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Seasonal and within-event dynamics of rainfall and throughfall chemistry in an open tropical rainforest in Rondônia, Brazil

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Abstract Prolonged dry periods, and increasingly the generation of smoke and dust in partially-deforested regions, can influence the chemistry of rainfall and throughfall in moist tropical forests. We investigated rainfall and throughfall chemistry in a palm-rich open tropical rainforest in the southwestern Brazilian Amazon state of Rondônia, where precipitation averages 2300 mm $year^{-1}$ with a marked seasonal pattern, and where the fragmentation of remaining forest is severe. Covering the transition from dry to wet season (TDWS) and the wet season (WS) of 2004–2005, we sampled 42 rainfall events on event basis as well as 35 events on a within-event basis, and measured concentrations of DOC, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, SO_4^{2-}, NO_3^- and pH in rainfall and throughfall. We found strong evidence of both seasonal and within-event solute rainfall concentration dynamics. Seasonal volume-weighted mean (VWM_S) concentrations in rainfall of DOC, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{2-} and NO_3^- were significantly higher in the TDWS than the WS, while VWM_S concentrations in throughfall were significantly higher for all solutes except DOC. Patterns were generally similar within rain events, with solute concentrations declining sharply during the first few millimeters of rainfall. Rainfall and throughfall chemistry dynamics appeared to be strongly influenced by forest and pasture burning and a regional atmosphere rich in aerosols at the end of the dry season. These seasonal and within-event patterns of rainfall and throughfall chemistry were stronger than those recorded in central Amazônia, where the dry season is less pronounced and where regional deforestation is less severe. Fragmentation and fire in Rondônia now appear to be altering the patterns in which solutes are delivered to remaining moist tropical forests.

Keywords Amazonia · Nutrient fluxes · Rainfall chemistry · Sequential sampling · Throughfall chemistry · Tropical rain forest

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Introduction

Throughfall is an important component of nutrient cycles in tropical forests on strongly weathered soils (Bruijnzeel 1991; Parker 1983). While precipitation may be an important source of nutrients, nutrient fluxes in throughfall are typically much larger, and throughfall is an important source of directly

available nutrients for plants and forest floor microorganisms (Parker 1983; Stark and Jordan 1978). Solutes delivered in throughfall can be an important driver of biogeochemical processes at the soil surface, such as emissions of trace gases, which are linked to the availability of both carbon and nutrients (Davidsion et al. 2000; Garcia-Montiel et al. 2003).

The large leaf surface area in forest canopies can enhance the concentrations of solutes over those in precipitation by foliar leaching and by accumulation of dry deposition, which leads to higher rates of dry deposition in forests compared with open land (Lindberg and Lovett 1985). These controls on throughfall solute concentrations are likely of particular importance in highly fragmented landscapes where forests are subject to elevated aerosol concentrations because of land use in adjacent, non-forested lands.

Over large regions of the tropics, burning of forests and pastures in areas of intensive deforestation now leads to particulate emission to the atmosphere of black carbon, K^+, Cl^- and SO_4^{2-} (Yamasoe et al. 2000), organic material, NH_4^+, K^+, NO_3^-, SO_4^{2-} and organic anions (formate, acetate, and oxalate) (Andreae et al. 1988a). In addition, fragmented landscapes are subject to increased input of dust generated from roads, agricultural areas and additions such as lime and cattle supplements. How these factors might be linked to changes in forest nutrient cycling through alteration of throughfall concentrations is not known.

Seasonal as well as within-event dynamics of throughfall chemistry provide insight into the relative importance of internal cycling versus external deposition in controlling throughfall concentrations and total throughfall element fluxes. In regions of active deforestation, such as the state of Rondônia in the southwestern Brazilian Amazon, the dry season is marked by very high aerosol concentrations, while clear atmospheric conditions persist during the wet season (Artaxo et al. 2002). Dry and wet season aerosols consist of biomass emissions, pyrogenic emissions and soil dust, but the relative dominance shifts from pyrogenic emissions in the dry season to biogenic emissions in the wet season (Guyon et al. 2004). This seasonality can be reflected in throughfall solute concentrations. Studies in central Amazônia have revealed seasonal changes of throughfall concentrations, but because forest clearing and anthropogenic fires are relatively minor in this region, these changes were related primarily to a higher rainfall frequency during the wet season (Filoso et al. 1999; Forti and Moreira-Nordemann 1991). Little is known about both the seasonality and magnitude of throughfall solute fluxes in other Amazon regions, particularly those with greater densities of both roads and biomass fires.

Throughfall chemistry can also change rapidly in response to the initiation of rain events. In several laboratory experiments, Lindberg and Lovett (1985) and Potter and Ragsdale (1991) showed that elevated initial concentrations of solutes declined during events. Clement et al. (1972) also reported an initial increase in solute concentrations, followed by a decline. Similar patterns were found under natural rainfall conditions in temperate forests (Crockford et al. 1996; Hansen et al. 1994; Kubota and Tsuboyama 2003). Sequential sampling of throughfall has not been reported from tropical forest.

We measured throughfall solute concentrations in a tropical forest in central Rondônia, a region of the Amazon Basin where deforestation for cattle pasture has been historically high (INPE 2006) and where forest is now highly fragmented. Our objectives were: (1) to quantify within-event and seasonal patterns of throughfall solute dynamics, and (2) to compare our findings with other studies of throughfall concentrations in the Amazon basin conducted in less deforested regions.

Study area and methods

Study area

The study site, Rancho Grande ($10°18'$ S, $62°52'$ W, 143 m a.s.l.) is located about 50 km south of Ariquemes in the Brazilian state of Rondônia in the southwestern part of the Amazon basin. The forest vegetation at Rancho Grande is predominantly *terra firme* primary open tropical rainforest (Floresta Ombrófila Aberta) with a large number of palm trees. In Rondônia, open tropical rainforest amounts to 55% of the total vegetation area (Pequeno et al. 2002). Open tropical rainforest is the predominant vegetation type within the transition zone from dense rainforest to cerrado vegetation (savanna) in the southwest Amazon. The climate of Rondônia is

tropical wet and dry (Köppen's Aw). The mean annual temperature is about 27°C. Mean annual precipitation is 2300 mm year^{-1} with a marked dry period from July through September (average of the years 1984–2003 (Germer et al. 2006, Schmitz, personal communication)). Soils in the study area are classified as Kandiudults (Soil Survey Staff 1999). More details about soils, vegetation and climate at Rancho Grande can be found in Sobieraj et al. (2002) and Germer et al. (2006).

