Internal nutrient fluxes in a Puerto Rican rain forest

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ABSTRACT. Throughfall and soil solution chemistry were studied for 1 y in a tropical montane forest in the Luquillo Mountains of Puerto Rico. Passage of precipitation through the forest canopy resulted in an increase in the concentration and flux of all solutes except H^+ and NO_3^-. Throughfall chemistry showed no strong seasonal patterns, but concentrations of many solutes declined during weeks of high rainfall. Enrichment in throughfall relative to precipitation was similar to values reported recently for several other tropical sites, with the exception of NH_4^+, which was particularly high at this site. Based on net throughfall deposition of Cl^-, dry deposition of marine aerosols appears to be a relatively minor component (*c.* 15%) of total deposition. In soil solution, no seasonal patterns in concentration were evident and variability was highest for elements with high biological activity (especially N). Concentrations and fluxes of K^+ and dissolved organic carbon (DOC) showed the largest declines as throughfall passed through the soil profile; concentrations of most other elements increased or were relatively constant. Declining DOC flux through the soil profile appears to be due to sorption processes similar to those observed in many temperate forests. Concentrations and fluxes of HCO_3^- and SiO_2 increased substantially in soil solution, but never approached those observed in the stream. This suggests that additional weathering must occur as groundwater moves from this ridgetop site to the stream.

KEY WORDS: dissolved organic carbon, nitrogen, nutrient cycles, phosphorus, Puerto Rico, soil solution, throughfall, tropical rain forest

INTRODUCTION

The flow of water through terrestrial ecosystems links atmosphere, vegetation, soil and surface waters. In humid environments, nutrient cycles are closely tied to these hydrologic linkages. Nutrients are deposited in wet and dry deposition, produced or retained by the forest canopy, flushed into groundwater as throughfall infiltrates the soil profile, and exported from the catchment in stream water.

Interactions between hydrologic and nutrient cycles are well documented for

many temperate forests (e.g. Likens *et al.* 1977), but much less is known about such interactions in tropical forests. In his review, Bruijnzeel (1990) summarized the current understanding of nutrient and hydrologic cycles in tropical forests. He concluded that rates of litterfall and litter decomposition are well known, but that hydrologic fluxes (wet deposition, throughfall and groundwater) are poorly characterized. The extent to which the forest canopy is a source or sink of nutrients for water deposited to the canopy as rainfall or cloud water, for example, is unclear. Early work by Jordan *et al.* (1980) and Manokaron (1980) suggested that the canopy of tropical forests is a net sink for many elements, but more recent work at other sites shows it is a source, rather than a sink, for most solutes (Asbury *et al.* 1994, Forti & Moreira-Nordemann 1991, Veneklaas 1990).

Characterization of nutrient cycles in tropical forests is important from the perspective of both ecological theory and forest management. Early authors emphasized the 'tightness' of nutrient cycling in the humid tropics, and argued that this is a reflection of nutrient paucity in tropical soils. As more data have accumulated on nutrient cycles and soil chemistry in tropical forests, this ecological paradigm has begun to be seriously questioned (e.g. Whitmore 1989). Understanding nutrient cycles has great practical importance for forest management, where concerns for site degradation due to nutrient losses associated with harvesting may cause a rethinking of silvicultural practices (Bruijnzeel 1983).

The purpose of this study was to characterize the magnitude of internal elemental fluxes (throughfall and soil water) in a montane rain forest of Puerto Rico. Previously published estimates of hydrologic fluxes were combined with newly reported analyses of solution chemistry to generate elemental fluxes in throughfall and soil water. With the availability of previously published data on other fluxes such as wet deposition, litterfall, weathering and hydrologic export, the importance of these newly measured internal fluxes in overall nutrient cycling at the site can be assessed.

