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Rainwater and Throughfall Chemistry in a “Terra Firme” Rain Forest: Central Amazonia

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During the Global Tropospheric Experiment (GTE)–Amazon Boundary Layer Experiment (ABLE) 2B campaign in the Amazon basin, samples of rainwater and throughfall were obtained in a “terra firme” (nonflooded forest) rain forest at the Ducke Reserve (2°57’S, 59°58’W). The samples were collected during one wet period (April 1 to May 13, 1987) and one dry period (August 1 to October 1, 1987). All samples were analyzed for Na^+ , K^+ , Mg^{2+} , Ca^{2+} , NH_4^+ , Cl^- and SO_4^{2-} , and pH. The rainwater was acidic, with a volume-weighted mean pH of 4.6 for the two periods. Rainwater input from the dry period was 2 times greater for Na^+ , Mg^{2+} , NH_4^+ and SO_4^{2-} and about 4 times greater for K^+ than from the wet period. The ionic concentrations in throughfall were higher than those in rainwater, except for NH_4^+ during the dry period. This enrichment of throughfall is attributed to the interaction of precipitation with the forest canopy.

INTRODUCTION

The tropical rain forest has a large biomass per unit area, a greater variety of species compared to other forests, and vigorous biological activity that usually takes place throughout the year. Nevertheless, Nye and Greenland [1960] have shown that the luxuriant and tall tropical rain forest may grow on relatively nutrient poor, highly weathered substrates. Tropical rain forests have evolved mechanisms to efficiently utilize the nutrients in the soil solution, as well as those entering the forest from the atmosphere [Golley, 1983]. Nutrient distribution and cycling occur through the rainwater, mineral weathering and absorption/liberation of gases (including biological fixation) that depend mostly on climate, species composition, successional state and soil fertility [Forti, 1989].

The rainwater and throughfall chemistry in Central Amazonia have been studied by several authors [e.g., Nortcliff and Thornes, 1978; Franken and Leopoldo, 1984; Franken *et al.*, 1985; Brinkmann, 1985; Moreira-Nordemann *et al.*, 1986; Andreae and Andreae, 1988]. Most of these studies, however, consider only cations (Na^+ , K^+ , Mg^{2+} and Ca^{2+}) or only anions (Cl^- and SO_4^{2-}). There is a lack of studies where cations and anions are studied at the same time and place.

This work is part of the Global Tropospheric Experiment (GTE)–Amazon Boundary Layer (ABLE) [Harriss *et al.*, 1990] conducted during the wet (April–May) and dry (August–September) seasons of 1987. For each period a continuous record of rainwater and throughfall composition and amount, was obtained in a “terra firme” rain forest ecosystem, in Central Amazonia. The results of this study focus on the interaction of precipitation with the forest canopy (the throughfall), showing a seasonal and spatial variation of the ionic input by rainwater and throughfall.

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METHODS

Experimental Site

Precipitation samples were collected at the Ducke Reserve (02°57’S, 59°57’W), a 10,000-ha preserve near Manaus. Figure 1 shows a location map of the experimental site, situated in the “Barreiras” formation. Soils are mainly yellow latosols with small areas of podzolization, and the vegetation is typical of an undisturbed, natural Amazonian “terra firme” rain forest. A detailed description of this region can be found in the works by Livingston *et al.* [1988] and Forti [1989].

Samples were obtained at two stations (Figure 1): the first one in a clear-cut area of approximately 0.5 ha in the Barro Branco catchment area [Franken and Leopoldo, 1984] and the second one, 2 km away, close to a micrometeorological tower [Fitzjarrald *et al.*, 1988].

Collection

Samples were obtained with a collector composed of a polyethylene funnel (collecting area of 712 cm²), covered with a nylon screen (mesh ~ 2 mm), connected to a 2-L polyethylene bottle.

One collector was installed at the 43 m elevation on the 45-m-tall micrometeorological tower, and held away from the tower by a spar, in order to prevent the collection of rain splatter from the tower. During the April–May (wet) 1987 period, the samples from the tower corresponded to the bulk precipitation because the dry deposition over the collector could not be avoided; during the August–September (dry) 1987 period, this collector was washed daily with 2 L of deionized water to minimize the dry deposition.