Field sampling and laboratory analysis

A tipping bucket rain gauge (Hydrological Services P/L, Liverpool Australia) with a resolution of 0.254 mm and a Campbell Scientific data logger recorded 5-min rainfall intensity values on a pasture about 400 m from the forest. In addition, incident rainfall was collected with three trough-type collectors. The collectors, installed on supports 1 m above ground, were made from 150 mm diameter PVC pipes, which were connected via flexible tubes to 20 l plastic canisters or a sequential sampler. Between collector pipe and tubes, funnels with a thin-mesh nylon net pre-leached with deionized water (DIW) prevented coarse material from entering the canisters. The total collecting area per collector was 980 cm^2 (7 cm × 140 cm). One of the rainfall collectors was used for bulk event sampling and the other two were connected to one single sequential sampler for within-event sampling. Bulk throughfall was sampled on event basis with 20 collectors, which were cleaned of litter after each event. The samplers sampled dry plus wet deposition. Two additional collectors were connected to one sequential sampler for within-event sampling of throughfall. To minimize dry deposition from August through November the rainfall collector was rinsed daily with deionized water for those days with no precipitation. For the remaining year dry deposition is expected to be low. Samples were collected on an event basis from 22 August 2004 to 3 April 2005. Within-event sampling was carried out for the same period except the first month.

The sequential samplers (Fig. 1) were composed of 10 connected sampling bottles of different sizes that partitioned events into predefined rainfall depth intervals of 1.25 mm, 2.5 mm and 5 mm for the bottles 1 to 4, 5 to 6 and 7 to 9, respectively. This

Fig. 1 Sequential sampler design: Composite of two through collectors, a tipping bucket and 10 sampling bottles. The detail image in the lower right image corner shows individual sampling bottles and the connection tubing

arrangement allowed for a sequential sampling of the first 25 mm. For events exceeding 25 mm, the last bottle collected the surplus. After each event, bottles were replaced by empty bottles rinsed with deionized water.

Rainfall and throughfall volumes were measured and samples were collected for measurement of solute concentrations 2 h after every event, or alternatively the next morning for events that ended after 09:00 pm (Germer et al. 2006). Rainfall and throughfall samples of up to 1 l were collected in Nalgene polyethylene bottles that were pre-washed with dilute (5%) HCl then thoroughly rinsed with nanopure dionized water. All samples were returned to the field laboratory and stored on ice in coolers immediately after collection.

In the field laboratory, pH of unfiltered samples was measured with an Orion pH meter (Model 250A+) calibrated twice daily. For cation and anion determination, a 50 ml aliquot was filtered through glass fiber filters (Whatman, GF/F) pre-washed with 20 ml of sample. Samples were stored in acid washed polyethylene bottles, preserved with thymol and frozen. An additional 50 ml aliquot was filtered for DOC determination. Samples for DOC were stored in pre-combusted and acid washed 30 ml glass vials with acid washed Teflon lid liners. Samples for DOC were preserved with $HgCl_2$ at a final concentration of 300 μM and refrigerated. DOC samples were packed with the frozen cation/anion samples and shipped in Styrofoam coolers to CENA in Piracicaba, where they arrived still partially frozen. Cation/anion

samples were maintained frozen and DOC samples maintained refrigerated until analysis.

Concentrations of cations (Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+) and anions (Cl^-, SO_4^{2-} and NO_3^-) were analyzed using a Dionex ion chromatograph (model DX-500). A Shimadzu total carbon analyzer (model TOC 5000 A) was used to determine DOC concentrations by combustion at 720°C and detection of the evolved CO_2 in a non-dispersive infrared gas analyzer. For cations and anions, separate standard curves were prepared for each batch of 80 samples. In addition a certified reference sample of soft river water (Trois-94, Quebec, Canada, National Water Research Institute of Canada) was included in each sample run. The results were acceptable when the R^2 of the correlation between standards and peak areas is 0.99 or above. Differences in concentrations determined daily for the certified water sample were maintained within 1% of that specified in the certificate. The detection limits were (in μM): Cl^-= 1.41, SO_4^{2-} = 0.52, NO_3^- = 0.81, Na^+ = 2.17, NH_4^+ = 2.77, K^+=1.28, Mg^{2+} = 2.06, Ca^{2+} = 1.25 and DOC = 10. Analytical variability of solute concentrations was always less than 10%. Sample blanks of DIW and DIW passed through PVC collectors were below detection limits.

Data analysis

The first set of events from August to the end of November 2004 and the second set of events from January to April 2005 were grouped into the transition from dry to wet season (TDWS) and wet season (WS), respectively.

Volume-weighted means (VWM_E) per event E were used to express mean throughfall solute concentration of individual events. The VWM_E per event was calculated as

$$VWM_E = \left(\sum_{n=1}^{i} C_{i,E}V_{i,E}\right)\left(\sum_{n=1}^{i} V_{i,E}\right)^{-1} \quad (1)$$

for all sampled events, where $C_{i,E}$ and $V_{i,E}$ are the concentration and volume at collector i for event E.

Seasonal VWM_S (VWM_{TDWS}, VWM_{WS}, $VWM_{TDWS+WS}$) were further calculated using the VWM_E in throughfall and the measured concentrations in rainfall for all sampled events of the TDWS and WS, respectively. For this calculation, equation 1 still applies, replacing the notation E with TDWS or WS for the season and the notation i with E for events.