METHODS

Study site

The study site is located in the Luquillo Mountains of northeastern Puerto Rico, in the Luquillo Experimental Forest (Figure 1). The Luquillo Mountains are of volcanic origin with a geological age of mid- to late-Cretaceous (Seiders 1971). Bedrock is andesitic igneous rock that contains some interbedded mudstones of marine origin, and soils are acidic clays (ultisols of the Los Guineos Series; Boccheciamp 1977). Hydrologic flow paths through these ultisols tend to be shallow: in a riparian site in the nearby Bisley catchment, McDowell *et al*. (1992) found that most flow through the soil profile appeared to occur as shallow interflow at depths of 40–60 cm. Total exchangeable cations are
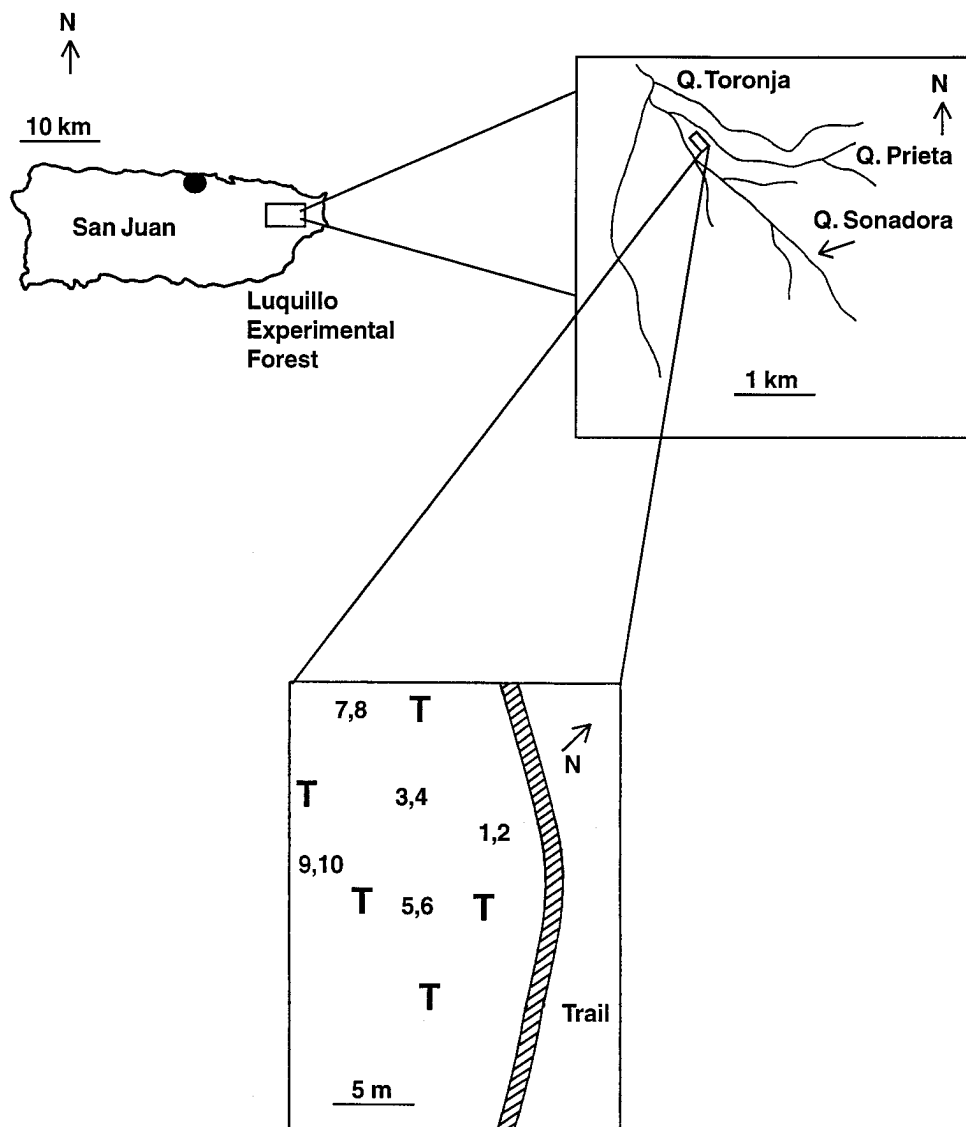
Figure 1. Location of the study plot in the Luquillo Experimental Forest, Puerto Rico. T = throughfall collector. Numbers refer to lysimeters.

12.5 cmol kg^{-1} soil in ridgetop soils of the Luquillo Experimental Forest, and are similar to levels found in other montane tropical forests (Silver *et al.* 1994). Organic matter content in surface horizons averages 9.6%, and declines with depth to 1.4% at 30–60 cm. Total nitrogen also declines with depth, ranging from 0.34% at the surface to 0.08% at 30–60 cm depth, and is somewhat lower than concentrations typically found in tropical montane forest (Silver *et al.* 1994). The plant community is dominated by the tabonuco (*Dacryodes excelsa*

Vahl) forest type (Brown *et al.* 1983). Prior to inclusion in the National Forest system *c*. 70 y ago, the site was part of a small farm with coffee, fruit and charcoal production.

Peak precipitation at the site occurs in May and from August to November (McDowell & Estrada-Pinto 1988). Hurricanes and tropical depressions produce individual rainfall events which are highly unpredictable and of high intensity, and hurricanes play a major role in structuring plant community dynamics and life histories (e.g. Zimmerman *et al.* 1995). Elemental fluxes including wet and bulk deposition, litterfall, and hydrologic export are known for the site (McDowell *et al.* 1990, McDowell & Asbury 1994, Zou *et al.* 1995).

Field sampling

The study was conducted on a 25-m × 25-m plot located near the El Verde field station, on a steep ridge (slopes up to 100%) between Quebrada Sonadora and Quebrada Prieta at *c*. 390 m elevation (Figure 1). The site itself was relatively flat, however, with slopes of *c*. 5% and a general downward trend from NE to SW. Rainfall was collected on a 25-m walk-up tower *c*. 40 m upslope of the study plot and inputs for the study period were obtained from previously published data (McDowell *et al.* 1990). Elemental flux in stream water was obtained from a nearby gauged catchment (Quebrada Toronja; Figure 1) using data reported previously by McDowell & Asbury (1994). Lysimeters (porous cup ceramic tension lysimeters, Soil Moisture Corporation) were installed at depths of 40 and 80 cm at five locations in the plot (Figure 1). Prior to installation, lysimeters were acid-washed (10% HCl), rinsed copiously, and soaked in deionized water for 3 d, and the first litre collected from each lysimeter was discarded to allow porous cups to reach equilibrium with the soil solution (Debyle *et al.* 1988). A vacuum (0.3 MPa) was applied to each lysimeter following sample collection, and typically some vacuum was maintained until the next sample collection. Each lysimeter typically collected soil solution each week; only rarely (several times during the study) were soil conditions dry enough that no water was collected in one or more lysimeters.