The throughfall samples were collected near the tower where fifteen different points were selected over a 100-m transect. Over these points, five collector pairs were set up, approximately 1 m above the ground (the screens were daily changed), and their positions were changed randomly each 20 days.

Another pair of collectors was installed in a clearing (0.5 ha), close to the “Barro Branco igarape,” 1 m above the ground and 20 m from the forest edge. Their screens were changed daily.

Fig. 1. Localization map of sampling sites in Ducke Reserve, near Manaus.

The rainwater samples were collected every 24 hours, one event being considered as the total rainfall precipitated during this time interval; all the precipitation events that occurred during the collection periods were collected.

After the collection, the samples were preserved, to prevent algae growth, with prewashed chloroform (1% in volume) to eliminate Cl^- ions that might be present in the chloroform, and then sent to the Instituto de Pesquisas Espaciais (INPE) in São José dos Campos, São Paulo, Brazil, and stored at 4°C .

During the wet period (April 1 to May 13), 16 samples were collected at the tower; 18 pairs in the clearing (for the period April 1 to May 13) and 16 sets of throughfall samples (totaling 80 sample pairs) were taken. During the dry period (August 1 to October 1), 10 samples were collected at the tower, 11 pairs at the clearing and 10 sets of throughfall samples were taken (totaling 50 pairs).

For all samples, the pH was measured on the collecting day, utilizing a Digimed field pH meter with a combined plastic electrode, having an internal reference system of Ag/AgCl . The NH_4^+ ion was analyzed by potentiometry, with an Orion (model 811) electrode with NH_3 internal solution, and the readings were performed in June and

October, for the samples collected during the wet and dry period, respectively. Storage tests during a six month period showed that the NH_4^+ ion remained stable for this length of time (differences $<10\%$). The cations, Na^+ , K^+ , Mg^{2+} and Ca^{2+} , were analyzed by atomic absorption spectrometry, with Varian AA 1475 equipment [Thompson and Reynolds, 1978]. The samples collected during the wet period were analyzed in July 1987. One half of them were reanalyzed in January 1988, together with the samples from the dry season. Finally, in May 1988, all samples were reanalyzed. The results from the three analyzed sets ($\sim 5\%$) did not show significant differences. Ion chromatography, using EPA method [Pfaff, 1986], was used to quantify the anions Cl^- and SO_4^{2-} . The first nine samples collected at the tower were analyzed in Manaus in May 1987. In December 1987, the same samples and those collected from the clearing were analyzed in Centro de Pesquisas de Aguas Subterraneas, University of São Paulo (CEPAS/USP) laboratory. Finally, these samples, together with the remaining ones, were analyzed at INPE's laboratory during February 1989. The Cl^- and SO_4^{2-} concentrations did not change significantly with time, giving the same values for the means, although the mean NO_3^- values decreased. The volumetric weighted

TABLE 1. Rainwater and Throughfall NO_3^- During the Wet and Dry Periods

	Rainwater		Throughfall	
	Wet	Dry	Wet	Dry
Volumetric weighted mean	6.5	6.4	14.1	8.7
Standard deviation	10.2	6.5	32.4	9.0
Maximum	56.4	19.0	242	29.3
Minimum	0	0	0	0

Values are in micromoles of NO_3^- per liter.

means, standard deviations and maximum and minimum values for NO_3^- are presented in Table 1, to provide some indication of its importance in these samples.

Blanks of the deionized water as well as of the containers and screens were analyzed. The results for the analyzed ions were below the detection limit, obtained from the calibration curves, of the various methods. The blanks of deionized water with 1% chloroform, without the prewashed chloroform, showed $1 \mu\text{mol Cl}^-/\text{L}$, a result not detected with prewashing.

The screen which covered the tower collector during the wet period was taken out to analyze the soluble deposited material. The total mass deposited was obtained by gravimetry. The screen was immersed in 100 mL of deionized water and submitted to ultrasound for 30 min; the aqueous solution was taken out, filtered in a $4\text{-}\mu\text{m}$ porous Millipore filter and stored for later analysis.