We calculated separate VWM_S for the TDWS and the WS to compare our data with published results. The volume-weighted standard deviation was calculated and used to determine the 95% confidence limits of the VWM_S (Bland and Kerry 1998). The computation of annual or seasonal solute fluxes required estimates of solute concentrations for those events that were not sampled. The following procedure was executed for each solute for the TDWS and the WS, with the aim of finding the respective best models to estimate concentrations. Explanatory variables were transformed, if required, to get linear relations with the response variable. After including the explanatory variables, a step-wise regression using backward deletion of insignificant explanatory variables was performed. The explanatory variables included in the initial model were: the reciprocal of event size in mm (R^{-1}), event duration in h (D), antecedent dry period per event in h (ADP) and the reciprocal of mean rainfall intensity per event in mm h^{-1} (I^{-1}). The only interaction term included was the mean rainfall intensity, as it was calculated from the event size and duration. The response variable was the VWM_E concentration per event.

To calculate annual fluxes, we used the measured concentrations of all sampled events plus estimates of concentrations in unsampled events predicted with the best-fit model for each solute. If concentrations couldn't be predicted with the available explanatory variables, mean VWM_S concentrations per season were used. Fluxes were calculated as the product of the measured or modeled concentrations and rainfall or throughfall for all events with a rainfall depth greater than 3 mm. Smaller events were not sampled, as they did not yield enough sample volume for chemical analysis, which precluded the estimation via a step-wise regression. The uncertainty of seasonal fluxes was expressed by 95% confidence levels for all estimated fluxes. Correlations among solutes were calculated using Spearman's rank correlations after visual examination of the respective scatterplots. For all statistical analysis we used the language and environment of R (Version 2.2.1).

Results

The total incident rainfall at Rancho Grande from August 2004 to July 2005 was 2286 mm, similar to the mean annual rainfall from 1984 to 2003 of 2300 mm. Of 176 rainfall events from August 2004 to July 2005, we sampled 42 events on an event basis (total rainfall 1088 mm) and 35 events on a within-event basis (total rainfall 852 mm). Most of the events sampled within-events were also sampled on an event basis. The subset of events sampled for rainfall and throughfall chemistry covered the whole range of event sizes above 3 mm (Fig. 2).

Seasonal patterns of rainfall solute concentrations

In rainfall, VWM_S solute concentrations followed the pattern $DOC \gg Ca^{2+} = NH_4^+ > K^+ = Cl^- > Na^+ = SO_4^{2-} = Mg^{2+} = NO_3^-$, (with $Na^+ > Mg^{2+}$ and NO_3^-) (Table 1). In the TDWS, the pattern was $DOC \gg NH_4^+ = Ca^{2+} > K^+ = Cl^- = Mg^{2+} = NO_3^- = SO_4^{2-} = Na^+$ (with $K^+ > Mg^{2+}$ and $Cl^- > Na^+$), and in the WS the pattern was $DOC \gg Ca^{2+} = Cl^- = Na^+ = K^+ > Mg^{2+} = NH_4^+ = NO_3^- = SO_4^{2-}$, (with $Ca^{2+} > Na^+$ and K^+) (Table 1). The relative importance of K^+, Cl^- and Na^+ concentrations in rainfall increased and that of NH_4^+ concentrations decreased from the TDWS to the WS. Except for Na^+ and Cl^-, solute concentrations were significantly higher in the TDWS. TDWS:WS ratios of VWM_S concentrations were highest for NH_4^+, SO_4^{2-}, DOC and NO_3^-. Rainfall concentrations of NO_3^-, NH_4^+, SO_4^{2-} and K^+ peaked in bulk rainfall in mid-September, while Ca^{2+} concentrations were highest for the early season events and decreased in the TDWS (Fig. 3). The remaining solutes as well as pH showed no clear trends within the TDWS or the WS.

Correlations between rainfall solute concentrations in the TDWS were highest for SO_4^{2-}, NO_3^- and NH_4^+ (r^2 range: 0.85–0.90, $p < 0.001$). These three ions correlated as well with DOC (r^2 range: 0.66–0.74, p at least <0.01). Ca^{2+} showed weaker correlations with DOC, SO_4^{2-}, NO_3^- and Mg^{2+} (r^2 range: 0.61–0.67, p at least <0.01). A different pattern existed during the WS, where the highest correlations were found for Cl^-, Mg^{2+} and Ca^{2+} (r^2 range: 0.80–0.85, $p < 0.001$). Sulfate and NO_3^- showed a lower and less significant correlation in the WS compared to the TDWS (r^2=0.70, $p < 0.05$). Potassium correlated weakly with NO_3^- and Na^+ (r^2 range: 0.66–0.67, p at least <0. 01), but no significant correlation was found for NO_3^- and Na^+.

Within-event patterns of rainfall concentrations

Concentrations of many solutes in rainfall within events declined sharply during the initial few mm of rain during the TDWS. Figure 4 shows the typical pattern for three solutes during one event. By analyzing these within-event concentration plots of all 35 events for each solute, we found the following patterns: Initial concentrations of K^+ and Na^+ declined rapidly within early TDWS season events and reached constant concentration levels after 3–4 mm of rainfall. In the same events, the decline of initial concentrations was more gradual for Ca^{2+} and NH_4^+. From September to mid-October a re-increase after 15 mm of rainfall was found for Ca^{2+} and NH_4^+.