Five throughfall collectors were also installed in the plot. Each collector consisted of a primary (all-plastic) and secondary (all-glass) collector. The primary collector consisted of a 20-cm diameter polyethylene funnel attached with Tygon tubing to a 2-l plastic collection bottle. Evaporation from the collection bottle was minimized by use of a vapour lock (loop) in the tubing (Galloway & Likens 1976). The all-glass collector consisted of a funnel with ground glass fittings attached to a round-bottom flask. To exclude large particulate matter from both types of collectors, fibreglass mesh window screen covered the tops of the funnels and a plug of acid-washed glass wool was placed in their necks. All collectors were replaced weekly with a clean, acid-washed collector to minimize growth of microorganisms on the collector walls.

Each lysimeter and throughfall collector was sampled weekly from June 1984 to June 1985. Lysimeters were sampled and subsequently evacuated on the

same day; thus both lysimeter and throughfall samples could have been held in the field for up to 6 d prior to collection. Soil solution was collected on the day following rainfall and throughfall collection. The high frequency and unpredictable nature of rainfall made event sampling unfeasible. On most collecting dates, samples were taken from individual collectors and combined by type (primary and secondary throughfall collectors, 40-cm lysimeters, and 80-cm lysimeters).

Chemical analysis

Samples from the primary collectors were analyzed for pH (glass combination electrode, unstirred open-top vessel), conductivity, and dissolved inorganic carbon (DIC) at the El Verde field station *c*. 1 km from the study plot. Samples were then filtered through pre-combusted Whatman GF/F glass fibre filters (nominal pore size 0.7 μm) and held on ice or refrigerated until analysis in San Juan. DIC was analyzed using syringe stripping and infrared spectroscopy (Stainton 1973). Bicarbonate was calculated from temperature, DIC and pH. Dissolved organic carbon (DOC) was measured on samples from the all-glass secondary collector using the persulfate oxidation technique (McDowell *et al.* 1987). Adsorption of DOC by mineral soil was determined using the method of McDowell & Wood (1984) with soils collected from a single soil pit near the site. On three faces of the pit, two replicate composite samples were taken from 0 to 80 cm in the mineral soil. On the fourth face of the pit, soil was sampled by depth at 0–10 , 10–40 and 40–80 cm. A dried, ground (1-mm) sample of the litter layer at the site was extracted for 24 h in distilled water at room temperature (234 g in 4 l) to produce the solution used as a source of DOC in these sorption experiments. Results of the sorption experiments were analyzed using the initial mass technique of Nodvin *et al.* (1986).

Na^+ K^+, Ca^{2+} and Mg^{2+} were measured by flame atomic absorption spectrophotometry. Chloride (thiocyanate), silicate (molybdate blue), nitrate-nitrite (Cd-Cu reduction) and ammonium (phenol-hypochlorite) were measured using automated colorimetry (Technicon AutoAnalyzer II). Periodic testing showed no detectable nitrite concentrations, thus the results are reported as nitrate alone. Total dissolved phosphorus (TDP) was measured following persulfate digestion (Solorzano & Sharp 1980) in sealed glass ampoules; the resulting phosphate was measured using the automated molybdate blue method. Several solutes were sometimes present below detection limits; these included NO_3^--N (detection limit 0.01 mg l^{-1}), NH_4^+-N (0.002 mg l^{-1}), SiO_2 (0.1 mg l^{-1}) and TDP (0.002 mg l^{-1}). Analytical error was typically 20–30% near the detection limits, and 5% at higher concentrations.

Flux calculations

Elemental fluxes for the period 11 June 1984–10 June 1985 were calculated for rainfall, throughfall, soil solution and stream flow as the product of hydrologic flux and the volume-weighted mean concentration for the year. Hydrologic

fluxes were all based on measurements made in previously published studies. Rainfall volume and chemistry for the study period were obtained from data on bulk rainfall chemistry previously summarized by McDowell *et al.* (1990). Throughfall has varied little in several studies of the tabonuco forest type at various sites and times in the Luquillo Experimental Forest, and averages 59% of incident precipitation on an annual basis (Scatena 1990). Because the relatively small number of collectors used in this study (five) has a potential error of 25 % in measuring water flux in this plot (c.f. Bruijnzeel 1989), I have chosen to use the extensive data base on throughfall quantity summarized by Scatena (1990) to calculate elemental fluxes in throughfall. Stemflow ranges from 1.4 to 5% of precipitation on a storm-by-storm basis in the tabonuco forest (Clements & Colon 1975). Because it was not sampled in this study, no estimates of elemental fluxes in stemflow are presented here. Hydrologic flux in soil solution was assumed to be equal to streamflow, because 80% of tree roots (and presumably transpiration) occur in the upper 20 cm of the soil at this site (Lugo 1992). Hydrologic and nutrient fluxes in deep soil solution may be overestimated due to the likelihood that some soil water moves laterally through the soil profile as shallow interflow at depths of 0–40 cm below the soil surface (McDowell *et al*. 1992). Streamflow for the study period was estimated as 50% of incident precipitation, based on runoff from Quebrada Toronja, a small gauged stream (16.2-ha catchment area) within 1 km of the study plot (McDowell & Asbury 1994).

