assumed that the canopy uptake (CU) of NH_4^+ and H^+ is counterbalanced by an equivalent release of base cations (Cronan and Reiners 1983). In this reference approach only the flux balance between canopy uptake of H^+ and NH_4^+ and canopy leaching of base cations (K^+, Ca^{2+}, and Mg^{2+}) is considered, which due to the ion charge balance of the canopy is assumed to be equal (Eq. 7):

$$CU_{NH_4+H} = CL_{BC} \qquad (7)$$

To partition the ion uptake between H^+ and NH_4^+ (Eq. 8a) the relative uptake efficiency factor xH is applied assuming that the exchange capacity of H^+ per mol is six times greater than that of NH_4^+ ($xH = 6$). Dry deposition of H^+ and NH_4^+ is then calculated based on Eq. 3. Canopy uptake of NO_3^- is calculated based on preferential uptake of NH_4^+ compared to NO_3^-, using an efficiency factor of NH_4^+ versus NO_3^- uptake (xNH_4) with a proposed value of 6 (Eq. 8b). xNH_4 has been found to be very close to this assumed value, being 6.4 for detached tree branches at the same forest site (Hinko-Najera Umana and Wanek 2010) as evaluated by $^{15}NH_4^+$ versus $^{15}NO_3^-$ retention rates. Dry deposition of NO_3^- is again calculated by Eq. 3.

$$CU_{NH_4} = \frac{(TF)_{NH_4}}{(TF)_{NH_4} + xH * (TF)_H} * CL_{BC} \qquad (8a)$$

$$CU_{NO_3+NH_4} = \frac{xNH_4 * (TF)_{NH_4} + (TF)_{NO_3}}{xNH_4 * (TF)_{NH_4}} * CU_{NH_4} \qquad (8b)$$

Canopy leaching of weak acids When weak acid (WA) leaching is included in the canopy budget model, it is assumed that canopy leaching of base cations (K^+, Ca^{2+}, and Mg^{2+}) is due to canopy uptake of $H^+ + NH_4^+$ and canopy leaching of WA (Eq. 9).

$$CU_{NH_4+H} = CL_{BC} - CL_{WA} \qquad (9)$$

CL_{WA} is calculated by subtracting TD (=WD + DD) from TF of WA. To estimate the concentration of WA in water samples organic anion concentrations are estimated from DOC concentrations and corresponding pH values using a model proposed by (Oliver et al. 1983) so that the dissociation ($HA = H^+ + A^-$) can be estimated by Eq. 10:

$$A^- = \frac{K[DOC]}{K + [H^+]} \qquad (10)$$

where A^- is the organic anion concentration, DOC is the organic carbon concentration and K is the mass action quotient estimated from sample pH using Eq. 11:

$$pK = 0.96 + 0.90pH - 0.039(pH)^2 \qquad (11)$$

Statistical analyses

Statistical analyses such as one-way analysis of variance (ANOVA), multiple regression analysis and principle component analysis (PCA) were computed with STATISTICA for Windows 7.5 (STAT-SOFT 2005). Differences in fluxes between study sites were investigated by one-way ANOVA after testing whether the assumptions underlying ANOVA were met by Levene's Test (homogeneity of variance) and test for normality (with/without log-transformation of data). Tukey HSD multiple range tests at the 95% level were calculated to test for differences between sites. Kruskal-Wallis ANOVA was calculated for data which did not meet homogeneity of variances and normality after log-transformation.

Principle component analysis was applied as a factor analytical technique to reduce the number of

variables and to detect structure in the relationships between variables that is to classify variables (event-based NTF of different solutes, based on single trap results) and compare the forest sites. In compliance with the Scree Test and the Kaiser Criterion (Eigen values > 1) four principle components were extracted and subsequent Varimax Rotation (orthogonal arrangement of factors) was used to allow specific interpretation of data.

Statistical analysis investigating species assemblages were computed with PRIMER 6.0 (Clarke and Gorley 2006). Fisher's alpha index, fitting best for species-rich areas as it accounts especially for rare single species (singletons), was computed to test for differences in species assemblages of study sites. Analysis of similarity (ANOSIM) based on correlating Bray Curtis matrices (Non-metric-multidimensional scaling) and Spearman rank correlations showed whether forest plots form clusters according to forest type. Analysis of similarity percentage (SIMPER) was applied to estimate percentages of similarity and reveal most dissimilar species between forest sites. After Bray Curtis distances of square rooted data were calculated for ionic composition and tree diversity, respectively, the two matrices where related by Spearman matrix rank correlation to test for significant relationships between nutrient fluxes and tree species assemblages on the respective forest site. Another Spearman rank correlation, analysing non-parametric data by the formation of ranks, investigated the relationship between ion fluxes and plant area index above a given throughfall trap.

Results

Soils

Bulk densities ranged from 0.41 g cm^{-3} (at site PRi) to 0.61 g cm^{-3} (at site PRa) (Table 1). Soil pH (CaCl$_2$) ranged between 3.28 and 3.68 and was lowest at site PRi. Soil C$_{tot}$ and N$_{tot}$ concentrations were high for the topsoil (0–5 cm, after removal of organic horizon), ranging between 4.8 and 8.6% for C and between 0.37 and 0.64% for N, and were lowest at site SRa (Table 1). Similar to soil solutions, extractable soil NO$_3^-$ was highest at site PRa, while NH$_4^+$ was highest at site PRi. Extractable K$^+$ and HPO$_4^{2-}$ did not differ between sites, but HPO$_4^{2-}$

Table 1 Soil characteristics (pH; bulk density, BD, in g cm^{-3}) and concentrations of CaCl$_2$ (10 mM)-extractable soil nutrients (0–5 cm, in mg kg^{-1}; g kg^{-1} for C$_{tot}$ and N$_{tot}$)

	pH (CaCl$_2$)	BD	Na$^+$	NH$_4^+$	K$^+$	Mg^{2+}	NO$_3^-$	SO$_4^{2-}$	HPO$_4^-$	C$_{tot}$	N$_{tot}$
PRi	3.28 ± 0.02 a	0.41 ± 0.06 a	29.3 ± 12.1	24.4 ± 3.8 b	173 ± 79.8	225 ± 31.3	18.8 ± 4.0 a	11.4 ± 3.8	0.7 ± 0.0	85.9 ± 8.1	6.2 ± 0.3
PRa	3.68 ± 0.04 b	0.61 ± 0.08 b	25.9 ± 4.9	11.5 ± 1.7 a	122 ± 17.2	250 ± 37.0	49.6 ± 7.6 b	9.3 ± 1.3	2.1 ± 0.4	77.8 ± 4.6	6.4 ± 0.3
SRa	3.56 ± 0.04 b	0.49 ± 0.06 a	17.3 ± 3.5	6.9 ± 0.8 a	200 ± 51.8	147 ± 21.5	9.0 ± 1.3 a	8.6 ± 0.9	4.8 ± 2.3	48.0 ± 4.5	3.7 ± 0.2

Data are means ± 1 standard error for the respective forest sites, i.e. primary ridge (PRi), primary ravine (PRa) and secondary ravine (SRa) forest (Piedras Blancas National Park, SW Costa Rica). Significant differences between forest sites are indicated by different letters (one-way ANOVA, $p < 0.05$)

showed a trend towards greater availability in soil solution at site PRa (and site SRa) compared to site PRi ($p < 0.10$). Concentrations of K^+, Mg^{2+} and Ca^{2+} in soil solution did not differ significantly between sites (Table 2).

Throughfall hydrochemistry

One-way ANOVA showed no statistically significant differences in throughfall volumes between forest sites, for rainfall events ranging from 5 to 168 mm. Throughfall comprised between 87% (SRa), 90% (PRa) and 92% (PRi) of bulk precipitation volume, on an annual basis. Annual precipitation during the study year was 5720 mm.

Generally variations in nutrient concentration between collectors within each forest type were relatively high, with CVs ranging between 8–26% for bulk precipitation and 20–160% for throughfall. Due to this high spatial variability few significant differences were found in nutrient concentrations between forest types (Table 2). Statistical analysis of volume weighted mean concentrations and net throughfall fluxes of solutes produced the same significant differences between sites as they are mathematically related i.e. multiplication of volume weighted mean concentration times volume of annual throughfall gives net throughfall flux. Statistical analysis of volume weighted mean concentrations produced the same significant differences as that of throughfall fluxes, which were calculated by multiplying volume weighted mean concentrations times volume of annual throughfall (see results below). Sodium concentrations in throughfall were highest at PRi, HPO_4^{2-} highest in throughfall at PRa and NO_3^- lowest in throughfall at SRa (Table 2).

Nutrient fluxes and throughfall modelling

In the Esquinas forest stemflow contributed <1% to hydrological fluxes and nutrient fluxes in stemflow were well below 5% of that in throughfall at all sites (data not shown), similar to values reported previously (Herwitz and Levia 1997). Stemflow was therefore excluded from further discussion and will be presented in a separate paper.

Bulk precipitation inputs of dissolved ions ranged from 0.4 (HPO_4^{2-}) to 20.0 kg ha^{-1} year^{-1} (Ca^{2+}). Inputs for dissolved organic carbon (DOC) and total

Table 2 Solute concentrations (μg l^{-1}) in bulk precipitation and throughfall (volume weighted means) and in soil water

	H⁺	Na⁺	NH₄⁺	K⁺	Mg²⁺	Ca²⁺	Cl⁻	NO₃⁻	SO₄²⁻	HPO₄⁻	DOC	DON	TDN
Bulk precipitation	25.2 ± 2.9	170 ± 13.8	96.6 ± 11.2	160 ± 31.3	77.8 ± 12.2	297 ± 36.1	149 ± 21.3	43.4 ± 4.2	80.3 ± 6.4	6.2 ± 3.1	623 ± 55.2	33.6 ± 19.6	173 ± 11.1
Throughfall													
PRi	8.1 ± 2.8	198 ± 25.3 b	67.2 ± 5.6	700 ± 82.1	129 ± 9.7	357 ± 20.0	362 ± 46.2	16.8 ± 1.4 b	122 ± 16.1	9.3 ± 3.1 a	1272 ± 146	93.8 ± 18.2	178 ± 11.9
PRa	4.2 ± 1.7	131 ± 9.2 a	96.6 ± 9.8	1482 ± 512	177 ± 26.7	485 ± 40.1	376 ± 67.5	19.6 ± 1.4 b	106 ± 9.6	31.0 ± 9.3 b	1704 ± 401	120 ± 25.2	236 ± 16.9
SRa	7.8 ± 2.3	127 ± 9.2 a	109 ± 23.8	946 ± 117	136 ± 9.7	449 ± 28.1	266 ± 14.2	12.6 ± 1.4 a	93.1 ± 6.4	15.5 ± 3.1 a	1548 ± 139	112 ± 15.4	234 ± 18.6
Soil water													
PRi	3.5 ± 1.0	495 ± 115	141 ± 44.8 b	1114 ± 102	374 ± 21.9	866 ± 84	1243 ± 351	25.2 ± 7.0 a	199 ± 86.7	3.1 ± 0.0	1944 ± 398	26.6 ± 78.4	193 ± 44.5
PRa	3.5 ± 2.1	589 ± 212	50.4 ± 5.6 a	1529 ± 414	498 ± 114	1395 ± 240	888 ± 266	304 ± 190 b	196 ± 83.5	15.5 ± 9.3	1644 ± 602	147 ± 51.8	501 ± 131
SRa	3.2 ± 0.9	545 ± 36.8	65.8 ± 5.6 ab	1595 ± 375	399 ± 70.5	1098 ± 148	1058 ± 245	8.4 ± 2.8 a	151 ± 61.0	9.3 ± 3.1	2952 ± 923	115 ± 5.6	193 ± 5.4