The volume of each sample was measured with an accuracy of 10%. These values were used to calculate the volume weighted mean for the ionic content, and the mean pH was obtained from the volumetric weighted mean of the calculated H^+ concentrations.

RESULTS AND DISCUSSION

The Rainwater pH

The rainwater pH varied between 4.0 and 5.3, with a volume weighted mean of 4.6 ± 0.1 for the wet period and 4.5 ± 0.1 for the dry period. Other authors obtained similar pH values for different tropical rain forests (Table 2). The acidity of rainwater observed in this study is in accordance with current results, which indicate that the rainwater is acidic with values between 4.5 and 5.0 [Rodhe *et al.*, 1988] in tropical rain forests.

TABLE 2. Rainwater pH Values for Some Tropical Rain Forests

Locale	pH		Reference
	Mean	Range	
Amazonia	5.1	4.7–5.7	Stallard and Edmond [1981]
Venezuela	4.6	3.8–6.2	Steinhardt and Fassbender [1979]
Venezuela	4.8	4.4–5.2	Galloway <i>et al.</i> [1982]
Costa Rica	5.3	4.8–6.3	Hendry <i>et al.</i> [1984]
Trinidad	5.8	5.3–6.4	McDowell [1988]
Australia	4.8	4.2–5.4	Galloway <i>et al.</i> [1982]
Amazonia	4.7	4.0–5.3	this work

Above the Canopy Versus the Clearing Rainwater Chemical Composition

The mean ionic concentration of the rainwater samples collected above the canopy (tower collection) and from the clearing indicated different results, in spite of being only 2 km apart. Table 3 presents the volumetric weighted means, mean standard deviations, superior and inferior confidence intervals of 5%, in micromoles per liter, and sampled volumes, obtained for the two sites during the wet and dry periods.

Part of the observed differences between the mean ionic concentrations in the rainwater samples above the canopy and the clearing is due to the dry deposition in the tower collector, mainly during the wet period, when only bulk precipitation samples were obtained. The analyses of the aqueous solution of the screen which covered the tower collector, during the wet period, presented the following values: $0.75 \mu\text{g Na}^+/\text{g}$, $0.95 \mu\text{g K}^+/\text{g}$, $0.08 \mu\text{g Mg}^{2+}/\text{g}$, $0.33 \mu\text{g Ca}^{2+}/\text{g}$, $1.30 \mu\text{g NH}_4^+/\text{g}$, $1.20 \mu\text{g Cl}^-/\text{g}$, and $17.65 \mu\text{g SO}_4^{2-}/\text{g}$. The total mass deposited was $103 \mu\text{g}$, indicating that the amount of dry deposition was not negligible. However, the dry deposition cannot be considered as the main factor which determined the composition differences found in the two sampled locations. For example, during the dry period, when the dry deposition was minimized, the difference between the mean values of the concentrations remained. Another potential source of this observed difference is differences in the sampled volumes [Lloyd and Marques, 1988]; however, these did not occur (see Table 3).

According to Brinkmann [1985], the roughness of the forest canopy surface generates vortices due to turbulent flow, even at low speed winds. Raupach *et al.* [1980] studied the effect of the turbulent flux on rough closed canopies, showing that gradient measurements over these surfaces must be done above the level

$$Z = h + 1.5d \quad (1)$$

where h and d are the height and the transverse length scale of the roughness elements, respectively. Measurements need to be made above this height (Z) to minimize the effects of the roughness sublayer, a region where significant vertical transport of momentum, and consequently, mass occur. Viswanadham *et al.* [1990] estimated a Z value of 39 m, for the tower region; as the collector was at 43 m height, there was a high probability of its being in the interior of the roughness sublayer (Y. Viswanadham, personal communication, 1989). The washout effect of this roughness sublayer by rainfall could be the main cause of the enrichment of the samples collected from the tower, in relation to those collected in the clearing. Due to this effect, the rainwater samples collected in the clearing will be considered in this work as representative of the atmospheric input by rainwater.