RESULTS

Total ionic strength increased throughout the solution profile from precipitation to stream. Dominance shifted, as the Na^+ and Cl^- derived from marine aerosols were replaced by Ca^{2+}, Mg^{2+} and HCO_3^- derived from weathering reactions (Table 1). Nitrogen, P, K and DOC showed different patterns, with highest concentrations in internal fluxes (throughfall and soil solution) and lowest in inputs and outputs. The concentration and flux of all elements except H^+ and NO_3^- increased as precipitation passed through the forest canopy (Table 1).

Concentrations of some ions in throughfall were related to rainfall quantity, with concentrations highest during periods of low precipitation (e.g. Figure 2). Significant relationships were obtained between log (concentration) and rainfall volume for Cl^-, Na^+, Mg^{2+}, Ca^{2+} and SiO_2 ($r^2 = 0.16$ to 0.41; $P < 0.05$). No significant relationship with volume was observed for NO_3^-, NH_4^+, TDP, K^+ or DOC. No seasonal trends in any solute were evident in throughfall chemistry. When the five throughfall collectors were analyzed individually on 4 of the 47 weekly samples, average coefficients of variation (CVs) ranged from 23% for Cl^- to 103% for K^+.

Temporal variability in soil solution was particularly high for NO_3^- and NH_4^+, and relatively low for Cl^- (Figure 3). Analytical variability was small relative

Table 1. Volume-weighted mean concentrations in bulk precipitation, throughfall, soil solution (40 and 80 cm depth) and stream water in a tropical rain forest at El Verde, Puerto Rico. Rainfall chemistry is taken from data summarized by McDowell *et al.* (1990); stream chemistry (Quebrada Toronja) is from McDowell & Asbury (1994).

| | Rainfall | | Throughfall | | Soil solution at depth (cm) | | | | Stream water | |
| | | | | | 40 | | 80 | | | |
	mg l^{-1}	µeq l^{-1}	mg l^{-1}	µeq l^{-1}	mg l^{-1}	µeq l^{-1}	mg l^{-1}	µeq l^{-1}	mg l^{-1}	µeq l^{-1}
H$^+$	0.01	5.0	0.00	0.6	0.00	1.63	0.00	3.39	0.00	0.05
NH$_4^+$-N	0.02	1.4	0.16	11.6	0.82	58.6	0.26	18.5	0.01	0.79
Na$^+$	1.81	78.7	3.94	171	5.87	255	5.07	221	6.46	281
K$^+$	0.13	3.4	2.50	63.9	0.31	7.9	0.25	6.3	0.28	7.16
Ca^{2+}	0.37	18.6	1.10	54.8	1.17	58.4	0.87	43.4	5.03	251
Mg^{2+}	0.24	20.1	0.65	53.5	1.46	120	0.95	78.1	3.43	282
NO$_3^-$-N	0.03	2.4	0.01	0.62	0.02	1.09	0.03	1.91	0.06	4.43
Cl$^-$	3.44	97.0	6.86	194	9.12	257	9.25	261	8.35	235
HCO$_3^-$	0.00	0.00	3.15	51.6	21.5	352	7.85	129	30.6	501
SiO$_2$	0.00	–	0.52	–	3.42	–	3.44	–	18.9	–
DOC[1]	0.96	–	6.16	–	5.26	–	2.44	–	1.86	–
TDP[2]	0.01	–	0.02	–	0.00	–	0.00	–	0.00	–

[1] Dissolved organic carbon.
[2] Total dissolved phosphorus.

to the temporal fluctuations in NH$_4^+$ concentrations, but may have made a significant contribution to variability in NO$_3^-$ concentrations, which were often near the detection limit in soil solution. Concentrations of NH$_4^+$ in shallow soil solution (40 cm depth) were especially high in two lysimeters, and often exceeded 7 mg l^{-1} (Figure 4). Concentrations and fluxes of NH$_4^+$ and DOC were considerably higher in soil solution than in the nearby Quebrada Toronja (Tables 1 and 2). In contrast, the concentrations and fluxes of Ca^{2+}, Mg^{2+}, SiO$_2$ and HCO$_3^-$ were all much lower in soil solution than in stream water.

The flux of dissolved organic carbon through the soil profile appeared to be regulated by soil sorption processes. Dissolved organic carbon was sorbed very efficiently from solution by shallow soils collected at the site. For the composite soil samples (0–80 cm depth), the partition coefficient (slope of the sorption 'isotherm') ranged from 0.39 to 0.59, and equilibrium DOC concentration (X-axis intercept, the concentration at which DOC is neither sorbed nor released from the solid phase) ranged from 0 to 0.7 mg l^{-1}. These equilibrium DOC concentrations were lower than those observed in the field in soil solution (2.4 mg l^{-1} at 40 cm and 1.9 mg l^{-1} at 80 cm; Table 1). Samples collected deeper in the soil profile were more retentive of DOC than shallow soils, as indicated by their lower equilibrium DOC concentrations and higher partition coefficients (Figure 5).