Data are means ± 1 standard error for the respective forest sites, i.e. primary ridge (PRi), primary ravine (PRa) and secondary ravine (SRa) forest (Piedras Blancas National Park, SW Costa Rica). Significant differences between forest sites are indicated by different letters (one-way ANOVA, $p < 0.05$). *n.d.* not determined

dissolved nitrogen (TDN) were 30.9 and 7.7 kg ha^{-1} year^{-1}, respectively. Throughfall fluxes of dissolved ions ranged from 0.4 (HPO$_4^{2-}$) to 80.4 kg ha^{-1} year^{-1} (K$^+$). Fluxes of DOC and TDN were found as high as 94.9 and 13.8 kg ha^{-1} year^{-1} in throughfall, respectively (Table 3). We found significant differences in solute fluxes between bulk precipitation and throughfall (full model: $F_{(39)} = 3.9$, $p < 0.001$). Compared to throughfall, bulk precipitation (BP) showed higher annual fluxes of H$^+$ (BP > PRa) and NO$_3^-$ (BP > PRi) and lower fluxes of Na$^+$ (BP < PRi), K$^+$ (BP < PRa), Cl$^-$ (BP < PRi) and SO$_4^{2-}$ (BP < PRi). However the greatest differences were found in fluxes of K$^+$ and NO$_3^-$, where fluxes of NO$_3^-$ were higher and K$^+$ lower in bulk precipitation compared to throughfall at all sites. Between forest sites we found significant differences in throughfall fluxes for Na$^+$ (one-way ANOVA, $p = 0.01$) being highest at PRi, NO$_3^-$ ($p = 0.01$) being lowest at SRa and HPO$_4^{2-}$ ($p = 0.002$) being highest at PRa (Table 3). Positive net throughfall fluxes indicated pronounced net increases of K$^+$ and DOC, with lower enrichments found for Cl$^-$, TDN, DON, Ca^{2+}, Mg^{2+}, Na$^+$, SO$_4^{2-}$ and HPO$_4^{2-}$ (in decreasing order, Fig. 1). In contrast negative values of net throughfall fluxes pointed to marked net retention and/or uptake of NO$_3^-$, NH$_4^+$ and H$^+$ (Fig. 1). Statistics of site-specific differences in net throughfall fluxes were consistent with that of throughfall fluxes due to their close mathematical relationship (Eq. 3).

The multiple regression model of event-based net throughfall was highly significant for most solutes, except NH$_4^+$, NO$_3^-$ and HPO$_4^{2-}$ (Table 4). As the intercepts of the multiple regression models were not significant (i.e. not significantly different from zero) for any solute and forest type, they were omitted from final multiple regression analyses. However it should be noted that for regressions that are forced through the origin, the properties of the resulting regression line are different than for an unforced regression. As a consequence, residuals of regressions through the origin must be interpreted with care and the sum of the squared residuals may exceed the total sum of squares, so that R^2 has no clear meaning for regressions through the origin (Neter et al. 1996). Application of regression models with and without intercept terms showed that omitting intercept terms in these regressions resulted in more adequate estimates of canopy exchange and dry deposition (NTF = CE + DD) that differed from calculated net

throughfall (NTF = TF − BP) by a factor of only 0.96 ± 0.08 compared to a factor of 0.78 ± 0.09 from regressions comprising intercept terms.

No significant differences in canopy exchange or dry deposition between forest types were evident, considering overlapping confidence intervals (CI) of their estimates for the three forest sites (CI calculated as the product of SE times 1.96; Table 3). Therefore for comparative analyses of canopy exchange versus litterfall fluxes (Fig. 2), and of dry deposition versus total deposition (Fig. 3), results of the multiple regression model combined for all sites were used. Canopy exchange fluxes were positive in most cases, indicating leaching from the forest canopy; exceptions were NH$_4^+$ (PRi) and NO$_3^-$ (all sites) showing negative canopy exchange estimates. Dry deposition estimates were in some cases negative i.e. Na$^+$ (PRi, PRa), NO$_3^-$ (all sites) and DOC (PRi). Though most multiple regression models were highly significant a large uncertainty in dry deposition coefficients for some solutes (Na$^+$, HPO$_4^-$, NO$_3^-$, and NH$_4^+$) caused dry deposition estimates not to be significantly different from zero. They are still the best estimates of the deposition rate, even if they were not statistically significant from zero. NTF was mostly dominated by canopy exchange compared to dry deposition for Na$^+$, K$^+$, Mg^{2+}, and SO$_4^{2-}$ while dry deposition dominated NTF for TDN and DON and both, canopy exchange and dry deposition, contributed equally to NTF of Ca^{2+}, Cl$^-$ and DOC.

Compared to the multiple regression model the canopy budget model (filtering approach) produced markedly higher estimates of dry deposition for most elements (e.g. for Na$^+$) and particularly for the exposed PRi forest site. Higher dry deposition estimates were found for Na$^+$, NH$_4^+$, Mg^{2+}, Ca^{2+}, and SO$_4^{2-}$ in the canopy budget model compared to the multiple regression model, resulting in lower estimates of canopy exchange fluxes i.e. lower canopy leaching or enhanced canopy uptake in the canopy budget model. In contrast, dry deposition calculated by the canopy budget model was lower compared to the multiple regression model for K$^+$ and DON, resulting in higher estimates of canopy leaching of these solutes. For Cl$^-$, DOC and TDN dry deposition estimates varied between both models, and therefore the resulting canopy exchange fluxes differed in their response between sites and models. At PRi Na$^+$ throughfall fluxes were highest among sites, translating into an

Table 3 Annual solute fluxes from external sources (atmospheric deposition via bulk and dry deposition), mixed sources (throughfall) and internal sources (litterfall, canopy exchange)

	H^+	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HPO_4^-	DOC	DON	TDN
Bulk precipitation	1.4 ± 0.1	6.9 ± 1.0	5.1 ± 0.9	6.2 ± 0.4	5.4 ± 0.8	20.0 ± 1.5	6.3 ± 0.4	2.0 ± 0.1	3.3 ± 0.1	0.4 ± 0.1	30.9 ± 1.0	0.6 ± 0.9	7.7 ± 1.9
Throughfall													
PRi	0.6 ± 0.2	14.3 ± 2.5	4.3 ± 0.4	45.5 ± 5.6	8.4 ± 0.7	21.9 ± 2.8	18.7 ± 3.2	0.9 ± 0.1	6.0 ± 0.4	0.4 ± 0.1	74.7 ± 9.7	5.2 ± 1.4	10.5 ± 1.3
PRa	0.3 ± 0.1	9.5 ± 1.0	6.7 ± 0.8	80.4 ± 22.2	10.5 ± 1.4	26.9 ± 2.4	17.7 ± 2.6	1.0 ± 0.1	5.2 ± 0.4	1.6 ± 0.5	94.9 ± 18.9	6.0 ± 1.5	13.8 ± 1.2
SRa	0.5 ± 0.1	8.9 ± 0.8	7.3 ± 1.6	58.8 ± 7.3	7.6 ± 0.4	22.3 ± 1.2	15.1 ± 0.9	0.7 ± 0.1	5.3 ± 0.3	0.8 ± 0.2	87.4 ± 7.7	5.3 ± 0.7	13.2 ± 2.0
Dry deposition													
Multiple regression													
PRi		−0.5 ± 0.8	0.5 ± 0.4	5.1 ± 2.4	0.3 ± 0.4	0.5 ± 0.8	2.9 ± 1.8	−0.2 ± 0.2	0.2 ± 0.3	0.0 ± 0.1	−0.8 ± 19.5	1.2 ± 2.0	1.5 ± 2.6
PRa		−0.1 ± 0.4	0.4 ± 0.5	6.7 ± 4.5	0.5 ± 0.4	1.3 ± 0.9	2.4 ± 1.2	−0.1 ± 0.2	0.2 ± 0.1	0.1 ± 0.2	44.4 ± 12.7	6.6 ± 2.0	7.0 ± 2.7
SRa		0.1 ± 0.4	0.2 ± 0.7	5.5 ± 2.0	0.4 ± 0.4	1.3 ± 0.8	2.5 ± 1.0	−0.2 ± 0.2	0.3 ± 0.1	−0.1 ± 0.1	31.4 ± 14.9	9.1 ± 2.2	9.0 ± 3.2
Filtering app.													
PRi	1.5 ± 0.0	7.4 ± 0.0	5.4 ± 0.0	6.7 ± 0.0	5.8 ± 0.0	21.4 ± 0.0	6.7 ± 0.0	2.2 ± 0.0	3.5 ± 0.0	0.7 ± 0.0	33.1 ± 0.0	0.6 ± 0.0	8.2 ± 0.0
PRa	0.6 ± 0.0	2.6 ± 0.0	2.0 ± 0.0	2.4 ± 0.0	2.1 ± 0.0	7.7 ± 0.0	2.4 ± 0.0	0.8 ± 0.0	1.3 ± 0.0	0.2 ± 0.0	11.9 ± 0.0	0.2 ± 0.0	2.9 ± 0.0
SRa	0.4 ± 0.0	2.0 ± 0.0	1.5 ± 0.0	1.8 ± 0.0	1.5 ± 0.0	5.7 ± 0.0	1.8 ± 0.0	0.6 ± 0.0	0.9 ± 0.0	0.2 ± 0.0	8.8 ± 0.0	0.2 ± 0.0	2.2 ± 0.0
Reference app.													
PRi	−0.4 ± 0.3	7.4 ± 0.0	0.6 ± 0.7	6.7 ± 0.0	5.8 ± 0.0	21.4 ± 0.0	6.7 ± 0.0	−1.1 ± 0.1	3.5 ± 0.0	0.7 ± 0.0	33.1 ± 0.0	0.6 ± 0.0	8.2 ± 0.0
PRa	−0.5 ± 0.2	2.6 ± 0.0	18.5 ± 8.8	2.4 ± 0.0	2.1 ± 0.0	7.7 ± 0.0	2.4 ± 0.0	−0.6 ± 0.2	1.3 ± 0.0	0.2 ± 0.0	11.9 ± 0.0	0.2 ± 0.0	2.9 ± 0.0
SRa	−0.1 ± 0.2	2.0 ± 0.0	7.2 ± 2.2	1.8 ± 0.0	1.5 ± 0.0	5.7 ± 0.0	1.8 ± 0.0	−1.2 ± 0.1	0.9 ± 0.0	0.2 ± 0.0	8.8 ± 0.0	0.2 ± 0.0	2.2 ± 0.0
Weak acid app.													
PRi	0.2 ± 0.5	7.4 ± 0.0	0.6 ± 0.7	6.7 ± 0.0	5.8 ± 0.0	21.4 ± 0.0	6.7 ± 0.0	−1.1 ± 0.1	3.5 ± 0.0	0.7 ± 0.0	33.1 ± 0.0	0.6 ± 0.0	8.2 ± 0.0
PRa	0.5 ± 0.6	2.6 ± 0.0	18.5 ± 8.8	2.4 ± 0.0	2.1 ± 0.0	7.7 ± 0.0	2.4 ± 0.0	−0.6 ± 0.2	1.3 ± 0.0	0.2 ± 0.0	11.9 ± 0.0	0.2 ± 0.0	2.9 ± 0.0
SRa	−0.1 ± 0.2	2.0 ± 0.0	7.2 ± 2.2	1.8 ± 0.0	1.5 ± 0.0	5.7 ± 0.0	1.8 ± 0.0	−1.2 ± 0.1	0.9 ± 0.0	0.2 ± 0.0	8.8 ± 0.0	0.2 ± 0.0	2.2 ± 0.0
Canopy exchange													
Multiple regression													
PRi	8.0 ± 1.7		−0.8 ± 0.8	25.0 ± 4.9	1.6 ± 0.9	1.3 ± 1.7	5.1 ± 2.9	−0.5 ± 0.3	2.1 ± 0.5	0.1 ± 0.1	30.4 ± 10.9	3.2 ± 0.3	2.0 ± 1.4
PRa	3.3 ± 0.7		0.5 ± 1.0	51.4 ± 9.3	3.8 ± 0.7	4.1 ± 1.9	5.4 ± 2.0	−0.4 ± 0.3	1.4 ± 0.2	0.9 ± 0.4	34.8 ± 7.1	1.4 ± 0.2	1.5 ± 1.5
SRa	1.5 ± 0.7		2.0 ± 1.5	34.4 ± 4.2	1.4 ± 0.7	0.7 ± 1.6	2.5 ± 1.6	−0.6 ± 0.3	1.2 ± 0.2	0.4 ± 0.2	25.2 ± 8.4	−0.2 ± 0.0	1.2 ± 1.8
Filtering app.													
PRi	−2.4 ± 0.2	0.0 ± 2.5	−6.2 ± 0.4	32.6 ± 5.6	−2.7 ± 0.7	−19.6 ± 2.8	5.7 ± 3.2	−3.3 ± 0.1	−0.8 ± 0.4	−0.7 ± 0.2	10.8 ± 9.7	4.1 ± 1.4	−5.4 ± 1.3
PRa	−1.7 ± 0.1	0.0 ± 1.0	−0.3 ± 0.8	71.8 ± 22.2	3.1 ± 1.4	−0.8 ± 2.4	9.0 ± 2.6	−1.8 ± 0.1	0.6 ± 0.4	1.5 ± 0.8	52.2 ± 18.9	5.2 ± 1.5	3.2 ± 1.2
SRa	−1.4 ± 0.1	0.0 ± 0.8	0.7 ± 1.6	50.8 ± 7.3	0.7 ± 0.4	−3.5 ± 1.2	7.0 ± 0.9	−1.9 ± 0.1	1.1 ± 0.3	0.4 ± 0.3	47.7 ± 7.7	4.5 ± 0.7	3.4 ± 2.0
Reference app.													
PRi	−0.4 ± 0.2	0.0 ± .5	−1.4 ± 0.5	32.6 ± 5.6	−2.7 ± 0.7	−19.6 ± 2.8	5.7 ± 3.2	0.0 ± 0.0	−0.8 ± 0.4	−0.7 ± 0.2	10.8 ± 9.7	4.1 ± 1.4	−5.4 ± 1.3
PRa	−0.7 ± 0.1	0.0 ± 1.0	−16.8 ± 8.8	71.8 ± 22.2	3.1 ± 1.4	−0.8 ± 2.4	9.0 ± 2.6	−0.4 ± 0.2	0.6 ± 0.4	1.5 ± 0.8	52.2 ± 18.9	5.2 ± 1.5	3.2 ± 1.2
SRa	−0.9 ± 0.2	0.0 ± 0.8	−5.0 ± 1.3	50.8 ± 7.3	0.7 ± 0.4	−3.5 ± 1.2	7.0 ± 0.9	−0.1 ± 0.0	1.1 ± 0.3	0.4 ± 0.3	47.7 ± 7.7	4.5 ± 0.7	3.4 ± 2.0