The Rainfall Ionic Input

Figure 2 presents mean monthly rainfall (in millimeters), measured in Ducke Reserve for the years 1966–1988 and the monthly rainfall during 1987. For the months of April and May, the rainfall was 35% lower in relation to the long time averages, while for August and September 1987, it was 32% higher. We also observe that the total rainfall for the wet

TABLE 3. Volumetric Weighted Mean Values, Mean Standard Deviations, 5% Confidence Intervals, and Total Sampled Volumes for the Tower and Clearing Samples for the Wet and Dry Periods

	Na ⁺ , μmol/L	K ⁺ , μmol/L	Mg ²⁺ , μmol/L	Ca ²⁺ , μmol/L	NH ₄ ⁺ , μmol/L	Cl ⁻ , μmol/L	SO ₄ ²⁻ , μmol/L	Sampled Volume, L
<i>Tower Wet Period N = 16</i>								
Volumetric weighted mean	29.5	7.91	1.61	3.33	2.14	15.3	5.15	12.1
Mean standard deviation	7.20	2.40	0.38	0.51	0.30	2.82	1.40	
Superior 5% confidence interval	45.1	13.1	2.43	4.44	2.80	21.4	8.17	
Inferior 5% confidence interval	14.0	2.74	0.79	2.23	1.48	9.20	2.14	
<i>Tower Dry Period N = 10</i>								
Volumetric weighted mean	20.4	7.14	2.22	6.46	11.0	36.5	10.6	8.3
Mean standard deviation	7.91	1.95	0.74	1.71	6.43	8.90	2.90	
Superior 5% confidence interval	38.3	11.6	3.89	10.3	25.6	56.6	17.2	
Inferior 5% confidence interval	2.53	2.72	0.55	2.59	-3.53	16.4	4.06	
<i>Clearing Wet Period N = 18</i>								
Volumetric weighted mean	3.13	0.58	0.31	2.40	2.41	7.73	3.04	12.2
Mean standard deviation	0.86	0.15	0.10	0.47	0.61	3.33	1.65	
Superior 5% confidence interval	4.93	0.90	0.53	3.39	3.71	14.8	6.52	
Inferior 5% confidence interval	1.33	0.27	0.10	1.41	1.11	0.71	-0.44	
<i>Clearing Dry Period N = 11</i>								
Volumetric weighted mean	9.57	3.58	0.76	3.07	8.57	11.8	7.23	9.3
Mean standard deviation	3.96	1.22	0.28	0.72	5.06	3.56	2.46	
Superior 5% confidence interval	18.4	6.31	1.39	4.67	20.0	19.8	12.7	
Inferior 5% confidence interval	0.74	0.86	0.13	1.46	-2.87	3.87	1.75	

N denotes sample number.

period (379 mm) was not much higher than for the corresponding value for the dry period (261 mm). Therefore, the periods covered by this work do not have characteristic rainfall, when compared to the long-term mean values.

Rainfall input of the elements in kilograms per hectare for the two periods is seen in Table 4. These results show that during the dry period, the inputs of Na⁺, Mg²⁺, NH₄⁺ and SO₄²⁻ are approximately twice as great as for the wet period; the input of K⁺ is 4 times that of the wet period and the inputs of Ca²⁺ and Cl⁻ are equivalent for both periods.

In an experiment conducted in the same place during 1977, Franken *et al.* [1985] observed that the fluxes of these

elements were higher during the rainy season than during the dry one. Similar results were obtained by Lewis [1981] in a study conducted at Lake Valencia in 1977. However, two important points must be considered when comparing these results: (1) the rainfall in the Ducke Reserve in April–May 1977, was 659 mm, while it was 379 mm in 1987; and during August–September 1977, it was 188.9 mm against 261.2 mm in 1987; and (2) the forest burnings were less intense in 1977. During the dry season in 1987, the number and extent of the fires were extensive [Setzer *et al.*, 1988].

The Na⁺, K⁺, Mg²⁺, NH₄⁺ and SO₄²⁻ ions have higher inputs during the dry period. The deposition by rainfall

Fig. 2. Mean monthly pluviometric values for 1966–1988 and 1987 for the Ducke Reserve.