DISCUSSION

The combination of plot- and catchment-level measurements which I have used in calculations of nutrient flux is not ideal. Catchment-level estimates of streamflow are generally the most appropriate means of obtaining minimum
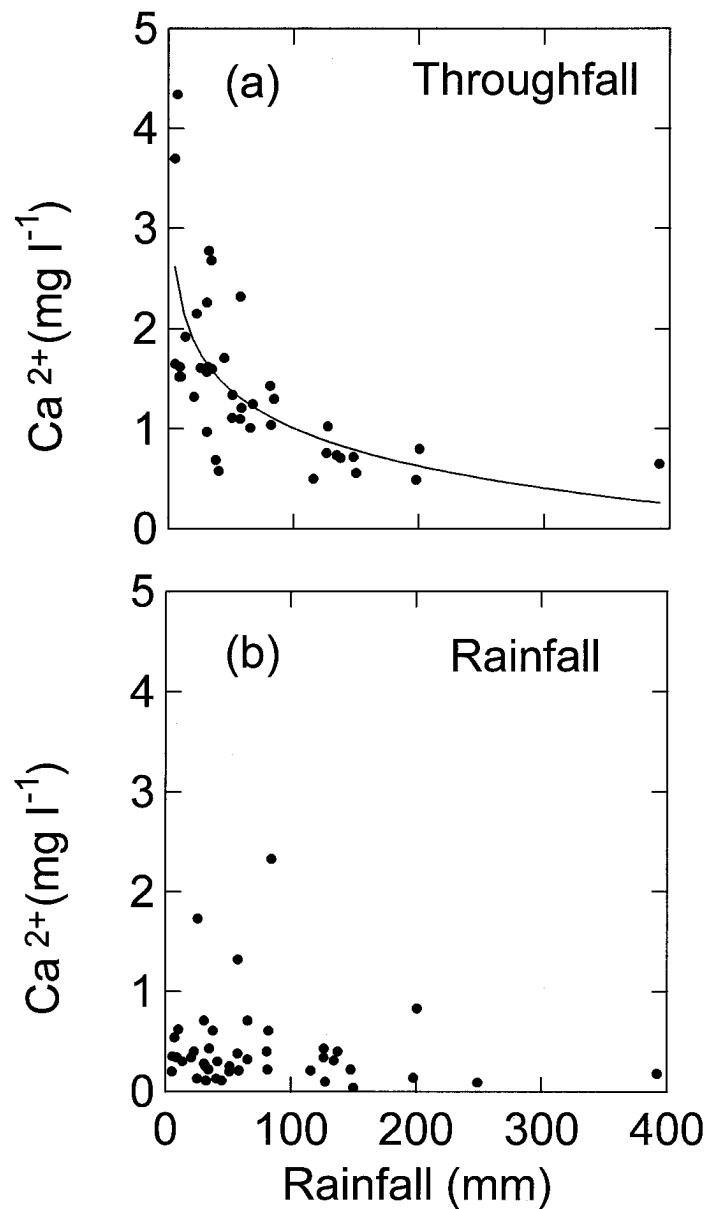
Figure 2. Concentrations of calcium in (a) throughfall, and (b) rainfall as a function of weekly rainfall volume. A logarithmic fit is shown (ln $[Ca^{2+}] = 0.56-0.005*$ volume; $r^2 = 0.41$; $P < 0.05$). Concentrations of Ca^{2+} in rainfall were not related to volume ($P > 0.05$).

estimates of soil water and groundwater fluxes, but these basin-wide results can only be applied to any particular plot within the catchment with caution. Considerable spatial variability in rates of saturated and unsaturated flow in a catchment is likely, and hence these rates are hard to predict at any particular plot without extensive hydrologic monitoring (Bruijnzeel 1990). Despite these
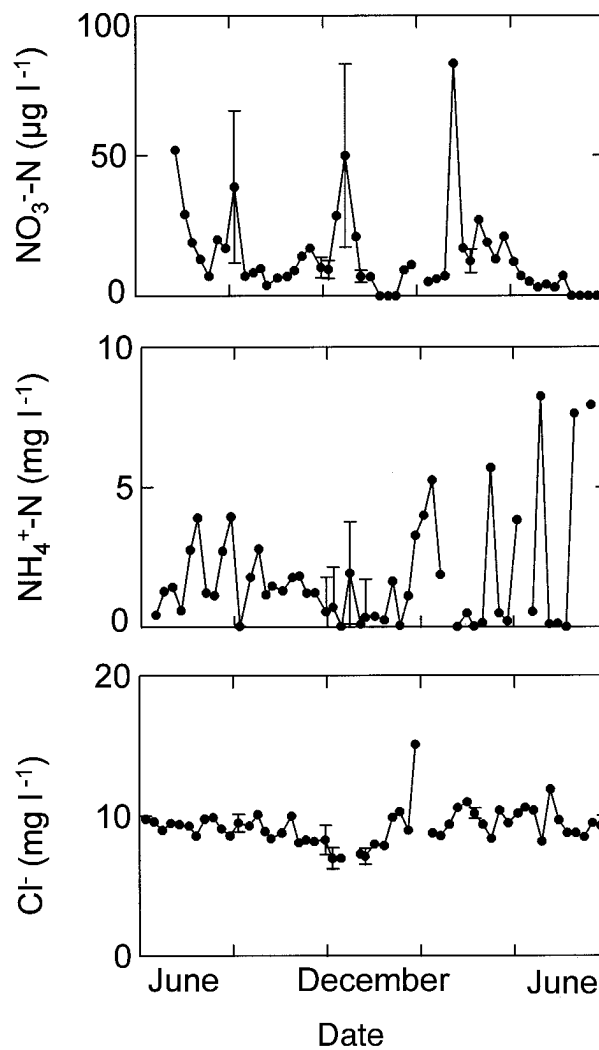
Figure 3. Concentrations of chloride, nitrate- and ammonium-nitrogen in soil solution collected at a depth of 40 cm from 1984 to 1985. Samples were bulked from five lysimeters prior to analysis; on six dates, ± SE of the mean for the five individual lysimeter samples is shown as a vertical bar. Note that on some dates, error bars are too small to be visible.

uncertainties, I believe that the values presented here are useful estimates of the relative magnitude of various internal elemental fluxes in this tropical rain forest. Study of multiple plots stratified by elevation and topographic position would be necessary to further refine my estimates of fluxes in throughfall and soil solution and obtain values representative of the entire catchment.