Table 3 continued

	H$^+$	Na$^+$	NH$_4$$^+$	K$^+$	Mg^{2+}	Ca^{2+}	Cl$^-$	NO$_3$$^-$	SO$_4$$^{2-}$	HPO$_4$$^-$	DOC	DON	TDN
Weak acid app.													
PRi	−1.1 ± 0.4	0.0 ± 2.5	−1.4 ± 0.5	32.6 ± 5.6	−2.7 ± 0.7	−19.6 ± 2.8	5.7 ± 3.2	0.0 ± 0.0	−0.8 ± 0.4	−0.7 ± 0.2	10.8 ± 9.7	4.1 ± 1.4	−5.4 ± 1.3
PRa	−1.7 ± 0.6	0.0 ± 1.0	−16.8 ± 8.8	71.8 ± 22.2	3.1 ± 1.4	−0.8 ± 2.4	9.0 ± 2.6	−0.4 ± 0.2	0.6 ± 0.4	1.5 ± 0.8	52.2 ± 18.9	5.2 ± 1.5	3.2 ± 1.2
SRa	−0.8 ± 0.2	0.0 ± 0.8	−5.0 ± 1.3	50.8 ± 7.3	0.7 ± 0.4	−3.5 ± 1.2	7.0 ± 0.9	−0.1 ± 0.0	1.1 ± 0.3	0.4 ± 0.3	47.7 ± 7.7	4.5 ± 0.7	3.4 ± 2.0

	Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}	P$_{tot}$	C$_{tot}$	N$_{tot}$
Litter fall							
PRi	1.9 ± 0.2	32.7 ± 4.7	16.1 ± 1.9	97.6 ± 9.2	5.2 ± 1.3	4406 ± 467	101 ± 11.1
PRa	2.6 ± 0.3	57.1 ± 6.2	35.1 ± 4.2	200 ± 23.3	10.6 ± 1.4	6232 ± 519	185 ± 15.7
SRa	2.2 ± 0.2	38.9 ± 5.0	18.1 ± 2.6	151 ± 23.1	6.3 ± 0.8	5050 ± 607	116 ± 13.2

Data are means ± 1 standard error (kg ha^{-1} year^{-1}). Significant differences in annual nutrient fluxes between forest sites i.e. primary ridge (PRi), primary ravine (PRa) and secondary ravine (SRa) forest (Piedras Blancas National Park, SW Costa Rica) are indicated by different letters (one-way ANOVA, $p < 0.05$)
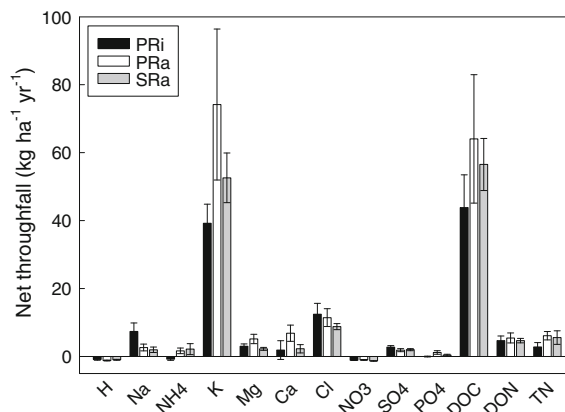

Fig. 1 Net throughfall fluxes (NTF; in kg ha^{-1} year^{-1}) of solutes in primary ridge (PRi), primary ravine (PRa) and secondary ravine (SRa) forests (Piedras Blancas National Park, SW Costa Rica). Values represent means ± 1 SE ($n = 15$ collectors per site)

enhanced dry deposition factor and increased dry deposition of many solutes. The reference approach yielded even higher estimates of canopy retention of NH$_4$$^+$ and lower estimates for NO$_3$$^-$ and H$^+$. The application of the weak acid approach slightly affected the H$^+$ estimates though not those of NH$_4$$^+$.

A detailed investigation of possible model flaws of the multiple regression model and canopy budget model estimates is given in the discussion section. Based on this we used multiple regression model estimates of canopy exchange and dry deposition for evaluation of nutrient budgets. Litterfall represented the major aboveground pathway of internal cycling of elements (i.e. C$_{tot}$, N$_{tot}$, Ca^{2+}, K$^+$, Mg^{2+} and HPO$_4$$^{2-}$, Fig. 2). Canopy exchange resulted in marked leaching of DOC and K$^+$ and less so of Cl$^-$, Na$^+$, Mg^{2+}, Ca^{2+} and SO$_4$$^{2-}$. However, contributions by canopy exchange to aboveground cycling were large for Na$^+$ (69%), K$^+$ (53%), Mg^{2+} (12.3%) and HPO$_4$$^{2-}$ (8.2%), while for Ca^{2+}, C$_{tot}$ and N$_{tot}$ contributions were <2% (full model: $F_{11,24} = 24.892$, $p < 0.0001$). Furthermore, canopy exchange led to significant retention of NO$_3$$^-$, and less so of NH$_4$$^+$, though this was not statistically significant (Fig. 2, Table 3). Dry deposition contributed most to total atmospheric inputs of DON (90%), K$^+$ (48%), DOC (45%), TDN (43%) and Cl$^-$ (29%) and to a lesser extent of Ca^{2+}, Mg^{2+}, SO$_4$$^{2-}$ and NH$_4$$^+$ (Fig. 3; full model: $F_{11,24} = 3.1509$, $p = 0.0091$). Bulk deposition estimates therefore would underestimate total atmospheric deposition to this tropical

Table 4 Results of the multiple regression model (Lovett and Lindberg 1984) of event net throughfall ($n = 12$) against rain volume (mm) and number of antecedent rain free days

	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HPO_4^-	DOC	TDN
PRi											
b2	5.9 ± 1.3	−1.0 ± 1.0	10.9 ± 2.1	1.1 ± 0.6	0.5 ± 0.7	2.5 ± 1.4	−0.6 ± 0.4	1.1 ± 0.3	0.0 ± 0.1	43.4 ± 15.5	2.4 ± 1.8
b1	−27.1 ± 46.0	44.4 ± 36.3	164.6 ± 75.9	17.6 ± 21.4	16.4 ± 25.0	100.9 ± 65.1	−14.3 ± 16.1	7.0 ± 13.2	0.2 ± 3.6	−80.8 ± 2027	133.7 ± 230.3
R^2	**0.70**	0.18	**0.81**	0.35	0.13	0.40	0.29	**0.63**	0.04	**0.50**	0.27
p-value	**0.004**	0.412	**0.001**	0.140	0.535	0.078	0.182	**0.007**	0.808	**0.044**	0.250
PRa											
b2	2.5 ± 0.6	0.6 ± 1.3	22.5 ± 4.1	2.7 ± 0.5	1.8 ± 0.8	2.6 ± 1.0	−0.5 ± 0.4	0.8 ± 0.1	0.5 ± 0.2	49.7 ± 10.1	1.8 ± 1.8
b1	−6.4 ± 19.5	39.3 ± 44.5	215.7 ± 144.7	26.6 ± 18.3	39.4 ± 29.3	85.1 ± 43.8	−11.8 ± 17.4	7.1 ± 3.9	2.8 ± 9.7	4625 ± 1320	621.0 ± 240.1
R^2	**0.69**	0.12	**0.81**	**0.79**	0.47	**0.58**	0.19	**0.90**	0.36	**0.87**	**0.56**
p-value	**0.005**	0.558	**0.001**	**0.001**	0.056	**0.013**	0.346	**<0.001**	0.103	**<0.001**	**0.026**
SRa											
b2	1.1 ± 0.6	2.4 ± 1.8	15.1 ± 1.8	1.0 ± 0.5	0.3 ± 0.7	1.2 ± 0.8	−0.7 ± 0.4	0.6 ± 0.1	0.2 ± 0.1	35.9 ± 11.9	1.5 ± 2.2
b1	4.7 ± 19.6	14.3 ± 63.5	176.8 ± 65.0	22.1 ± 18.6	40.5 ± 24.9	88.9 ± 34.9	−16.7 ± 18.1	10.4 ± 5.3	−2.7 ± 5.4	3270 ± 1556	807.6 ± 282.4
R^2	0.33	0.19	**0.91**	0.41	0.27	**0.52**	0.32	**0.80**	0.27	**0.70**	**0.57**
p-value	0.161	0.388	**<0.001**	0.093	0.246	**0.026**	0.144	**<0.001**	0.205	**0.004**	**0.023**
All sites											
b2	3.2 ± 0.5	0.7 ± 1.2	16.2 ± 2.1	1.6 ± 0.5	0.9 ± 0.4	2.1 ± 0.9	−0.6 ± 0.4	0.8 ± 0.1	0.3 ± 0.1	43.0 ± 7.6	1.9 ± 1.6
b1	−9.6 ± 17.6	32.6 ± 42.2	185.7 ± 75.0	22.1 ± 15.9	32.1 ± 15.5	91.6 ± 40.3	−14.2 ± 16.9	8.2 ± 5.5	0.1 ± 4.7	2605 ± 989	520.8 ± 207.9
R^2	**0.82**	0.12	**0.90**	**0.66**	**0.54**	**0.57**	0.27	**0.85**	0.38	**0.87**	**0.56**
p-value	**<0.001**	0.574	**<0.001**	**0.008**	**0.030**	**0.015**	0.200	**<0.001**	0.089	**<0.001**	**0.024**