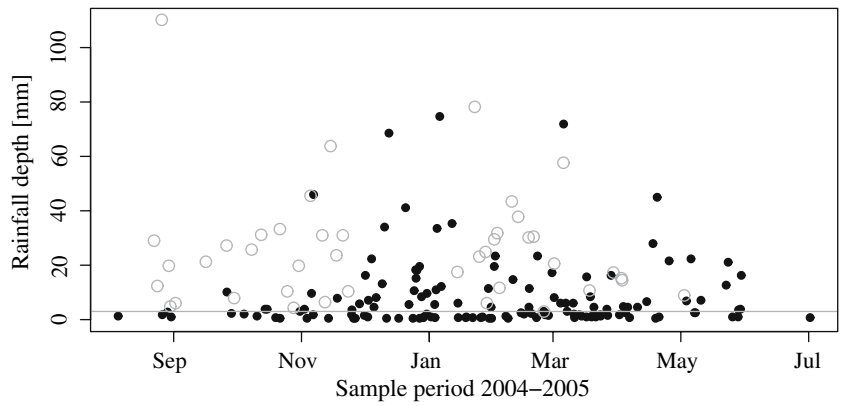

Fig. 2 Overview of all events from August 2004 to July 2005 grouped into those sampled on event basis (*grey open circles*) and the remaining not-sampled events (*black solid circles*). The grey line at 3 mm rainfall depth represents the minimum sample size

Table 1 VWM_S rainfall solute concentrations and lower (lwr) and upper (upr) confidence limits (where provided by the authors) in µmol per liter measured for different rainforests (*n* is the sample size). Where available, results are separately listed for the dry season (DS) or the transition from dry to wet season (TDWS) and the wet season (WS)

Site	Details	pH					DOC [µmol l^{-1}]				Cl^-[µmol l^{-1}]				SO_4^{2-}[µmol l^{-1}]				NO_3^-[µmol l^{-1}]			
		mean	range	lwr	upr	n	mean	lwr	upr	n	mean	lwr	upr	n	mean	lwr	upr	n	mean	lwr	upr	n
our study																						
Amazonia (SW) [a]	all events	6.3	5.2–6.8	6.2	6.4	41	591.8	375	808.6	37	11.4	8.8	13.9	38	4.5	2.7	6.4	27	4.1	2.4	5.8	37
Amazonia (SW) [a]	WS	6.2	5.5–6.8	6.1	6.4	19	280.8	81.1	480.5	17	11.4	8.8	14	20	0.7	–0.1	1.6	9	1.1	0.8	1.4	18
Amazonia (SW) [a]	TWDS	6.3	5.2–6.8	6.3	6.4	22	838.3	595.4	1081	20	11.3	8	14.6	18	6.5	4.6	8.4	18	7.1	5.1	9	19
previous studies																						
Amazonia (central) [b]	all events	5	–	–	–	30	110	–	–	30	2.1	–	–	30	6.2	–	–	30	8.1	–	–	30
Amazonia (central) [b]	WS	5.2	–	–	–	12	120	–	–	12	1.2	–	–	12	3.2	–	–	12	3.3	–	–	12
Amazonia (central) [b]	DS	4.8	–	–	–	18	110	–	–	18	4.1	–	–	18	13	–	–	18	18	–	–	18
Amazonia (central) [c]	all events	4.7	–	–	–	95	–	–	–	–	4.6	–	–	95	4	–	–	95	12.6	–	–	95
Amazonia (central) [c]	WS	5	–	–	–	72	–	–	–	–	4.6	–	–	72	3.2	–	–	72	9.9	–	–	72
Amazonia (central) [c]	DS	4.5	–	–	–	23	–	–	–	–	4.5	–	–	23	5.6	–	–	23	19.2	–	–	23
Amazonia (central) [d]	WS	5	–	–	–	13	68	–	–	13	4	–	–	13	1.6	–	–	13	1.3	–	–	13
Amazonia (central)[e]	all events[**]	4.3	–	4.2	4.4	90	–	–	–	–	18.9	3.9	33.6	30	8.3	5.5	11.1	20	–	–	–	–
Amazonia (central) [f]	WS	4.7	4.0–5.3	–	–	29	–	–	–	–	7.7	0.7	14.8	18	3	–0.4	6.5	18	–	–	–	–
Amazonia (central) [f]	DS						–	–	–	–	11.8	3.9	19.8	11	7.2	1.8	12.7	11	–	–	–	–
Amazonia (E) [g]		–	–	–	–	1	–	–	–	–	289	–	–	1	29.9	–	–	1	–	–	–	–
Amazonia (central)[g]		4.8	4.7–4.9	–	–	1[*]	–	–	–	–	27.3	–	–	1[*]	7.9	–	–	1[*]	3	–	–	1[*]
Amazonia (cent.-W) [g]	5.3	–	–	–	1	–	–	–	–	8.4	–	–	1		5.7	–	–	4.3	–	–	1	
Amazonia (W) [g]		5.7	–	–	–	1	–	–	–	–	3.4	–	–	1	1.9	–	–	1	–	–	–	–
Amazonia (NW) [h]	all events	5	–	4.9	5.1	35	328.3	281.9	374.7	35	25.4	21.2	29.6	35	36.9	28.3	45.5	35	6.4	5	7.8	35

Site	Details	Na^+ [µ mol l^{-1}]				NH_4^+ [µ mol l^{-1}]				K^+ [µ mol l^{-1}]				Mg^{2+} [µ mol l^{-1}]				Ca^{2+} [µ mol l^{-1}]			
		mean	lwr	upr	n	mean	lwr	upr	n	mean	lwr	upr	n	mean	lwr	upr	n	mean	lwr	upr	n
Amazonia (SW) [a]	all events	7	5.9	8.1	37	24	13	34.9	39	13.1	8.2	17.9	39	4.3	2.9	5.8	39	25.4	20.1	30.7	37
Amazonia (SW) [a]	WS	7.5	6	9	20	1.5	–0.2	3.1	20	7.5	4.6	10.3	20	1.6	0.8	2.3	20	15.1	12.2	17.9	20
Amazonia (SW) [a]	TWDS	6.4	5.2	7.6	17	47.1	35.3	59	19	18.8	12.6	25.1	19	7.2	5.6	8.8	19	36.9	31.5	42.4	17
previous studies																					
Amazonia (central) [b]	all events	5.1	–	–	30	2.2	–	–	30	0.9	–	–	30	3	–	–	30	11.8	–	–	30
Amazonia (central) [b]	WS	3.6	–	–	12	0.5	–	–	12	0.6	–	–	12	1.6	–	–	12	7	–	–	12
Amazonia (central) [b]	DS	8.4	–	–	18	5.8	–	–	18	1.6	–	–	18	5.6	–	–	18	22.2	–	–	18
Amazonia (central) [c]	all events	2.4	–	–	95	3	–	–	95	0.8	–	–	95	1.8	–	–	95	4.8	–	–	95
Amazonia (central) [c]	WS	2.1	–	–	72	1.2	–	–	72	0.7	–	–	72	2	–	–	72	4.8	–	–	72
Amazonia (central) [c]	DS	3.4	–	–	23	7.4	–	–	23	1.2	–	–	23	1.2	–	–	23	4.8	–	–	23