Alteration of precipitation chemistry by contact with the canopy appears to be similar in a wide variety of environments. Based primarily on studies of temperate forests, Parker (1983) concluded that throughfall tended to be enriched in base cations and DOC, and depleted in NH_4^+ and NO_3^- relative to
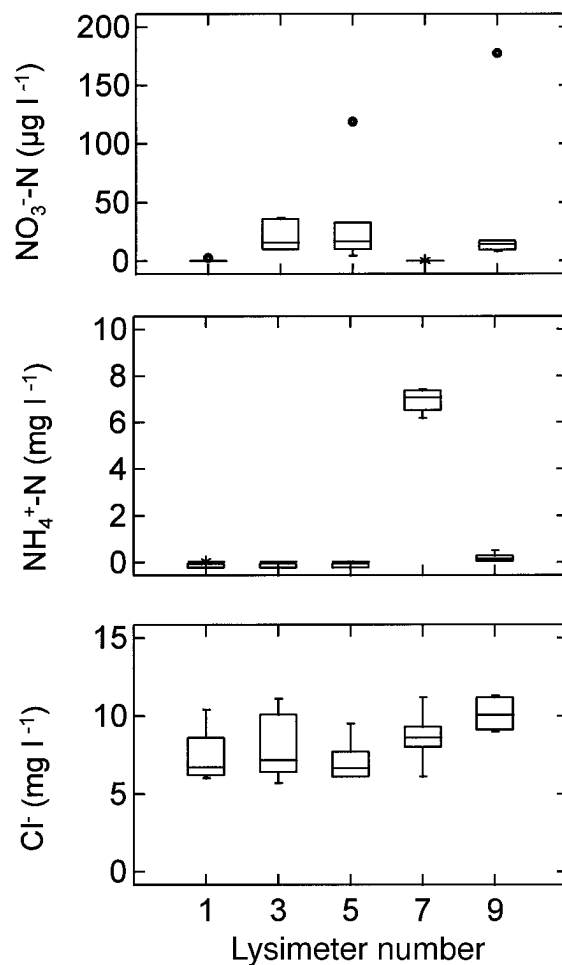
Figure 4.   Box-and-whisker plot showing spatial variability of chloride, nitrate- and ammonium-nitrogen in soil solution collected from individual lysimeters on six dates between June 1984 and June 1985. Note that for samples collected from lysimeter numbers 3 and 5, NH_4^+ concentrations and error bars are too small to be visible.

precipitation. My results and those of other recent studies in tropical rain forests show a clear pattern of increased base cation fluxes in throughfall compared to precipitation. This is particularly true for K^+; fluxes of K^+ in throughfall are typically 5–10 times higher than those in rainfall (Asbury *et al.* 1994, Forti & Moreira-Nordemann 1991, Sinun *et al.* 1992, Strigel *et al.* 1994, Veneklaas 1990). Studies of N and C production or retention by the forest canopy are still too few to allow generalizations for tropical rain forests.

Differences between the flux of Cl^- in precipitation and throughfall (net throughfall) are indicative of the magnitude of dry deposition of marine aerosols. The high humidity of this tropical forest should be conducive to high rates of dry deposition (McDowell 1988), but throughfall is enriched in chloride by

Table 2. *Annual hydrologic and elemental fluxes in a tropical rain forest at El Verde, Puerto Rico. All values are in kg ha^{-1} y^{-1} except for hydrologic fluxes (cm). Fluxes were calculated as the product of the volume-weighted mean concentrations shown in Table 1 and hydrologic fluxes. Details of hydrologic estimates are provided in the text.*

| | Rainfall | Throughfall | Soil solution at depth (cm) | | Stream water |
			40	80	
Hydrologic flux (cm)	350	206	175	175	175
H^+	0.17	0.01	0.03	0.06	0.00
NH_4^+-N	0.69	3.34	14.4	4.5	0.19
Na^+	63.3	81.3	103	88.6	113
K^+	4.69	51.6	5.4	4.3	4.9
Ca^{2+}	13.0	22.7	20.5	15.2	87.9
Mg^{2+}	8.53	13.4	25.5	16.6	60.0
NO_3^--N	1.2	0.18	0.27	0.47	1.1
Cl^-	120	142	159	162	146
HCO_3^-	0.00	65.0	376	137	535
SiO_2	0.00	10.6	59.8	60.1	330
DOC	33.6	127	92.0	42.7	32.5
TDP	0.20	0.45	0.02	0.02	0.03

only about 18% on a flux basis (Table 2). Wet deposition appears to be the dominant pathway (85% of total) for deposition of marine aerosols at this site. Although throughfall is greatly enriched in K^+ relative to precipitation, based on the molar ratio of K:Cl in marine aerosols (0.0188; Keene *et al.* 1986), only 3% of this enrichment could be due to marine sources.