Multiple regression models showed that intercepts were not significant; data presented here are values from multiple regression models calculated without intercepts. Values are given for bulk precipitation constant (b2), dry period constant (b1), adjusted R square (R^2 adj.) and p-values from primary ridge (PRi), primary ravine (PRa) and secondary ravine (SRa) forests and combined site analysis (Piedras Blancas National Park, SW Costa Rica). Data represent means ± 1 standard error. Bold values indicate statistically significant regressions of NTF of the respective nutrients against precipitation magnitude and number of dry days before the event ($p < 0.05$)
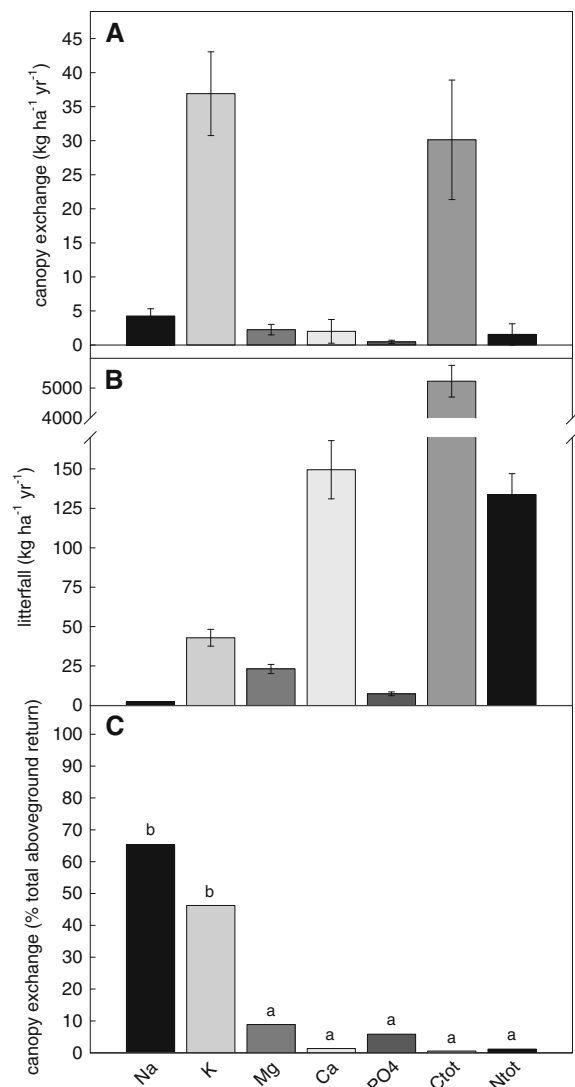
Fig. 2 Internal nutrient fluxes of **a** canopy exchange (in kg ha^{-1} year^{-1}), **b** litterfall and **c** canopy exchange as percentage of aboveground nutrient return to the forest floor i.e. canopy exchange plus litterfall in the Piedras Blancas National Park, SW Costa Rica. Values represent means ± 1SE of all sites and plots combined. Different letters denote significant differences between solutes (one-way ANOVA, LSD, $p < 0.05$)

Fig. 3 External nutrient inputs by **a** bulk precipitation (in kg ha^{-1} year^{-1}), **b** dry deposition and **c** dry deposition as percentage of total deposition i.e. bulk plus dry deposition in the Piedras Blancas National Park, SW Costa Rica. Values represent means ± 1SE of all sites and plots combined. Different letters denote significant differences between solutes (one-way ANOVA, LSD, $p < 0.05$)

rainforest by e.g. ∼2-fold (K$^+$, DOC, TDN, Cl$^-$) and 10-fold for DON.

Sources of nutrients in net throughfall

In a third approach (besides the multiple regression and the canopy budget model) a principal component analysis was calculated to assess sources of solutes in

net throughfall fluxes (Table 5). At a threshold of 0.5 for factor loadings, principle component PC 1 (37.2% variance explained) was found to group solutes such as K$^+$, Mg^{2+}, Ca^{2+}, DON and DOC i.e. plant nutrients and dissolved organic matter. Principle component PC 2 (14.6% variance explained) showed clustering of typical sea-salt ions (Na$^+$, Cl$^-$, Mg^{2+}, SO$_4^{2-}$) together with NO$_3^-$, while principle

Table 5 Results of principal component analysis (PCA)

Variables	PC 1	PC 2	PC 3	PC 4
H^+	−0.03	−0.01	−0.11	**−0.81**
Na^+	0.05	**0.81**	0.03	−0.26
NH_4^+	0.09	0.08	**0.88**	−0.10
K^+	**0.55**	0.26	−0.01	**0.64**
Mg^{2+}	**0.58**	**0.56**	0.00	0.38
Ca^{2+}	**0.67**	0.45	0.18	0.05
Cl^-	0.38	**0.66**	−0.11	0.39
NO_3^-	−0.33	**0.59**	0.47	0.06
SO_4^{2-}	0.22	**0.74**	0.04	0.24
HPO_4^-	0.11	−0.05	**0.74**	0.47
DOC	**0.86**	0.22	−0.08	0.20
DON	**0.79**	−0.13	0.12	−0.01
Eigen values	4.46	1.75	1.56	1.06
% Variance explained	37.19	14.58	12.99	8.79

Bold values indicate factor loadings above 0.5 or below −0.5 and thus common sources of solutes in annual net throughfall of single throughfall collectors. Factor loadings, Eigen values and percentage of variance explained for each principle component (PC 1–4) are given for 12 events for three forest sites (Piedras Blancas National Park, SW Costa Rica)

component PC 3 (13.0% variance explained) was determined by NH_4^+ and HPO_4^{2-}. Principle component PC 4 (8.8% variance explained) was determined by solutes H^+ and K^+ which were negatively correlated (Table 5). Together the four components accounted for 73.5% of total variance in net throughfall fluxes. The factor values were then tested by one-way ANOVA for differences between forest sites. PC 1 showed highest values at SRa, differing from PRi. PC 2 was highest at site PRi, differing from SRa. PC 3 was highest at the PRa site and lowest at PRi. For PC 4 no differences between sites were evident (Fig. 4).

Effects of seasonality and vegetation on net throughfall fluxes

In throughfall volume weighted mean concentrations of most solutes (except NH_4^+ and Ca^{2+}) were significantly higher in the dry season (events ranging from 5 to 61 mm) than in the wet season (events between 57 and 168 mm) (one way ANOVA, $p < 0.001$). Similarly, seasonality also affected throughfall fluxes, being significantly higher for Cl^-, NO_3^-, SO_4^{2-}, HPO_4^{2-} ($p < 0.001$) and DOC ($p < 0.01$) during the dry season and for NH_4^+ and

Ca^{2+} ($p < 0.001$) and Mg^{2+} ($p = 0.01$) during the wet season.

Plant area index (PAI) (Table 6), based on light absorbance by the canopy, was higher for PRa compared to SRa and PRi ($p < 0.001$). Values of PAI calculated by hemispherical photography did not differ between sites but showed the same trend as PAI from light absorbance measurements. The Spearman-Rank correlations between PAI measured above each throughfall collector and NTF of solutes were not significant (Supplementary Table 2).

Fisher's alpha value demonstrated that forest types differed significantly in species diversity for tree species above 10 cm dbh (Fisher's alpha 11–86) while species of trees between 2.5 and 10 cm in diameter at breast height did not (Fisher's alpha 20–26, Table 6). Analysis of similarity (ANOSIM) of species assemblages showed weak differences (high similarity) between forest types for trees between 2.5 and 10 cm dbh (Global Model's $R = 0.87$, $p = 0.001$). PRa differed from PRi and SRa ($R = 0.79$–1.00, $p = 0.03$) whilst SRa and PRi showed no differences in species assemblage ($R = 0.63$, $p = 0.10$). For trees > 10 cm dbh species assemblages showed greater differences between sites (Global Model's $R = 0.10$, $p = 0.002$) with generally high differences in species between all sites ($R = 0.01$, $p = 0.003$–0.02). Analysis of similarity percentage (SIMPER) confirmed that for trees > 10 cm dbh forests differed most significantly in species composition (average dissimilarity: PRa/PRi: 100%, SRa/PRa: 98.2% and SRa/PRi: 92.1%; Supplementary Table 3). Relating Bray Curtis distance matrices of tree species and ionic composition by Spearman-matrix-rank correlation, however, showed no influence of species composition on throughfall solute fluxes (Supplementary Table 2).

Discussion

Comparison of the multiple regression and canopy budget model approaches

In comparing the two model approaches to partitioning the contribution of canopy exchange and dry deposition to NTF in forest ecosystems, we found that both the multiple regression model and the canopy budget model involved several caveats that should be considered.
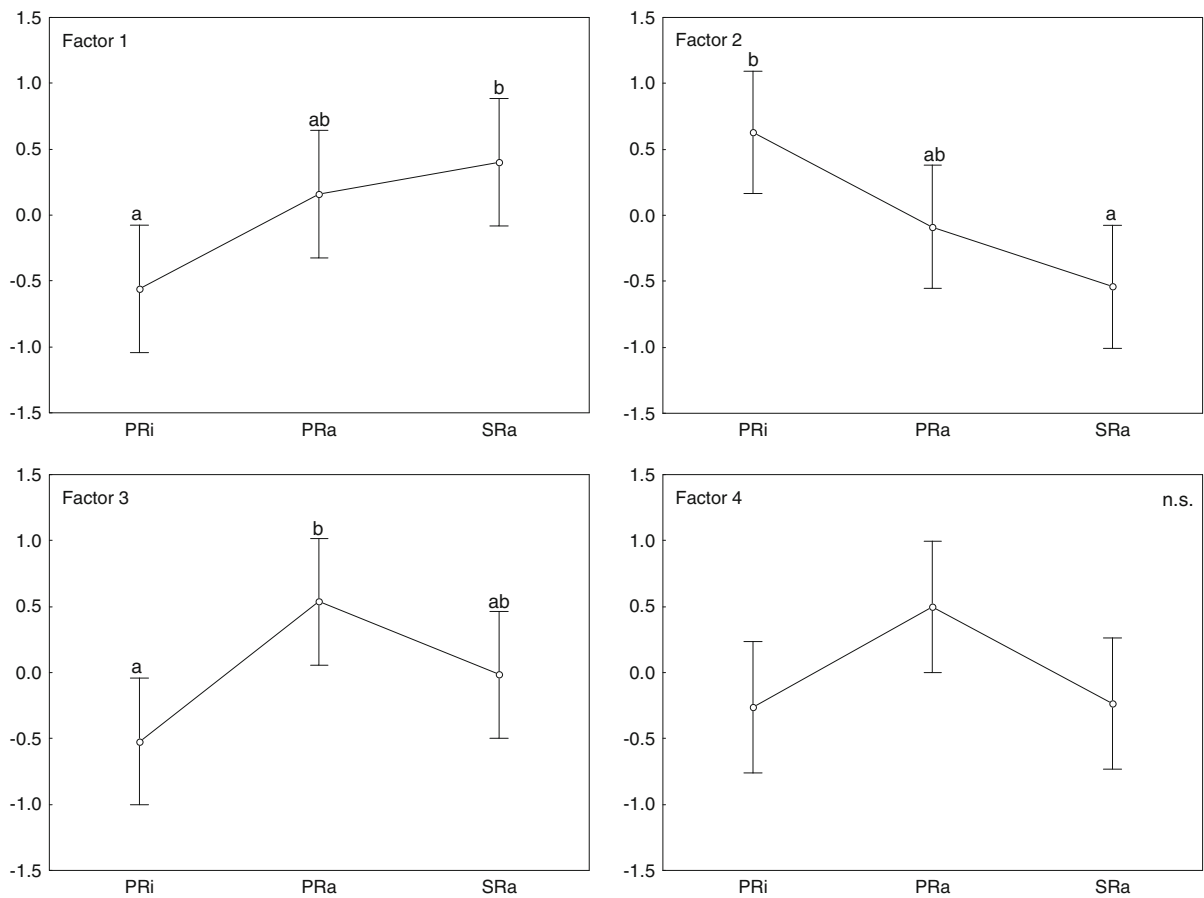
Fig. 4 Mean values ± confidence intervals of the factor loadings of principal components of annual net throughfall fluxes (presented in Table 5). Significant differences between sites i.e. primary ridge (PRi), primary ravine (PRa) and secondary ravine (SRa) forests (Piedras Blancas National Park, SW Costa Rica) for each factor (1–4) are presented by different letters (one-way ANOVA, LSD, $p < 0.05$). *ns* not significant