Table 1 continued

Site	Details	Na^+[µmol l^{-1}]				NH_4^+[µmol l^{-1}]				K^+[µmol l^{-1}]				Mg^{2+}[µmol l^{-1}]				Ca^{2+}[µmol l^{-1}]			
		mean	lwr	upr	n	mean	lwr	upr	n	mean	lwr	upr	n	mean	lwr	upr	n	mean	lwr	upr	n
Amazonia (central) [d]	WS	4.4	–	–	13	4.7	–	–	13	1.8	–	–	13	–	–	–	–	–	–	–	–
Amazonia (central) [e]	all events [**]	17	11.3	22.6	30	–	–	–	–	5.9	–0.5	12.3	30	–	–	–	–	–	–	–	–
Amazonia (central) [f]	WS	3.1	1.3	4.9	18	2.4	1.1	3.7	18	0.6	0.3	0.9	18	0.3	0.1	0.5	18	2.4	1.4	3.4	18
Amazonia (central) [f]	DS	9.6	0.7	18.4	11	8.6	–2.9	20.0	11	3.6	0.9	6.3	11	0.8	0.1	1.4	11	3.1	1.5	4.7	11
Amazonia (E) [g]		232	–	–	1	–	–	–	–	4.7	–	–	1	30.6	–	–	1	4.2	–	–	1
Amazonia (central)[g]		24.5	–	–	1[*]	1.1	–	–	1[*]	1.1	–	–	1[*]	2.2	–	–	1[*]	1.3	–	–	1[*]
Amazonia (cent.-W) [g]	9.9	–	–	1	0.4	–	–	1	1	–	–	1	1	–	–	1	1.4	–	–	1	
Amazonia (W) [g]		1.7	–	–	1	–	–	–	–	1	–	–	1	0.8	–	–	1	4.6	–	–	1
Amazonia (NW) [b]	all events	20	17.5	22.5	35	11.5	8.6	14.4	35	9	6.4	11.6	35	2.8	2.2	3.4	35	6.8	6	7.6	35

[a] This study, [b] Filoso et al. (1999), [c] Williams et al. (1997), [d] Andreae et al. (1990), [e] Franken and Leopoldo (1984), [f] Forti and Moreira-Nordemann (1991), [g] Stallard and Edmond (1981), [h] Tobon et al. (2004)

[*] Rainfall was collected sequentially during one event (8 subsamples), [**] mean instead of VWM_S concentrations, – no data provided

After mid-October, these cations reached constant concentration levels after 6–7 mm of rainfall. For Ca^{2+}, constant concentration levels were reached already after 3–4 mm of rainfall from January and through the WS. The decrease of the initial concentration of Mg^{2+} fell between the fast within-event concentration decline for K^+ and Na^+ and the more gradual decline for Ca^{2+} and NH_4^+, which reached low concentrations after 5 mm of rainfall. Chloride, SO_4^{2-} and NO_3^- showed a concentration decline within events similar to that of cations. A fast initial decline (first 3–4 mm) was found for Cl^- and SO_4^{2-} while the decline for NO_3^- was more gradual, reaching constant concentration levels after 6–7 mm of rainfall in early events of the TDWS. Within-event DOC concentrations were highly variable and showed clear declining concentration for few events. From September to mid-October, pH declined for the first 15 mm of rainfall and subsequently rose again with pH differences of up to 0.5 per event. For the rest of the study period pH did not show any trends during events, except during one week in February (12th–19th) with trends corresponding to those of the early season.

In addition to within-event dynamics, we analyzed the seasonal concentration dynamics of different event stages: the first 2.5 mm of rain and 7.5–10.0 mm. Higher initial event concentrations as well as the later event stage concentrations declined within the TDWS for SO_4^{2-}, NO_3^-, NH_4^+ and Ca^{2+} and did not show any changes within the WS (Fig. 5). No clear seasonal pattern of the two event stages was identified for the remaining solutes. Other than slightly elevated pH values in initial event concentrations in the beginning of early season events, the two event stages did not show any seasonal trends for rainfall.

Seasonal patterns of throughfall solute concentrations

In throughfall, VWM_S solute concentrations over the entire year decreased in the pattern $DOC \gg K^+ > Cl^- = NH_4^+ = Ca^{2+} > Na^+ = Mg^{2+} = NO_3^- = SO_4^{2-}$ (with $Mg^{2+} > SO_4^{2-}$) (Table 2). In the TDWS the pattern was $DOC \gg K^+ > Cl^- = NH_4^+ = Ca^{2+} > Na^+ = Mg^{2+} = NO_3^- = SO_4^{2-}$ (with $Mg^{2+} > SO_4^{2-}$), and in the WS the pattern was