Elemental fluxes in throughfall can be comparable to or greater than those in leaf fall, another major internal flux (Figure 6). The flux of K^+ in throughfall, for example, is 52 kg ha^{-1} y^{-1}, and K^+ in leaf fall was only 20 kg ha^{-1} y^{-1} at El Verde in 1981 (average of two sites reported by Zou *et al.* 1995). Throughfall fluxes of Ca^{2+} and Mg^{2+} are 50 and 75% of leaf fall values, respectively, but nitrogen is only 5% of the flux in leaf fall reported by Zou *et al.* (1995). Even for elements with a relatively small flux, however, throughfall may be ecologically significant because all of the flux is soluble and hence readily available to microbes in the forest floor (Lodge *et al.* 1994).

The biogeochemistry of DOC in this forested ecosystem is similar in many respects to that observed in temperate forests (e.g. McDowell & Likens 1988). Rainfall represents a small input of DOC, throughfall is enriched in DOC to approximately 7–10 mg l^{-1}, and concentrations decrease with depth in the soil profile (Table 1). The decrease at depth appears to be due to abiotic retention of DOC by mineral soil (Figure 5), which also occurs in the temperate hardwood forests of New Hampshire and southern Ontario (McDowell & Wood 1984, Moore *et al.* 1992). The major difference in DOC dynamics in the Luquillo Forest and most of its temperate counterparts appears to be the relative lack of DOC production in the very thin forest floor. Although I have not directly measured DOC concentrations immediately below the forest floor in the Luquillo Experimental Forest, results of the soil sorption experiments suggest that DOC production there is minimal. The equilibrium DOC concentration in upper mineral soils (0–10 cm) is 3.4 mg l^{-1}, much lower than the
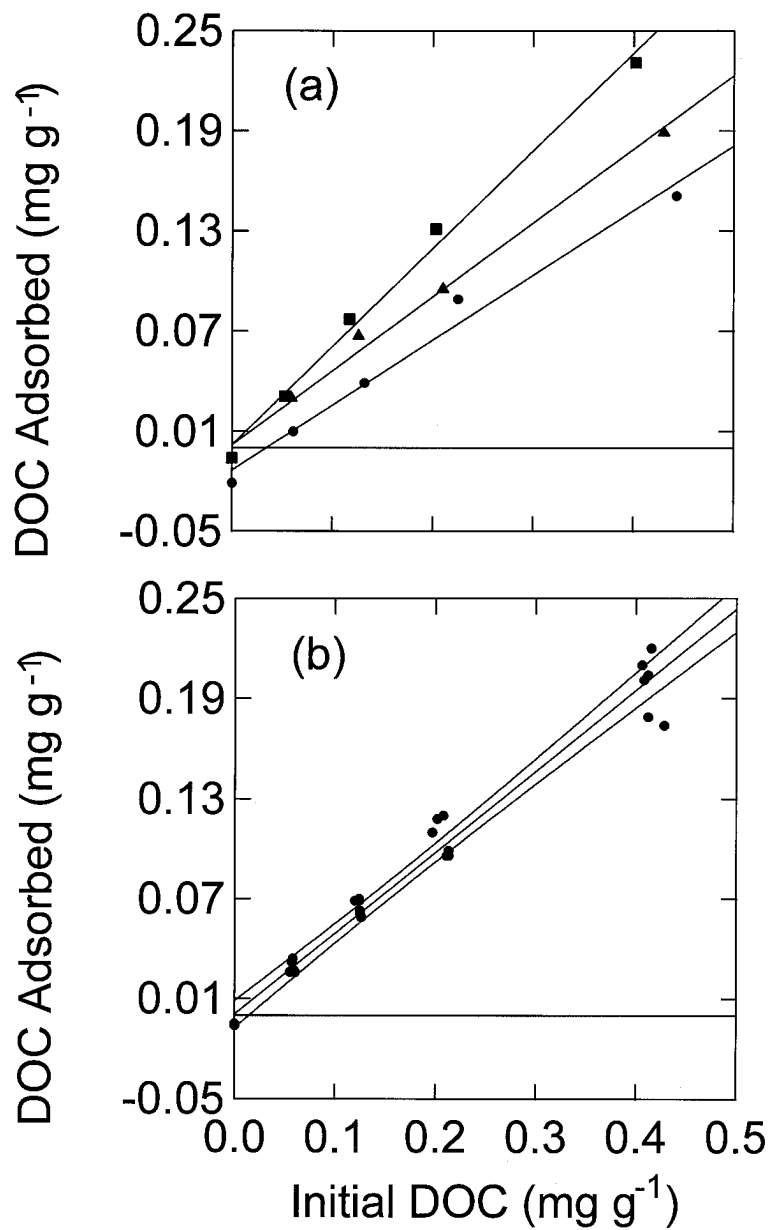
Figure 5. Sorption isotherms for dissolved organic carbon (DOC) and mineral soil collected from (a) different depths, and (b) six samples collected from 0–80 cm. Depths of samples in (a) are 0–10 cm (circles), 10–40 cm (triangles), and 40–80 cm (squares). Using the initial mass analysis of Nodvin *et al.* 1986, the equilibrium DOC concentrations are 3.4, 0, and 0 mg l^{−1} for depths of 0–10, 10–40 and 40–80 cm, respectively. For the samples shown in (b), the average equilibrium DOC concentration of the individual soil samples is 0.2 mg l^{−1} and the average partition coefficient (slope) is 0.48. The 95% confidence interval-band about the linear regression describing DOC sorption by the six soil samples taken as a single group is shown.
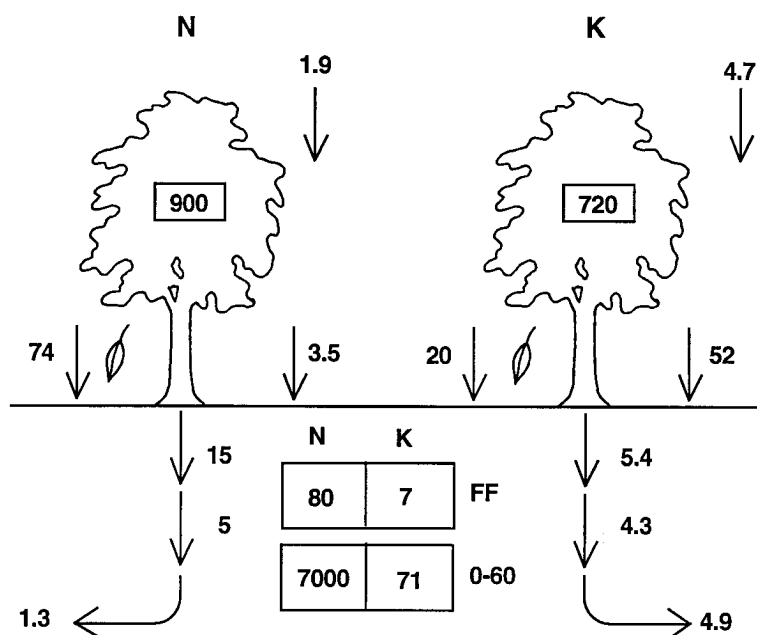
Figure 6. Fluxes (arrows) and standing stocks (boxes) of N and K in the tabonuco forest type of the Luquillo Experimental Forest. Data on fluxes in precipitation, throughfall, soil solution and stream water are from Table 2. Litterfall fluxes are from Zou *et al.* (1995), and standing stocks are from Silver *et al.* (1994).