Table 6 Vegetation characteristics of primary ridge (PRi), primary ravine (PRa) and secondary ravine (SRa) forests (Piedras Blancas National Park, SW Costa Rica)

	Trees 2.5–10 cm dbh (0.03 ha)			Trees > 10 cm dbh (0.12 ha)			Tree height		PAI (Sundata)		PAI (Hemiview)	
Site	Total species	Total individuals	Fisher's alpha	Total species	Total individuals	Fisher's alpha	Mean	CV%	Mean	CV%	Mean	CV%
PRi	52	167	26	25	29	86	16.6	38.8	7.1	18.2	4.1	14.8
PRa	18	28	22	21	29	34	17.4	43.2	8.3	23.4	4.7	24.4
SRa	29	65	20	15	31	11	21.5	41.0	6.9	16.7	4.1	24.7
Sum	99	260		61	89							

Total species and total individual numbers of tree species below and above 10 cm in diameter at breast height (dbh) are presented. Fisher's alpha index is given as an indicator of species diversity. Means and coefficients of variation (CV%) are given for height of trees; plant area index (PAI) investigated by Sundata and Hemiview System of the respective forest sites

The multiple regression model was designed for application in temperate regions where the distribution of dry days and precipitation magnitude is more or less equally throughout the year. The power of multiple regression analysis will be weakened when there is little variation in one of the variables (see

Eq. 4) among events such as here in the length of antecedent dry period that varied only between 0 and 2 days. Therefore the following limitations of the regression model have to be considered: (1) The relationships between (i) precipitation amount and canopy exchange and (ii) antecedent period and dry deposition flux are assumed to be linear. (2) Material accumulated between events is assumed to be washed off the canopy completely and quickly, and the efficiency of this wash-off is assumed to be unrelated to the amount of precipitation (events < 5 mm are excluded from analysis). Dry-deposited material that is retained in the canopy and is not included in NTF and therefore dry deposition may be underestimated for some substances. (3) The dry deposition component includes material that migrates from inside the leaves and branches to surfaces during the antecedent period, and also material accumulating in the TF funnels during the antecedent dry period, such as debris from the canopy, both leading to an overestimation of the dry deposition component. According to these assumptions and limitations the model has proven highly valuable to estimate canopy exchange and dry deposition in areas with convective storms and extended dry weather periods (Lovett et al. 1996; Puckett 1990) but was found less useful in areas characterized by frequent low-intensity rainfall and relatively short dry periods (Draaijers et al. 1994; Lindberg et al. 1990). The high mean annual precipitation of approximately 5800 mm in the study region with an average of 260 rainy days per year (data not shown) therefore indicates unfavourable conditions according to factor (1) but less restrictions by factors (2) and (3) for the application of this approach to correctly estimate the dry deposition component of NTF. For the 30 precipitation events collected the mean number of antecedent dry days was ∼0.5, and in the study year only 80 dry days occurred. We therefore anticipate that the local meteorological conditions result in high contributions of canopy exchange to NTF in the study area while contributions of dry deposition to NTF remain sparse and statistically uncertain, as demonstrated.

One more concern with the multiple regressions is the choice of model. Forcing regressions through the origin is commonly not advised and may lead to large uncertainties in calculated dry deposition and canopy exchange rates. However, in this study models without intercepts performed better than those with

intercepts i.e. models with intercepts led to underestimation of measured NTF by $22 \pm 1\%$ compared to $4 \pm 1\%$ underestimation by models forced through the origin. The discrepancy mainly derives from the difficulties in interpreting and partitioning the intercept value which neither represents dry deposition nor canopy exchange per se, following the assumptions of the multiple regression model. The intercept value would represent a net throughfall flux per rain event that is not related to precipitation amount (which presumably scales with canopy exchange flux) and to the length of antecedent dry period (which presumably scales with dry deposition flux). The exact nature of this flux remains obscure but in this study was not related to contamination of samples or collectors. The application of multiple regression models computed with intercepts can therefore lead to underestimations of the contributions of canopy exchange and dry deposition to net throughfall flux in tropical rainforests. This finding indicates that the multiple regression model computed without intercept terms (despite legitimate statistical scepticism) constitutes a more adequate instrument for the estimation of canopy exchange and dry deposition fluxes, provided that intercept terms are not significant.

The multiple regression model was not significant for NTF of NH_4^+, NO_3^- and HPO_4^{2-} ions that in tropical rainforest canopies are expected to be highly dynamic, to be exchanged between canopy compartments and to be biochemically transformed (e.g. NH_4^+ to NO_3^-, or inorganic to organic PO_4). The different dynamics of NH_4^+ and HPO_4^{2-} are also represented by the principal component analysis of NTF of individual throughfall traps, i.e. in their strong positive relation to principal component PC3. However, any estimates presented for canopy exchange and dry deposition of these ions have to be taken cautiously as model outputs were non-significant.

Interestingly dry deposition of the tracer ion, Na^+, of the canopy budget model was close to zero, NTF being dominated by canopy exchange processes which would prevent application of the canopy budget model in the study area. Though other tracer ions (e.g. Cl^-, Ca^{2+}) have also rarely been used (Staelens et al. 2008), Na^+ is the most commonly used tracer ion and we therefore calculated the canopy budget model with Na^+ to be compared with the multiple regression model.

The canopy budget model has been validated for areas with high wet and dry deposition rates of N and S (Draaijers and Erisman 1995). The filtering approach is based on medium to high dry deposition rates of Na^+ and base cations and the reference approach particularly applies where deposition of H^+ and NH_4^+ is high and therefore is a major driver of ion-exchange processes in the canopy. In the reference approach deposition of H^+ and NH_4^+ is neutralized by an equivalent release of base cations. The canopy budget model is therefore considered to be built on several assumptions of mechanisms which are sometimes questionable. When a specific assumption is not valid this propagates into successive calculations by which an accumulation of errors may arise (Staelens et al. 2008). We might expect that in remote and in clean air areas the processes being dominant in high deposition areas are not representative and that therefore the canopy budget model is based on a 'wrong' mechanistic basis. This becomes evident from the strong deviations in anticipated solute relationships based on the canopy budget model and those found by principal component analysis of NTF (Table 5). Principal component PC1 was controlled by NTF of base cations (which would fit canopy budget model assumptions) but also by NTF of DOC and DON indicating a similar canopy leaching mechanism. PC2 was strongly dominated by NTF of sea salts i.e. Na^+, Mg^{2+}, Cl^- and SO_4^{2-} but also of NO_3^-, indicating a strong dry deposition component that also affected NTF of NO_3^-. PC3 was related to NTF of NH_4^+ and HPO_4^{2-}, two elements that most probably have similar biological sink/source relationships in the forest canopy. Only in PC4 we find a typical ion-exchange component as indicated by the negative relation between NTF of H^+ and K^+ and predicted by the canopy budget model.

The major weakness of the filtering approach is the assumed relation between wet and dry deposition of particles (Draaijers et al. 1996). The assumption of the filtering approach that Mg^{2+}, Ca^{2+}, Cl^- and K^+ containing particles are deposited with equal efficiency as Na^+ containing particles will certainly introduce an error as the particle-size distribution of these constituents is not the same. In general mass median diameters of aerosols containing Ca^{2+} and to a lesser extent Mg^{2+} were found to be larger than those of Na^+, while mass median diameters of K^+

aerosols can be considered smaller (Ruijgrok et al. 1997). As a result dry deposition of Ca^{2+} and to a lesser extent of Mg^{2+} containing particles will be underestimated by the model and dry deposition of K^+ containing particles will be overestimated (Draaijers et al. 1997). In this study, however, we found very high estimates for dry deposition of most elements but especially Ca^{2+} in the exposed PRi forest site (compared to the multiple regression model). These high dry deposition estimates further translate into much higher rates of canopy uptake of NO_3^-, NH_4^+ and TDN and especially unrealistically high canopy uptake of Ca^{2+} at PRi compared to the multiple regression model estimates. The most plausible explanation of low NTF but high dry deposition and therefore canopy uptake fluxes of Ca^{2+} at PRi is the enhanced TF:BP ratio (DDF) for Na^+ at this site which gives rise to high dry deposition fluxes of all base cations in the filtering approach. In a study by Staelens et al. (2008) it was reported that part of NTF of Na^+ may actually result from canopy leaching instead of dry deposition and that canopy exchange of Na^+ is most critical in regions with low marine deposition inputs, which would impair the use of Na^+ as a tracer in remote areas. In contradiction, previous research suggests that the enrichment of Na^+ in TF is mainly derived from dry deposition although evidence for the canopy inertness of Na^+ is scarce (Staelens et al. 2008). Further error is introduced when based on these dry deposition values, canopy leaching of base cations is computed which in turn is used to calculate canopy uptake of H^+ and NH_4^+ in the reference approach. Application of the weak acid approach assumes generally larger canopy leaching of base cations, since weak acid leaching may release extra base cations from the plant tissues. Although in this study the application of the weak acid approach resulted in minor changes in H^+ but not base cation estimates, it has been reported that base cations leached in association with weak acids accounted for 6–30% of canopy leaching of base cations (Zhang et al. 2006). In the latter two approaches (reference and weak acid approaches) we found negative dry deposition for NO_3^- and H^+. Such negative dry deposition fluxes are actually impossible, but result from calculating dry deposition of H^+ and NH_4^+ as NTF minus estimated canopy exchange, where the latter depends on the calculated canopy leaching of base cations. This shows how errors in the estimated

base cation fluxes result in erroneously negative H^+ and NH_4^+ flux estimates (Staelens et al. 2008).

Some differences between the multiple regression and canopy budget model reported above might be explained by the fact that the characteristics of wet tropical climates with high relative humidity (>90%), large rainfall volumes and frequent rain events will generally accelerate element cycling and in particular enhance canopy leaching or more generally canopy exchange processes. Moreover, relatively long residence times during drizzle (e.g. in tropical regions) were shown to account for relatively high leaching rates compared to short rain periods with large rainfall intensities (Lovett and Lindberg 1984), and the amount of rainfall is one of the most important factors controlling the leaching of K^+ and DOC and the exudation of weak acids from plant tissues (Likens et al. 1996; Prescott 2002). Based on the discussion above we used the multiple regression model estimates of canopy exchange and dry deposition, as they are relatively unbiased in terms of assumptions on the underlying canopy ion-exchange and dry deposition processes compared to the canopy budget model. For future applications of the canopy budget model, more studies of dry deposition and canopy exchange fluxes in tropical rainforest canopies should be performed to generate a realistic mechanistic basis of canopy exchange processes applicable to remote and high-precipitation forests.

Contribution of canopy exchange and dry deposition to net throughfall

Based on NTF only we could not distinguish whether the enrichment in throughfall of solutes (Fig. 1) was due to dry deposition, canopy leaching, both processes, or dry deposition exceeding canopy uptake. Multiple linear regression analysis, however, demonstrated that on average NTF of Na^+, HPO_4^{2-}, SO_4^{2-}, K^+, Mg^{2+}, NH_4^+, Ca^{2+}, and DOC (in declining order) was controlled by canopy exchange processes (>50% canopy exchange of NTF). For DOC and K^+ strong net throughfall enrichment was linked to canopy leaching. Potassium and DOC are considered to be highly soluble substances that are easily washed out from canopy materials (Tobón et al. 2004b), explaining the highest canopy leaching fluxes at all three sites. Ca^{2+} and Mg^{2+} leaching were shown to depend on the nutrient status of the forest site (Filoso

et al. 1999), as shown here by highest canopy leaching of both ions at PRa where soil solution concentrations were highest.