TABLE 4. Ecosystem Input by Rainwater for the Wet and Dry Periods

	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	NH ₄ ⁺	Cl ⁻	SO ₄ ²⁻
Wet	0.25	0.07	0.02	0.30	0.15	0.86	0.91
Dry	0.49	0.31	0.04	0.28	0.34	0.93	1.54

Values are in kilograms per hectare.

through the washout depends on the soluble aerosol residence time, washed component solubility, rainfall regime and the quantity of the injected aerosols in the atmosphere [Junge, 1963]. As a consequence, measurements on a short time scale are more susceptible to these variations, getting larger fluxes, mostly during the dry season, when the rainfall intervals are larger and an increase of the aerosols in the atmosphere (e.g., by the fires) takes place.

The Ca²⁺ inputs are equivalent for the two periods. We expected the Ca²⁺ input to be similar to the other ions but during the wet period the input was smaller. However, another Ca²⁺ source is the soil, but the soils of this region are depleted in soluble cations [Stark, 1971]. Talbot *et al.* [1990] discuss a similar behavior for the soluble aerosols in this region, suggesting that they are introduced in the Central Amazon region, through air masses coming from Central Brazil and the northern hemisphere.

The Throughfall Ionic Input

The quality of precipitation falling on the forest is altered during a brief but significant interaction with the surfaces of the plants, resulting in a transfer of additional mineral matter to the forest floor. Throughfall and stemflow are the major pathways in the nutrient recycling. As stemflow transfers only 5–20% of the total nutrients in rainwater [Brinkmann and dos Santos, 1971], it was not considered in this work.

Table 5 shows the volumetric weighted means, mean standard deviations, superior and inferior confidence intervals of 5% and the ionic input in kilograms per hectare by the throughfall. These values are expressed in net content, defined as the amount of nutrients added to the precipitation as it passes through the canopy, during the two studied periods. By this process it can be observed that all the

elements are enriched in the throughfall, except the NH₄⁺; this ion seems to be absorbed in the dry period. The small return or even absorption of NH₄⁺ may be attributed to the foliar absorption by the microflora and other populations usually existing on the leaves, trunk and branches [Franken *et al.*, 1985].

In Table 5 the percent values of the ratio (*R/T*) of the ions transported by rainwater (*R*) to the throughfall (*T*) are also shown. It can be noticed that the *R/T* ratios for Na⁺ and Mg²⁺ are equivalent during the two periods; for K⁺ it is higher during the dry period; in contrast Ca²⁺, Cl⁻ and SO₄²⁻ *R/T* ratios are smaller during this same period.

The ionic return in throughfall has the following sequence: Mg²⁺ > K⁺ > Na⁺ > Ca²⁺ > NH₄⁺ > SO₄²⁻ > Cl⁻ (wet) and Mg²⁺ > K⁺ > Ca²⁺ ~ Na⁺ > Cl⁻ > SO₄²⁻ (dry).

The throughfall is a very important source of Mg and K for the soil. Of the total ionic input reaching the soil, only about 10% comes from rainwater, the difference being added to precipitation as it passes through the canopy. These elements, according to Vitousek and Sanford [1986], participate in the forest internal recycling.

The *R/T* ratio for Na⁺ is equal for the two periods. Because higher Na⁺ quantities enter the ecosystem by rainwater, during the dry period, the Na⁺ is being transferred in larger quantities from the vegetation to the throughfall during this period. Franken *et al.* [1985] found evidence of the Na absorption during the periods of high rainfall (wet season), relating the Na absorption and elimination in different periods of the year to metabolic processes of some plants and, based on the Na/K ratio, they also suggested that a substitution of K by Na in the system may be occurring.

The Ca²⁺ species is the smallest contributor to this enrichment process during the two periods. For example, during the dry period the leaching is even smaller. This transference pattern is found in different tropical forest systems, particularly in those with lower fertility soils [Vitousek and Sanford, 1986], where the Ca²⁺ values in tree leaves are relatively low.