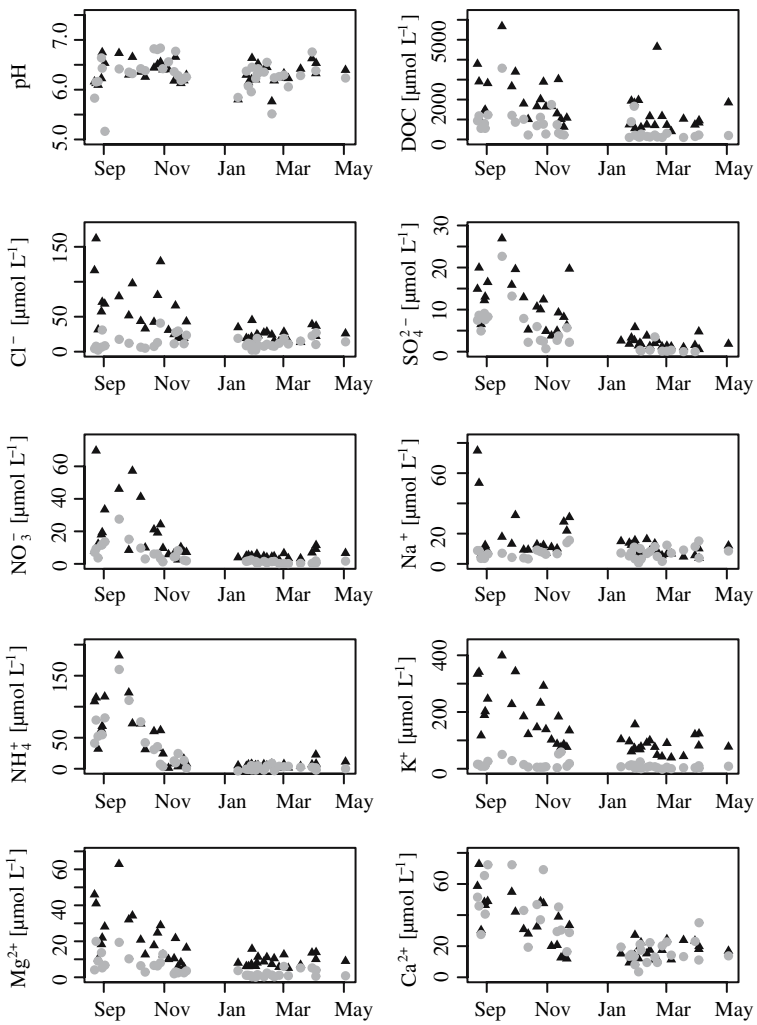

Fig. 3 Rainfall (*grey solid circles*) and throughfall VWM_E (*black solid triangles*) solute concentrations plotted over time for all events sampled on event basis

$DOC \gg K^+ > Cl^- > Ca^{2+} > Na^+ = Mg^{2+} > NH_4^+ = NO_3^- > SO_4^{2-}$ (Table 2). The sequences of both seasons were very similar, despite the lower relative abundance of NH_4^+ in the WS. In the TDWS, the relative abundance of K^+, Cl^- and Na^+ increased from rainfall to throughfall, while in the WS, only the relative abundance of K^+ and Cl^- increased. VWM_S concentrations in throughfall samples were significantly higher in the TDWS than in the WS for all solutes except DOC. The VWM_S of pH was higher in the WS. The VWM_E's of bulk throughfall samples decreased for all solutes during the TDWS, but did not show temporal trends during the WS (Fig. 3). The VWM_E pH in throughfall ranged from 4.5 to 7.1 but did not show any seasonal trend.

To assess the effect of the canopy on throughfall solute concentration, we subtracted rainfall concentrations from VWM_E throughfall concentrations. The resulting net throughfall (TF_{net}) concentrations per event were always positive for K^+, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-} and DOC. TF_{net} for Na^+, Ca^{2+} and NH_4^+ was negative for some events. While negative net throughfall concentrations for Ca^{2+} occurred over the whole study period, negative values for Na^+ occurred only in the WS and negative values for NO_3^- and NH_4^+ occurred only in the TDWS.

The correlations of solute concentrations during the TDWS were strong and significant for most of the solutes (r^2 range: 0.60–0.95, p at least <0.01). Correlations were highest for Cl^-, K^+, Mg^{2+} and Ca^{2+} ($r^2 \geq 0.90$, $p < 0.001$). For the WS fewer solutes correlated, but all of these correlations were highly significant ($p < 0.001$). The highest correlations were found for Cl^- with K^+ and Mg^{2+} (r^2: 0.90 and 0.81, respectively) and Na^+ and SO_4^{2-} (r^2=0.82).

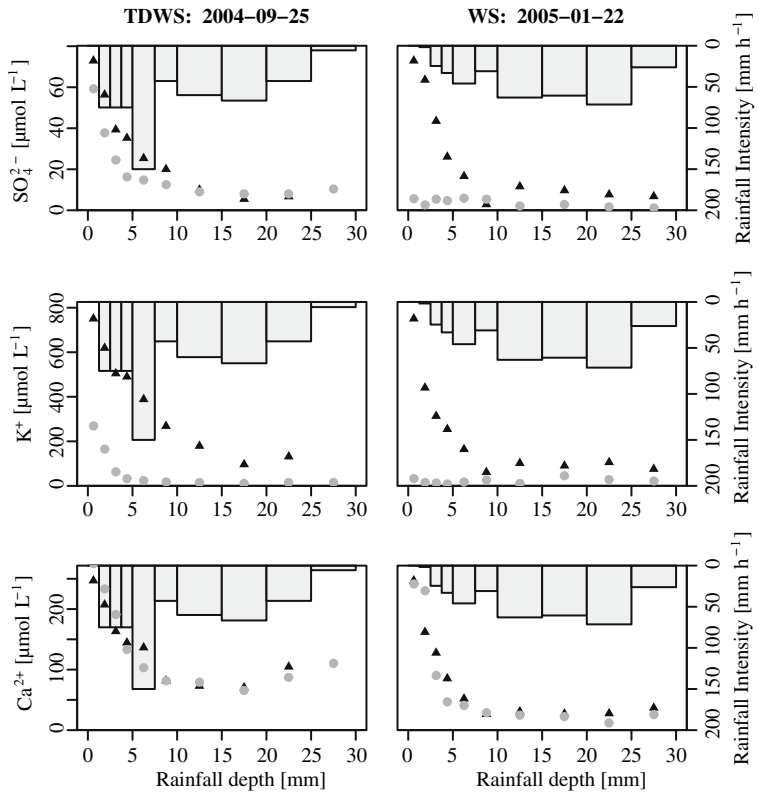

Fig. 4 Typical within-event solute concentration dynamics in rainfall (*grey solid circles*) and throughfall (*black solid triangles*) for sulfate, potassium and calcium. The bars illustrate the rainfall intensity

Furthermore, strong correlations were found for the solute pairs: K^+–Mg^{2+}, Mg^{2+}–Ca^{2+} and NO_3^-–NH_4^+ (r^2 range: 0.72–0.82). There were no correlations between Na^+ and all other solutes, between DOC and NO_3^- as well as between NO_3^- and Ca^{2+} ($r^2 < 0.55$, $p \geq 0.05$).