For total nitrogen dry deposition was dominant, thereby probably masking the uptake of NH_4^+ and NO_3^- from rainfall. Canopy uptake of inorganic N (particularly NO_3^-) was to some extent balanced by canopy leaching of DON (and NH_4^+), resulting in net canopy leaching of TDN. The major source of DON to net throughfall in tropical forests has been considered to be foliar leaching or phyllosphere processes such as N_2 fixation by free-living diazotrophic organisms (Fürnkranz et al. 2008; Wanek and Pörtl 2005). Moreover, it has been debated whether NH_4^+ and NO_3^- uptake by the forest canopy is counterbalanced by DON release from epiphytes and epiphylls (Gaige et al. 2007; Wanek and Pörtl 2005). The latter pattern might hold to some extent in the study area where negative net throughfall of NO_3^- (and NH_4^+) pointed to net uptake of solutes from throughfall during passage through the canopy layer and DON increased in two out of three forest sites. Transformation of DIN to DON and N_2 fixation would most plausibly be subsumed under the dry deposition flux of DON while foliar leaching adds to the canopy exchange flux. However, N_2 fixation is highly dependent on sufficient surface moisture, therefore N_2 fixation products are thought to accumulate mostly during wet periods. In contrast the release of N fixed (DON, NH_4^+) occurs mostly after dry spells, eventually increasing with the length of dry period. A recent paper discusses this issue to some extent, noting that N_2 fixation did not greatly contribute to net throughfall fluxes of DON (Hinko-Najera Umana and Wanek 2010). Nitrogen is a major plant nutrient and in strongly nutrient limited forests, canopy uptake may supplement nutrients for plant growth. For instance, in boreal forests canopy uptake of N has been reported to meet up to 30% of the annual demand for net primary production (Lovett and Lindberg 1993). Similarly, uptake of essential nutrients such as N and P was found across a strong N to P limitation gradient in mangroves (Wanek et al. 2007) and across a soil nutrient gradient from nutrient-rich alluvial soils to nutrient-depleted upland terraces (Tobón et al. 2004b). Uptake of inorganic N forms in the canopy of our study site evidently was of less importance, as net canopy uptake of inorganic N occurred only at PRi site where the flux comprised

less than 2% of the annual litterfall N flux, and NTF of TDN demonstrated net release of N in the canopy.

Interestingly, we found a trend towards HPO_4^{2-} leaching from the forest canopy at all three sites, though lowland rainforests are considered to be P rather than N limited (Tanner et al. 1998). However, relatively low P use efficiencies and high litter P contents (Sigrid Drage, unpublished data) in this forest pointed to higher than average soil P availabilities, as a result of rapid land lift, enhanced erosion and weathering in the Golfo Dulce area (Gardner et al. 1992; Porder et al. 2006). Canopy leaching of HPO_4^{2-} can also be enhanced during the wet season or at sites of very high MAP where the net loss from the forest canopy is increased by the greater magnitude of heavy precipitation events (Filoso et al. 1999). The retention of H^+ (and NH_4^+) is considered to be the result of ion exchange processes with base cations in the forest canopy which decreases the acidity of rain and results in an enrichment of base cations and organic acids (Asman et al. 1998; Lovett et al. 1996). In support of the latter reaction principal component analysis of annual net throughfall based on individual throughfall traps yielded a principal component PC 4 in which the highly exchangeable elements H^+ and K^+ were negatively related. These reverse ion-exchange processes did not differ between forest type but followed more general physicochemical processes in the canopy (see also Tobón et al. 2004b).

Compared to canopy exchange dry deposition represented a large forest input of DOC, TDN, DON and K^+ and less for inputs of Cl^-, Ca^{2+}, Mg^{2+}, and SO_4^{2-}. Dry deposition controlled NTF of DON, TDN, Cl^- (and NO_3^-) i.e. contributed >50% to NTF. Sodium, Cl^-, Mg^{2+} and SO_4^{2-} are the major components of sea water, and external inputs are therefore commonly related to dry deposition of marine aerosols. Such a clear marine source of NTF of Na^+, Cl^-, Mg^{2+} and SO_4^{2-} was reflected in principle component PC 2 (Table 5). In contrast the multiple regression model indicated that dry deposition of Na^+ was negligible and the PCA results might therefore also be interpreted in terms of similar canopy exchange behaviour of these elements (see also discussion above). Potassium and Ca^{2+} are only minor solutes in sea water, and marine concentrations of NH_4^+ and DOC are negligible. These components are closely linked to biogenic emissions and biomass burning (Artaxo et al. 1998). Generally it is assumed

that dry deposition is of less importance than canopy exchange for base cations since they do not occur in gaseous phases and there is low aeolian transport of soil and dust particles in remote areas of continuous forests. In a Brazilian forest archipelago canopy exchange was therefore the dominant source of base cations to net throughfall, while dry deposition was important only during the dry season (Filoso et al. 1999). Although for SO_4^{2-} and Cl^- dry deposition was reported to be the main source to NTF in the Amazonian forest (Filoso et al. 1999), in our study this was the case for Cl^- but not for SO_4^{2-} which was dominated by canopy exchange processes. It has been shown that dry deposition changes seasonally with anthropogenic biomass burning during the dry season since forest burning increases emissions of NO_x, organic C and other elements such as K^+ and P and thus dry deposition of these compounds (Clark et al. 2001b). Biomass burning and natural background sources may therefore explain the dry deposition flux of P but especially that of DOC and DON in this study. Alternatively, dry deposition of DOC may represent migration of organic compounds from the interior of the leaf to the leaf surface to accumulate there during dry periods (Draaijers et al. 1997), while dry deposition of DON may be the same process, or N_2 fixation in the phyllosphere.

Dry deposition and canopy exchange represent the major mechanisms that control the chemical composition and deposition via NTF as shown above and discussed elsewhere (Filoso et al. 1999; Lovett and Lindberg 1984). It has been suggested that canopy exchange is mainly affected by species assemblage, vegetation structure, soil fertility and concentration of solutes in precipitation, whereas dry deposition is primarily influenced by climate (seasonality) and exposure of the canopy layer to atmospheric deposition (Levia and Frost 2006). Both dry deposition and canopy exchange vary in space and time since they are related to biological characteristics of the forest e.g. stand age, soil fertility, plant nutrient status, presence of insects, leaf area and epiphyte activity (Levia and Frost 2006). These seasonal and biological effects are discussed below.

Seasonal effects

In the tropics seasonal climate variations i.e. distinct wet and dry seasons can profoundly affect deposition

of elements resulting from differences in leaf area and litterfall patterns and in precipitation amounts. Season markedly affected throughfall fluxes, being due to higher volume weighted mean concentrations of most solutes (except NH_4^+, Ca^{2+}) during the dry season, and due to higher rainfall volumes in the wet season for NH_4^+, Mg^{2+} and Ca^{2+}. High dry season concentrations are directly linked to higher aerosol loads in air above the canopy that is washed out during precipitation events. In a Brazilian forest archipelago (Filoso et al. 1999) also a clear pattern of seasonality was found in NTF—in the rainy season the contribution of canopy exchange to NTF was significant for all ions except Na^+, whilst dry deposition significantly contributed to Cl^- only. During the dry season dry deposition affected NTF of most ions (except Cl^-, HPO_4^{2-} and H^+), whereas canopy exchange had an effect on all ions except Ca^{2+} and NH_4^+. These variations in volume weighted mean concentration and deposition of solutes between wet and dry seasons were also explained on the basis of large seasonal variations in rainfall depth and biogenic emissions (Filoso et al. 1999).

Topographic effects

Topography is strongly correlated with (i) altitude and exposure to wind, precipitation and aerosols and (ii) erosion and nutrient transfers from upland to downslope areas. While the first factor affects microclimate and deposition velocity, the second effectively controls soil fertility across topographic gradients. Topography may therefore increase dry deposition by exposure to aerosol laden air masses at ridges and canopy exchange by increasing soil fertility at downslope areas. We found clear evidence for increased dry deposition to the ridge forest (PRi) where NTF of Na^+ was significantly higher than at the ravine site (PRa). Moreover, principle component PC 2 from PCA analysis of net throughfall which was composed of sea salt ions (Na^+, Cl^-, Mg^{2+}, SO_4^{2-}) and NO_3^-, was significantly higher at the PRi site (compared to SRa) which was situated at a ridge at higher elevation and thus was more exposed to deposition of aerosols (see also (Eklund et al. 1997). The contribution of NO_3^- to principle component PC 2 may be explained by greater deposition of aerosols from biogenic origin or from biomass burning to the higher elevation site.

A significant effect of soil fertility and foliar nutrient concentration on NTF has been previously reported by Filoso et al. (1999) and Tobón et al. (2004b). Higher nutrient availability at the ravine site was supported by 12-fold higher soil water NO_3^- and 5-fold higher soil water HPO_4^{2-} concentrations at PRa compared to PRi (Table 2). This actually translated into higher NTF of NO_3^- and HPO_4^{2-} at the PRa site, and showed up in significantly higher factor loadings for principle component PC 3, which was determined by HPO_4^{2-} and NO_3^-. Greater NTF of HPO_4^{2-} can be attributed to higher soil fertility and lower nutrient use efficiency of N and P reflecting less nutrient limitation of the ravine site. This was also confirmed by nutrient inputs deriving from leaf litterfall (fine & coarse litter), where highest litterfall fluxes of C, N, Ca^{2+}, K^+, Mg^{2+} and P occurred at the PRa forest site, the site which turned out to be the most nutrient rich with fastest nutrient cycling rates (Table 3). Topography therefore had a significant effect on NTF in the Esquinas forest. Similarly NTF of K^+, P and Mg^{2+} were found to vary across other toposequences, with lower throughfall fluxes at upper slopes and higher ones at downslope sites in tropical forest sites in Mexico and Colombia (Campo-Alves 2003; Tobón et al. 2004b). Low NTF of N or P may be associated with a more economic use of these elements by trees and epiphytes at specific topographies. This would be in accordance with the conclusions of Veneklaas (1990) and Clark et al. (1998), suggesting limited availability and efficient use of N and P in tropical forests situated at higher altitudes.

Disturbance effects

Disturbance and forest regrowth have a strong impact on tree species composition, vegetation structure, and biomass and nutrient distribution. Tree species composition and vegetation structure were significantly affected by stage of succession (Table 6, Supplementary Table 3) but these parameters did not significantly affect NTF in secondary and primary ravine forests (Supplementary Table 2). However, the large demand for nutrients to allow regrowth and biomass accrual of secondary forests commonly leads to an intermittent decrease in soil nutrient availability (Hughes et al. 1999). Comparing primary ravine forest (PRa) and secondary ravine forest (SRa)

nutrient depletion was evident since NO_3^- and HPO_4^{2-} concentrations in soil water were 36- and 1.7-fold lower in the secondary forest (Table 2). Decreases in soil fertility at the SRa site also corresponded to significantly lower NTF of HPO_4^{2-} and NO_3^-. However, identification of sources of nutrients in net throughfall conducted by principal component analysis and further ANOVAs for differences between forest sites revealed that principle component PC 1 accounting for solutes that derived mainly from canopy exchange processes (K^+, Mg^{2+}, Ca^{2+}, DON and DOC) showed highest values at the SRa site. This result may be attributed to the characteristics of plant species in the secondary ravine forest in a relatively young stage of succession (~ 20 years after disturbance). Forests in different stages of succession exhibit differences in plant life forms, nutrient allocation and leaf traits of the characteristic species (Reich et al. 1992). Leaves of fast growing early successional species have a shorter leaf life time (Reich et al. 1991), are less sclerotic but are more nutrient rich (Poorter et al. 2004) and the present tree species at SRa are therefore more likely to leach readily soluble elements (Tukey 1970).