Of the quantity of Cl⁻ reaching the soil by the throughfall, our results show that the major fraction is introduced by rainwater, in the two periods, with a higher enrichment during the dry period. Similar findings were obtained by Franken *et al.* [1985]. They attributed this greater amount of

TABLE 5. Throughfall Volumetric Weighted Means, Mean Standard Deviation, 5% Confidence Intervals, Ionic Inputs and Rainwater/Throughfall Ratio (*R/T*) for the Wet and Dry Periods

	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	NH ₄ ⁺	Cl ⁻	SO ₄ ²⁻
<i>Wet Period, N = 75</i>							
Volumetric weighted mean	10.6	6.64	3.65	5.10	4.65	10.3	4.64
Mean standard deviation	0.99	0.72	0.42	0.55	0.70	0.91	0.042
Superior 5% confidence interval	12.6	8.07	4.49	6.20	6.05	12.1	5.49
Inferior 5% confidence interval	8.60	5.21	2.82	3.99	3.24	8.48	3.80
Input, kg/ha	0.45	0.67	0.24	0.29	0.08	0.19	0.36
<i>R/T</i> , %	36	10	8	51	65	82	72
<i>Dry Period, N = 48</i>							
Volumetric weighted mean	29.6	25.1	10.9	10.2	6.14	21.0	11.8
Mean standard deviation	2.66	2.27	0.87	0.96	1.17	1.84	0.80
Superior 5% confidence interval	35.9	29.6	12.6	12.1	9.49	24.7	13.4
Inferior 5% confidence interval	24.2	20.5	9.13	8.24	3.79	17.3	10.2
Input, kg/ha	0.88	1.67	0.50	0.55	-0.12	0.57	0.75
<i>R/T</i> , %	36	16	8	34	155	62	67

N denotes number of samples.

TABLE 6. Ionic Content in the Aqueous Solution of the Deposited Material Over the Screen During the Wet Period and Its Contribution to the Ionic Content in Throughfall

	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	NH ₄ ⁺	Cl ⁻	SO ₄ ²⁻
Ionic content, kg/ha	0.01	0.01	0.002	0.05	0.02	0.02	0.26
Contribution to throughfall, %	4	3	2	28	29	13	100

Cl⁻ in throughfall to its elimination by the predehiscent leaves, that occur mostly during the dry season.

The major fraction of the SO₄²⁻ ion in throughfall is from rainwater for both periods. Sulphur is an essential element for the vegetation and it might have been washed from the vegetation in its SO₄²⁻ form, thus enriching the throughfall.

The particulate deposition over the canopy, however, must be considered, and this elemental source may be a significant component of the throughfall. Gosz *et al.* [1983], (cited by Vose [1985]) suggested that the canopy can provide much more nutrient input from the atmosphere than that measured normally by bulk precipitation analysis, and McColl [1978] noticed that particulates impacted on the vegetation could supply 2 to 3 times greater inputs for certain ions than did rainfall.

From the analysis of aqueous solutions of the deposited material over the screen, the throughfall component due to the washout of soluble material deposited on the vegetation for the wet period was estimated [Parker, 1983]. The estimated values are presented in Table 6. These results suggest that during the wet period, the main component of throughfall for Na⁺, K⁺, Mg²⁺ and Cl⁻ was the leaching of these ions from the vegetation; for Ca²⁺ and NH₄⁺ the leaching may be an important process and for SO₄²⁻ the component due to the washout of impacted particulate on the leaves predominates over that due to the leaching.

CONCLUSIONS

As found in other tropical rain forests, the rainwater in Central Amazonia is acidic, with a volume-weighted mean pH, of 4.6, for the two periods studied (dry and wet seasons). The rainwater samples collected above the canopy are enriched in relation to those collected from a clearing, probably due to the washing of aerosols from the roughness sublayer above the forest canopy.

The throughfall ionic content is enriched in relation to the rainwater due to the interaction with the vegetation. The major elements transferred from the vegetation to the throughfall for the two periods are: Mg²⁺ and K⁺ (90%), Na⁺ (70%), Ca²⁺ (60%), Cl⁻ (25–40%) and SO₄²⁻ (40%). It is possible to observe NH₄⁺ absorption by the vegetation during the dry period. It may be inferred that during the wet period, the main source of Na⁺, K⁺, Mg²⁺ and Cl⁻ in the throughfall is from the leaching of the vegetation, in contrast to the SO₄²⁻ ion whose main source could be from the washing of the impacted particulate material from the vegetation.

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