Within-event patterns of throughfall concentrations

Throughfall solute concentrations decreased after the onset of rains for all solutes over the whole study period. Figure 4 shows this typical pattern for three solutes in two events. Constant concentration levels were generally reached later in throughfall than in rainfall, except for Ca^{2+}, whose pattern was similar to rainfall. The throughfall depth necessary for all solutes to reach constant concentration levels differed between events ranging from 6 to 15 mm and in some cases it was not reached within the first 20 mm of throughfall (Fig. 6). The within-event pH values were slightly higher than or equal to values in rain but differences rarely exceeded 0.5 pH units.

The initial concentrations in throughfall declined over the study period for DOC and most of the ions, except for NO_3^-, which decreased in the TDWS and then increased in the WS. A seasonal trend of the later event stage concentrations was not apparent for Cl^-, Mg^{2+}, Na^+ and SO_4^{2-} but decreased concentrations of DOC, NO_3^-, NH_4^+, K^+ and Ca^{2+} decreased during later event stages.

Plots of net throughfall against rainfall for sequential samples collected during events showed clearly the proportion of samples in which net throughfall is positive or negative for each solute (Fig. 7). All solutes showed negative TF_{net} in some portions of events. For the solutes SO_4^{2-}, NO_3^-, NH_4^+ and K^+, a frequent negative TF_{net} was found during the TDWS, while TF_{net} during the WS was mostly positive. In contrast, DOC and Ca^{2+} TF_{net} concentrations were consistently negative for high rainfall concentrations during the WS.

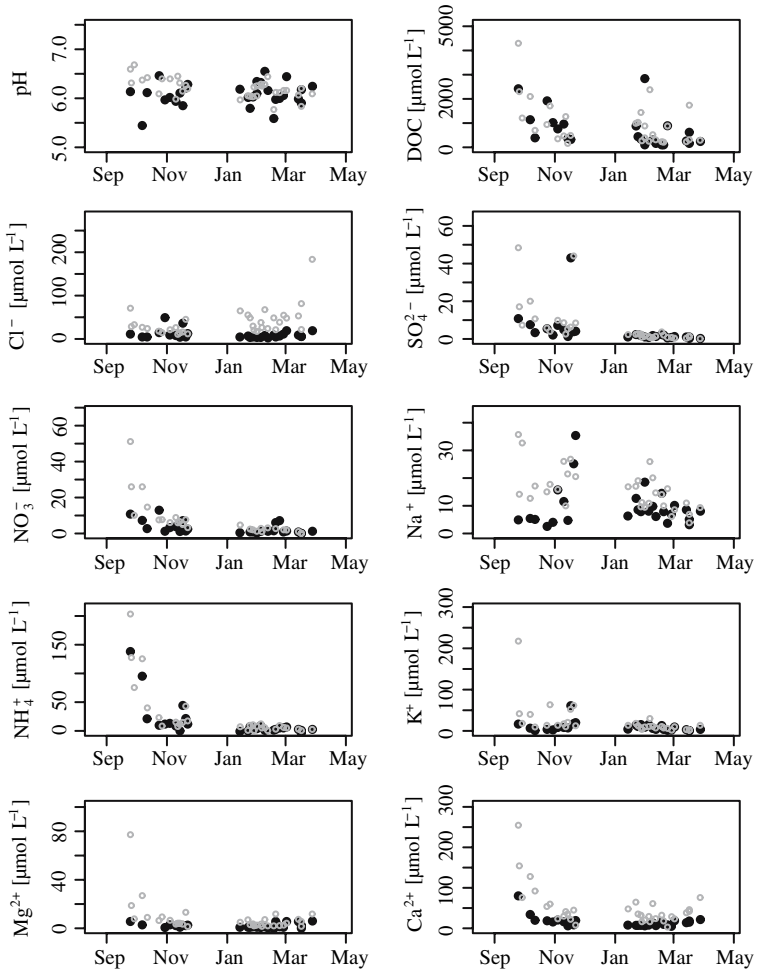

Fig. 5 Temporal dynamics in rainfall solute concentrations of different event stages. Solute concentrations of the first 2.5 mm per event (*open circles*) and of a later event stage represented by the event interval from 7.5 to 10 mm of rainfall (*solid circles*) are plotted over the study period

Modeling and annual solute fluxes

For rainfall, step-wise regression resulted in relatively few models capable of predicting solute concentrations (Table 3). This indicated that the predictor variables (*R*, *D*, ADP and *I*) were generally unable to predict rainfall concentrations of most solutes in particular events in either sampling period. Rainfall concentrations of H^+ and Cl^- were predicted by event size and event duration in the TDWS. Event size and antecedent dry period were significant for DOC in the WS. Rainfall intensity was useful to predict NO_3^- concentrations in the WS.

For throughfall, models with varying levels of significance were found for 7 of 10 solutes (Table 3). The antecedent dry period was more important in the TDWS than in the WS, and appeared as a significant predictor for 5 of the 7 solutes for which a predictive model was found. Furthermore, event size and event duration were helpful to predict throughfall concentrations for some solutes during the TDWS. For the WS, in contrast, the mean rainfall intensity was a highly significant predictor for throughfall Cl^-, K^+, Mg^{2+} and Ca^{2+} concentrations. The only other significant predictor for WS throughfall was the event duration for Ca^{2+}.

In rainfall, fluxes of SO_4^{2-}-S, NO_3^--N, NH_4^+-N and Mg^{2+} were significantly higher in the TDWS than in the WS (Fig. 8). Rainfall fluxes of Cl^- and Na^+ showed the opposite seasonal pattern, with higher fluxes in the WS than in the TDWS. There were no seasonal differences in seasonal rainfall fluxes of DOC, K^+ and Ca^{2+}.