Canopy characteristics and tree species composition

Microclimate and soil fertility are also key determinants of vegetation composition and canopy characteristics such as the plant area index, which differed between PRa and PRi. Plant area index as a proxy for canopy cover is a major determinant of NTF by increasing the surface area to which aerosols are deposited and where nutrients can be exchanged. (Schroth et al. 1999) clearly demonstrated this relationship for tropical mono- and poly-cultures with canopy covers ranging between 7 and 100%. In this study plant area indices measured by SunScan system were high and varied between 6.9 and 8.3 (Table 6). Plant area indices from hemispheric photography were markedly lower due to saturation effects with increased overlapping of leaves and leaf clumping. The plant area index was significantly higher at the PRa forest site where highest NTF was found for HPO_4^{2-} and a trend towards increased net throughfall of DOC, K^+, Mg^{2+} and Ca^{2+} compared to the other sites. A greater variability in canopy characteristics at PRa, as suggested by higher

coefficients of variation of plant area indices and tree height, also results in greater canopy roughness. Canopy roughness may further increase NTF by enhancing dry deposition processes and thus nutrient deposition (Hansen et al. 1994; Lovett 1992; Parker 1983). However, on an individual throughfall trap basis, we found no correlation between plant area index and NTF of any solute. At this small scale the variation in NTF is therefore not accounted by simple canopy structure measures as applied above, and more elaborate models of throughfall fluxes have to be adopted (Levia and Frost 2006). The magnitude of water and nutrient fluxes inside the canopy, however, is also affected by non-vascular plants (mosses, liverworts and lichens) which may account for a large part of the vegetation's aboveground biomass, particularly in montane rainforests (Hölscher et al. 2004). In the Esquinas rainforest year-round high humidity resulted in dense epiphyte colonisation of ravine but not of ridge forests (PRa > PRi), while after ~ 20-years of succession epiphytes in SRa were virtually absent (Roland Albert, data not shown).

ANOSIM and SIMPER analysis revealed significant differences in tree species composition between forest sites due to distinct stages of succession and different topography (Supplementary Table 3). Tree species composition has been shown to significantly affect the hydrology and fluxes of nutrients and thus contribute to spatial variability of throughfall fluxes, especially in species-poor tree-based land use systems (Schroth et al. 1999). In this study, however, Spearman matrix rank correlations did not show that species composition exerted a significant influence on NTF compared between primary and secondary forest stands and between ravine and ridge forests. This is probably the effect of high species diversity in tropical lowland rainforests (160 species on 0.36 ha total surveyed site) what seems to outweigh the impact of certain tree species in terms of nutrient deposition.

Internal nutrient cycling via litterfall and canopy exchange

Comparison of nutrient cycling showed that litterfall generally represented a higher quantity of element input to the forest floor compared to throughfall (Fig. 2). Element inputs by litterfall in this study ranged among the highest reported for tropical forest

sites (Wood et al. 2006) (Table 3). Whereas internal cycling of N, Ca^{2+} and P mainly is associated with litterfall, other nutrients (e.g. K^+) are more susceptible to leaching of the canopy layer (Cavelier et al. 1997; Johnson 1992; Tobón et al. 2004b; Veneklaas 1991) and thus mainly cycle via throughfall (Levia and Frost 2003; Parker 1983). Chuyong et al. (2004) reported that the percentage of rain-based input (TF + SF) to gross inputs including litterfall was about 77% (K^+), 42% (Mg^{2+}), 35% (P), 27% (Ca^{2+}) but only 4% (N) for two different forest sites in Cameroon.

However, in terms of internal element cycling, litterfall cannot be compared directly to throughfall or net throughfall but rather to canopy exchange. According to our knowledge, we here present the first direct comparison of internal nutrient cycling via litterfall and canopy exchange for tropical forest ecosystems. Our data indicate that the contribution of canopy exchange to aboveground inputs of elements to the forest floor was low to negligible for C, N and Ca^{2+}, contributed about 10% to Mg^{2+} and P but >50% to K^+ (Fig. 2). Therefore, canopy exchange contributed to aboveground nutrient cycling where solutes are easily leached from the canopies i.e. K^+, HPO_4^{2-} and Mg^{2+}, while naturally the contribution of canopy exchange to internal cycling of C was negligible (<1%). DON leaching was partly counterbalanced by NH_4^+ and NO_3^- uptake, and the contribution of canopy exchange of TDN was therefore only 1.5% for total N. However, the contributions were substantial for K^+, i.e. 53%, and for Mg^{2+} and P, i.e. 12.3% and 8.2%. In comparison, in pine and birch forests as well as regenerating forests stands in Belgium, canopy exchange did not contribute to aboveground cycling of N due to strong net canopy uptake of inorganic N (DON was not assessed) and little to Ca^{2+} (0–16%) while it contributed by 44–78% to K^+ and 17–48% to Mg^{2+} (De Schrijver et al. 2009; De Schrijver et al. 2004). This enhanced canopy exchange contribution was most probably due to strong acid and enhanced N deposition triggering base cation leaching and therefore enhanced canopy exchange fluxes for Ca^{2+} and Mg^{2+} compared to litterfall.

Quantification of external nutrient inputs via wet and dry deposition

Contributions of dry deposition to total atmospheric deposition (sum of bulk/wet and dry deposition) were greatest for DON (90%), high for DOC, TDN and K^+

(43–48%) and Cl^- (29%) but <10% for the other elements. Therefore bulk deposition fluxes would have to be corrected by a factor of approximately 1.0 to 1.9 (DON: 10.4) to estimate total atmospheric deposition to forests, depending on the element considered. For solutes such as Cl^-, NH_4^+, SO_4^{2-}, HPO_4^{2-}, Ca^{2+}, and Mg^{2+} the correction factor ranged from 1.0 to 1.4 while for K^+, DOC, TDN and DON it was between 1.8 and 10.4. Only few studies on tropical forests are available that reported estimates of dry deposition and bulk deposition fluxes and therefore allow us to assess total atmospheric deposition. Correction factors calculated from published data by far exceeded ours for specific solutes. For instance in an off-shore mangrove ecosystem dominated by *Rhizophora mangle* (Wanek et al. 2007) the correction factors ranged from 2.2 to 3.4 for base cations (K^+, Ca^{2+} and Mg^{2+}) and was 2.8 for SO_4^{2-}. Sea-salt derived solutes i.e. Na^+ and Cl^- were underestimated by a factor of 2.9 and 3.8. At a more remote site in a flooded forest archipelago at the Negro River in Brazil (Filoso et al. 1999) correction factors were even higher, and ranged between 1.5 and 35 for cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) and were 1.6 and 6.8 for SO_4^{2-} and HPO_4^{2-}. Although situated far from the coast values for Na^+ and Cl^- input had to be corrected by 1.6 and 3.2 (Filoso et al. 1999). These results therefore indicate that previous calculations of atmospheric inputs to tropical forest ecosystem have been profoundly underestimated, depending on the ionic form and element.

Conclusions

Two models, the multiple regression model and the canopy budget model, were tested for their suitability to partition NTF into canopy exchange and dry deposition contributions. In places with rainfall >5 m per year and an average dry period of <0.5 days between rain events it is very difficult to accurately estimate dry deposition based on the multiple regression model. Sampling and analysis of more rainfall events with greater variability in the length of the antecedent dry period may improve these estimates. Moreover, the high biological dynamic of N and P in the forest canopy resulted in non-significant models for NH_4^+, NO_3^- and HPO_4^-. Biochemical transformations such as mineralization and

assimilation reactions link the pools of inorganic and organic N forms (as well as P forms) and therefore did not allow using multiple regression models to dissect the contribution of dry deposition and canopy exchange to net throughfall of inorganic N and P though this was possible for the sum of inorganic and organic N. Based on the multiple regression model but considering the constraints presented above, we showed that former estimates, which accounted for bulk precipitation only, underestimated atmospheric deposition as external input of elements to tropical rainforests. Further, we demonstrated that factors affecting the amount and ratio of dry deposition and canopy exchange strongly affected NTF. Tree species composition did not explain the differences found in NTF between forest sites, and vegetation characteristics had no (tree height) or little effect (plant area index) on NTF. Compared to a mature forest, a younger forest had lower leaching of N and P but higher canopy exchange of highly leachable solutes. Topography most significantly affected NTF, possibly from enhanced dry deposition to higher elevation sites and higher soil fertility and canopy exchange at down slope sites. The application of approaches to partition NTF therefore will allow further insights into the biotic and geochemical controls of internal nutrient cycling of tropical rainforests, allowing better understanding of climatic versus nutrient controls of net primary production in times of globally changing environments.

References

Artaxo P, Fernandes ET, Martins JV, Yamasoe MA, Hobbs PV, Maenhaut W, Longo KM, Castanho A (1998) Large-scale aerosol source apportionment in Amazonia. J Geophys Res Atmos 103:31837–31847

Asman WAH, Sutton MA, Schjorring JK (1998) Ammonia: emission, atmospheric transport and deposition. New Phytol 139:27–48

Baker TR, Phillips OL, Malhi Y, Almeida S, Arroyo L, Di Fiore A, Erwin T, Higuchi N, Killeen TJ, Laurance SG, Laurance WF, Lewis SL, Monteagudo A, Neill DA, Vargas PN, Pitman NCA, Silva JNM, Martinez RV

(2004a) Increasing biomass in Amazonian forest plots. Philos Trans Roy Soc London Ser B Biol Sci 359:353–365

Baker TR, Phillips OL, Malhi Y, Almeida S, Arroyo L, Di Fiore A, Erwin T, Killeen TJ, Laurance SG, Laurance WF, Lewis SL, Lloyd J, Monteagudo A, Neill DA, Patino S, Pitman NCA, Silva JNM, Martinez RV (2004b) Variation in wood density determines spatial patterns in Amazonian forest biomass. Global Change Biol 10:545–562

Beringer J, McIlwaine S, Lynch AH, Chapin FS, Bonan GB (2002) The use of a reduced form model to assess the sensitivity of a land surface model to biotic surface parameters. Clim Dyn 19:455–466

Campo-Alves J (2003) Nutrient availability and fluxes along a toposequence with tropical dry forest in Mexico. Agrociencia 37:211–219

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

Chapin FS III, Matson PA, Mooney HA (2002) Principles of terrestrial ecosystem ecology. Springer-Verlag, New York

Chuyong GB, Newbery DM, Songwe NC (2004) Rainfall input, throughfall and stemflow of nutrients in a central African rain forest dominated by ectomycorrhizal trees. Biogeochemistry 67:73–91

Clark KL, Nadkarni NM, Schaefer D, Gholz HL (1998) Cloud water and precipitation chemistry in a tropical montane forest, Monteverde, Costa Rica. Atmos Environ 32:1595–1603

Clark DA, Brown S, Kicklighter DW, Chambers JQ, Thomlinson JR, Ni J (2001a) Measuring net primary production in forests: concepts and field methods. Ecol Appl 11:356–370

Clark DA, Brown S, Kicklighter DW, Chambers JQ, Thomlinson JR, Ni J, Holland EA (2001b) Net primary production in tropical forests: an evaluation and synthesis of existing field data. Ecol Appl 11:371–384

Clarke, Gorley RN (2006) PRIMER v6: User manual/tutorial, PRIMER-E, Plymouth UK, 192 pp

Cronan CS, Reiners WA (1983) Canopy processing of acidic precipitation by coniferous and hardwood forests in New-England. Oecologia 59:216–223

De Schrijver A, Nachtergale L, Staelens J, Luyssaert S, De Keersmaeker L (2004) Comparison of throughfall and soil solution chemistry between a high-density Corsican pine stand and a naturally regenerated silver birch stand. Environ Pollut 131:93–105

De Schrijver A, Geudens G, Wuyts K, Staelens J, Gielis L, Verheyen K (2009) Nutrient cycling in two continuous cover scenarios for forest conversion of pine plantations on sandy soil. I. Nutrient cycling via aboveground tree biomass. Can J For Res 39:441–452

Delta-T-Devices (1999) Hemiview Canopy Analysis Software V2.1 (1999) Delta-T Devices Ltd. http://www.delta-t.co.uk

Dixon RK (1994) Carbon pools and flux of global forest ecosystems (Vol 263, Pg 185, 1994). Science 265:171–171

Draaijers GPJ, Erisman JW (1995) A canopy budget model to assess atmospheric deposition from throughfall measurements. Water Air Soil Pollut 85:2253–2258

Draaijers GPJ, Vanek R, Bleuten W (1994) Atmospheric deposition in complex forest landscapes. Bound Layer Meteor 69:343–366

Draaijers GPJ, Erisman JW, Spranger T, Wyers GP (1996) The application of throughfall measurements for atmospheric deposition monitoring. Atmos Environ 30:3349–3361

Draaijers GPJ, Erisman JW, VanLeeuwen NFM, Romer FG, teWinkel BH, Veltkamp AC, Vermeulen AT, Wyers GP (1997) The impact of canopy exchange on differences observed between atmospheric deposition and throughfall fluxes. Atmos Environ 31(3):387–397