11–35 mg l^{-1} observed at Hubbard Brook at a similar depth in the mineral soil (McDowell & Wood 1984).

Concentrations of base cations, SiO_2 and DOC are within the range of those observed in soil solution of other tropical rain forests. Four forested sites in sub-Sahelian Africa all have higher concentrations of base cations in soil solution (Roose & Lelong 1981) than those observed in Puerto Rico. Concentrations of Ca^{2+}, for example, are 4–8 mg l^{-1} in the African forests and only 1 mg l^{-1} in Puerto Rico. Amazonian forests can have considerably lower soil solution concentrations, with values of 0.1 to 1 mg l^{-1} reported by Forti & Neal (1992) for 'terra firme' sites in central Amazonia. Less data are available for SiO_2 and DOC in soil solution; DOC concentrations are 2–12 mg l^{-1} in the African forests, and SiO_2 concentrations are typically 10 mg l^{-1}. In Puerto Rico, corresponding concentrations are 2–5 mg l^{-1} for DOC and 3 mg l^{-1} for SiO_2.

Soil solution which I have sampled does not appear to be representative of groundwater entering the stream channel, because the concentration and flux of Ca^{2+}, Mg^{2+} and SiO_2 are much less in soil solution than in stream water. Chloride flux, in contrast, is relatively constant from throughfall to stream runoff, indicating that my hydrologic budget is probably reasonably accurate. This discrepancy between concentrations of weathering products in soil solution and stream water suggests that weathering is physically displaced from my sampling site, occurring deeper in the solum, further downslope on the catena, or in the stream channel itself.

Recent work on soil chemistry in the Bisley catchments of the Luquillo Experimental Forest suggests that higher concentrations of weathering products in stream water than in soil solution could be the result of production or accumulation of weathering products in the riparian zone. Standing stocks of KCl-extractable Ca^{2+}, Mg^{2+} and K^+ are two to three times greater in riparian than ridgetop soils (Silver *et al.* 1994), suggesting that release from riparian soils may be important in determining stream chemistry and export. Use of tension rather than zero-tension lysimeters is probably not responsible for the discrepancy between lysimeter and stream chemistry. Elemental concentrations are typically higher in soil water collected from tension lysimeters compared to zero tension lysimeters (e.g. Fernandez *et al.* 1995). Thus, use of tension lysimeters would tend to minimize differences between soil and stream water, rather than cause them.

Hydrologic export of inorganic N from catchments in the Luquillo Experimental Forest is modest in the absence of large-scale disturbance (averaging 1.2 kg ha^{-1} y^{-1} for Quebrada Toronja; McDowell & Asbury 1994), but this does not appear to be the product of particularly tight internal recycling of N in the forest floor (Figure 6). Concentrations and fluxes of inorganic N are highest at 40-cm depth, and decline with depth in the soil profile. Because the flux at 80 cm is still four-fold higher than stream export, riparian processes (e.g. plant uptake or denitrification) are probably important in regulating losses of inorganic N in stream runoff (McDowell *et al.* 1992).

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