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

Field CB, Behrenfeld MJ, Randerson JT, Falkowski P (1998) Primary production of the biosphere: integrating terrestrial and oceanic components. Science 281:237–240

Filoso S, Williams MR, Melack JM (1999) Composition and deposition of throughfall in a flooded forest archipelago (Negro River, Brazil). Biogeochemistry 45:169–195

Fisch G, Tota J, Machado LAT, Dias M, Lyra RFD, Nobre CA, Dolman AJ, Gash JHC (2004) The convective boundary layer over pasture and forest in Amazonia. Theor Appl Climatol 78:47–59

Fürnkranz M, Wanek W, Richter A, Abell G, Rasche F, Sessitsch A (2008) Nitrogen fixation by phyllosphere bacteria associated with higher plants and their colonizing epiphytes of a tropical lowland rainforest of Costa Rica. Isme J 2:561–570

Gaige E, Dail DB et al (2007) Changes in canopy processes following whole-forest canopy nitrogen fertilization of a mature spruce-hemlock forest. Ecosystems 10(7):1133–1147

Gardner TW, Verdonck D, Pinter NM, Slingerland R, Furlong KP, Bullard TF, Wells SG (1992) Quaternary uplift astride the Aseismic Cocos Ridge, Pacific Coast, Costa-Rica. Geol Soc Am Bull 104:219–232

Hansen K, Draaijers GPJ, Ivens W, Gundersen P, Vanleeuwen NFM (1994) Concentration variations in rain and canopy throughfall collected sequentially during individual rain events. Atmos Environ 28:3195–3205

Harrington RA, Fownes JH, Vitousek PM (2001) Production and resource use efficiencies in N- and P-limited tropical forests: a comparison of responses to long-term fertilization. Ecosystems 4:646–657

Herwitz SR, Levia DF (1997) Mid-winter stemflow drainage from bigtooth aspen (Populus grandidentata Michx) in Central Massachusetts. Hydrol Process 11:169–175

Hinko-Najera Umana N, Wanek W (2010) Large canopy exchange fluxes of inorganic and organic nitrogen and preferential retention of nitrogen by epiphytes in a tropical lowland rainforest. Ecosystems 13(3):367–381

Holdridge LR (1967) Life zone ecology. Tropical Science Center, San Jose, Costa Rica

Hölscher D, Köhler L, Van Dijk AIJM, Bruijnzeel LAS (2004) The importance of epiphytes to total rainfall interception by a tropical montane rainforest in Costa Rica. J Hydrol 292:308–322

Hughes RF, Kauffman JB, Jaramillo VJ (1999) Biomass, carbon, and nutrient dynamics of secondary forests in a humid tropical region of Mexico. Ecology 80:1892–1907

Johnson DW (1992) Base cations. In: Johnson DW, Lindberg SE (eds) Atmospheric deposition and forest nutrient cycling. Springer-Verlag, New York, pp 233–235

Kolmer JA, Spaulding EH, Robinson HW (1951) Approved laboratory techniques. Appleton Century Crafts, New York

Kopacek J, Turek J, Hejzlar J, Santruckova H (2009) Canopy leaching of nutrients and metals in a mountain spruce forest. Atmos Environ 43:5443–5453

Levia DF, Frost EE (2003) A review and evaluation of stemflow literature in the hydrologic and biogeochemical cycles of forested and agricultural ecosystems. J Hydrol 274:1–29

Levia DF, Frost EE (2006) Variability of throughfall volume and solute inputs in wooded ecosystems. Prog Phys Geogr 30:605–632

Likens GE, Driscoll CT, Buso DC (1996) Long-term effects of acid rain on ecosystems of the Hubbard Brook Experimental Forest. Bull Ecol Soc Am 77:266

Lindberg SE, Bredemeier M, Schaefer DA, Qi L (1990) Atmospheric concentrations and deposition of nitrogen and major ions in conifer forests in the United States and Federal Republic of Germany. Atmos Environ 24A:2207–2220

Lovett GM (1992) Atmospheric deposition and canopy interactions of nitrogen. In: Johnson DW, Lindberg SE (eds) Atmospheric deposition and forest nutrient cycling. Springer-Verlag, New York, pp 152–166

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, Lindberg SE (1993) Atmospheric deposition and canopy interactions of nitrogen in forests. Can J For Res—Revue Canadienne De Recherche Forestiere 23:1603–1616

Lovett GM, Nolan SS, Driscoll CT, Fahey TJ (1996) Factors regulating throughfall flux in a New Hampshire forested landscape. Can J For Res 26:2134–2144

Malhi Y, Baker TR, Phillips OL, Almeida S, Alvarez E, Arroyo L, Chave J, Czimczik CI, Di Fiore A, Higuchi N, Killeen TJ, Laurance SG, Laurance WF, Lewis SL, Montoya LMM, Monteagudo A, Neill DA, Vargas PN, Patino S, Pitman NCA, Quesada CA, Salomao R, Silva JNM, Lezama AT, Martinez RV, Terborgh J, Vinceti B, Lloyd J (2004) The above-ground coarse wood productivity of 104 Neotropical forest plots. Global Change Biol 10:563–591

Martinelli LA (2004) A 'fantasy island' for tropical biogeochemistry: nutrient cycling and limitation by Peter Vitousek. Princeton University Press, 2004. (232 pages). Trends Ecol Evol 19:295

Melillo JM, McGuire AD, Kicklighter DW, Moore B, Vorosmarty CJ, Schloss AL (1993) Global climate-change and terrestrial net primary production. Nature 363:234–240

Neter J, Kutner MH, Nachtsheim CJ, Wasserman W (1996) Applied linear statistical models. WCB McGraw-Hill/Irwin, Boston, MA, pp 1408

Nobis M (2005) SideLook 1.1—Imaging software for the analysis of vegetation structure with true-colour photographs; http://www.appleco.ch

Oliver BG, Thurman EM, Malcolm RL (1983) The contribution of humic substances to the acidity of colored natural-waters. Geochim Cosmochim Acta 47:2031–2035

Pamperl S (2001) Der Boden als Standortfaktor eines baum-artenreichen Tieflandregenwaldes in Costa Rica. Formal- und Naturwissenschaftliche Fakultät (p 107+). University of Vienna, Vienna

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

Poorter L, de Plassche MV, Willems S, Boot RGA (2004) Leaf traits and herbivory rates of tropical tree species differing in successional status. Plant Biol 6:746–754

Porder S, Clark DA, Vitousek PM (2006) Persistence of rock-derived nutrients in the wet tropical forests of La Selva, Costa Rica. Ecology 87:594–602

Prescott CE (2002) The influence of the forest canopy on nutrient cycling. Tree Physiol 22:1193–1200

Puckett LJ (1990) Estimates of ion sources in deciduous and coniferous throughfall. Atmos Environ 24:545–555

Reich PB, Uhl C, Walters MB, Ellsworth DS (1991) Leaf life-span as a determinant of leaf structure and function among 23 Amazonian tree species. Oecologia 86:16–24

Reich PB, Walters MB, Ellsworth DS (1992) Leaf life-span in relation to leaf, plant, and stand characteristics among diverse ecosystems. Ecol Monogr 62:365–392

Ruijgrok W, Tieben H, Eisinga P (1997) The dry deposition of particles to a forest canopy: a comparison of model and experimental results. Atmos Environ 31:399

Schinner F, Öhlinger R, Kandeler E, Margesin R (eds) (1996) Methods in soil biology. Springer Verlag, Berlin

Schroth G, da Silva LF, Wolf MA, Teixeira WG, Zech W (1999) Distribution of throughfall and stemflow in multi-strata agroforestry, perennial monoculture, fallow and primary forest in central Amazonia, Brazil. Hydrol Process 13:1423–1436

Schroth G, Elias MEA, Uguen K, Seixas R, Zech W (2001) Nutrient fluxes in rainfall, throughfall and stemflow in tree-based land use systems and spontaneous tree vegetation of central Amazonia. Agric Ecosyst Environ 87:37–49

Schuur EAG (2003) Productivity and global climate revisited: the sensitivity of tropical forest growth to precipitation. Ecology 84:1165–1170

Staelens J, Houle D, De Schrijver A, Neirynck J, Verheyen K (2008) Calculating dry deposition and canopy exchange with the canopy budget model: review of assumptions and application to two deciduous forests. Water Air Soil Pollut 191:149–169

STATSOFT (2005) STATSOFT (2005): STATISTICA for Windows 7.1. Statsoft Inc, Tulsa, Oklahoma

Tanner EVJ, Vitousek PM, Cuevas E (1998) Experimental investigation of nutrient limitation of forest growth on wet tropical mountains. Ecology 79:10–22

ter Steege H, Pitman NCA, Phillips OL, Chave J, Sabatier D, Duque A, Molino JF, Prevost MF, Spichiger R, Castellanos H, von Hildebrand P, Vasquez R (2006) Continental-scale patterns of canopy tree composition and function across Amazonia. Nature 443:444–447

Tobón C, Sevink J, Verstraten JM (2004a) Litterflow chemistry and nutrient uptake from the forest floor in northwest Amazonian forest ecosystems. Biogeochemistry 69:315–339

Tobón C, Sevink J, Verstraten JM (2004b) Solute fluxes in throughfall and stemflow in four forest ecosystems in northwest Amazonia. Biogeochemistry 70:1–25

Tukey HB (1970) The leaching of substances from plants. Ann Rev Plant Physiol 21:305–324

Ulrich B (1983) Interaction of forest canopies with atmospheric constituents: SO_2, alkali and earth alkali cations and chloride. In: Ulrich B, Pankrath J (eds) Effects of accumulation of air pollutants in forest ecosystems. Reidel, Dordrecht, The Netherlands, pp 33–45

Vasquez MA (1989) Mapa de Suelos de Costa Rica

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

Veneklaas EJ (1991) Litterfall and nutrient fluxes in two montane tropical rain forests, Colombia. J Trop Ecol 7:319–336

Vitousek PM (1984) Litterfall, nutrient cycling, and nutrient limitation in tropical forests. Ecology 65:285–298

Vitousek P (2004) Nutrient cycling and limitation. Hawai'i as a model system. Princeton University Press, Oxford and Princeton

Wanek W, Pörtl K (2005) Phyllosphere nitrogen relations: reciprocal transfer of nitrogen between epiphyllous liverworts and host plants in the understorey of a lowland tropical wet forest in Costa Rica. New Phytol 166:577–588

Wanek W, Hofmann J, Feller IC (2007) Canopy interactions of rainfall in an off-shore mangrove ecosystem dominated by Rhizophora mangle (Belize). J Hydrol 345:70–79

Wanek W, Drage S, Hinko N, Hofhansl F, Pölz EM, Ratzer A, Richter A (2008) Primary Production and nutrient cycling in lowland rainforests of the Golfo Dulce region. In: Aubrecht G (ed) Natural and cultural history of the Golfo Dulce region, Costa Rica. Stapfia, Biologiezentrum des OÖ Landesmuseum, Linz, pp 155–177

Weber A, Huber W, Weissenhofer A, Zamora N & Zimmermann G (2001) An introductory field guide to the flowering plants of the Golfo Dulce Rain Forests, Costa Rica. Biologiezentrum des OÖ Landesmuseums

Weissenhofer A (1996) Ökologie und Struktur eines Tieflandregenwaldes in der Pazifikregion von Costa Rica. Diploma Thesis: University of Vienna

Weissenhofer A, Huber W, Mayer V, Pamperl S, Weber A (2008) Natural and cultural history of the Golfo Dulce region, Costa Rica. Stapfia, Biologiezentrum des OÖ Landesmuseum, Linz

Wood TE, Lawrence D, Clark DA (2006) Determinants of leaf litter nutrient cycling in a tropical rain forest: soil fertility versus topography. Ecosystems 9:700–710

Zhang G, Zeng GM, Jiang YM, Yao JM, Huang GH, Jiang XY, Tan W, Zhang XL, Zeng M (2006) Effects of weak acids on canopy leaching and uptake processes in a coniferous–deciduous mixed evergreen forest in central-south China. Water Air Soil Pollut 172:39–55