In throughfall, fluxes of SO_4^{2-}-S, NO_3^--N and NH_4^+-N were also higher in the TDWS than in the WS, but fluxes of Mg^{2+} were similar between sampling

Table 2 VWM_S throughfall solute concentrations and lower (lwr) and upper (upr) confidence limits (where provided by the authors) in μ M per liter measured for different rainforests (*n* is the sample size). Where available, results are separately listed for the dry season (DS) or the transition from dry to wet season (TDWS) and the wet season (WS)

Site	Details	pH					DOC [μ mol l^{-1}]				Cl^- [μ mol l^{-1}]				SO_4^{2-} [μ mol l^{-1}]				NO_3^- [μ mol l^{-1}]			
		mean	range	lwr	upr	n	mean	lwr	upr	n	mean	lwr	upr	n	mean	lwr	upr	n	mean	lwr	upr	n
our study																						
Amazonia (SW) [a]	all events	6.3	4.5–7.1	6.2	6.3	42	1354	1031	1678	40	31.4	24.2	38.5	41	5.3	3.7	7	41	8.7	5.7	11.8	42
Amazonia (SW) [a]	WS	6.3	4.5–6.9	6.2	6.4	22	1106	664.2	1547	19	22.4	18.8	25.9	20	2	1.5	2.4	20	4.6	3.9	5.4	20
Amazonia (SW) [a]	TDWS	6.3	5.1–7.1	6.2	6.3	20	1604	1261	1947	21	40.9	31.5	50.2	21	9.3	7.5	11.1	21	12.9	8.9	16.9	22
previous studies																						
Amazonia (central) [b]	all events	5.5	–	–	–	30	810	–	–	30	9.3	–	–	30	13	–	–	30	8.1	–	–	30
Amazonia (central) [b]	WS	5.7	–	–	–	12	720	–	–	12	4.3	–	–	12	7	–	–	12	1.5	–	–	12
Amazonia (central) [b]	DS	5.3	–	–	–	18	940	–	–	18	19.8	–	–	18	26	–	–	18	22.2	–	–	18
Amazonia (central) [c]	WS	–	–	–	–	–	–	–	–	–	10.3	8.5	12.1	16	4.6	3.8	5.5	16	–	–	–	–
Amazonia (central) [c]	DS	–	–	–	–	–	–	–	–	–	21	17.3	24.7	10	11.8	10.2	13.4	10	–	–	–	–
Amazonia (NW) [d]	sedimentary plain	5.2	–	5.2	5.2	35	459.6	436.4	482.8	35	22.9	21.2	24.5	35	59	52.1	66	35	23.7	17.2	30.1	35
Amazonia (NW) [d]	high terrace	5.5	–	5.5	5.5	35	558.1	511.7	604.5	35	38.1	33.5	42.7	35	77.5	62	93	35	16.6	11.3	22	35
Amazonia (NW) [d]	low terrace	5.3	–	5.3	5.3	35	558.1	525.6	590.6	35	35.6	32.2	39	35	84.9	65.9	103.8	35	33.2	21.7	44.8	35
Amazonia (NW) [d]	flood plain	5.5	–	5.5	5.5	35	525.3	497.4	553.1	35	40.6	36.5	44.8	35	70.1	53.7	86.5	35	39	17.9	60,2	35

Site	Details	Na^+ [μ mol l^{-1}]				NH_4^+ [μ mol l^{-1}]				K^+ [μ mol l^{-1}]				Mg^{2+} [μ mol l^{-1}]				Ca^{2+} [μ mol l^{-1}]			
		mean	lwr	upr	n	mean	lwr	upr	n	mean	lwr	upr	n	mean	lwr	upr	n	mean	lwr	upr	n
our study																					
Amazonia (SW) [a]	all events	13	9.2	16.8	40	21.7	10.8	32.6	42	109.7	87.9	131.5	42	12	8.8	15.2	42	21.6	17.5	25.7	40
Amazonia (SW) [a]	WS	9.7	7.8	11.6	20	5.2	3.8	6.5	20	76.3	63.6	89	20	8.1	6.8	9.4	20	15.4	13.1	17.6	20
Amazonia (SW) [a]	TDWS	16.9	11.6	22.2	20	38.6	24.6	52.5	22	143.8	117.2	170.3	22	16	11.8	20.2	22	28.3	23.3	33.3	20
previous studies																					
Amazonia (central) [b]	all events	10.2	–	–	30	2.2	–	–	30	43.4	–	–	30	27.2	–	–	30	33.8	–	–	30
Amazonia (central) [b]	WS	7.1	–	–	12	1.1	–	–	12	24.9	–	–	12	14	–	–	12	19.2	–	–	12
Amazonia (central) [b]	DS	16.5	–	–	18	4.6	–	–	18	80.5	–	–	18	53.6	–	–	18	63	–	–	18
Amazonia (central) [c]	WS	10.6	8.6	12.6	16	4.7	3.2	6.1	16	6.6	5.2	8.1	16	3.7	2.8	4.5	16	5.1	4	6.2	16
Amazonia (central) [c]	DS	29	24.2	35.9	10	6.1	3.8	9.5	10	25.1	20.5	29.6	10	10.9	9.1	12.6	10	10.2	8.2	12.1	10
Amazonia (NW) [d]	sedimentary plain	24	22.2	25.8	35	27.6	20.7	34.5	35	32.4	27	37.8	35	8.1	7.2	9	35	8.8	8.4	9.2	35
Amazonia (NW) [d]	high terrace	28	26.5	29.5	35	35.7	20.4	51	35	45	32.6	57.4	35	7.6	6.7	8.4	35	9.5	8.8	10.2	35
Amazonia (NW) [d]	low terrace	28	25.5	30.5	35	33.4	19.8	44.6	35	44.1	33.8	54.4	35	9	8	9,9	35	10.2	9.3	11	35
Amazonia (NW) [d]	flood plain	26	24.7	27.2	35	32.21	24.1	40.3	35	41.4	33.9	48.9	35	14.3	12.5	16	35	15	13.9	16	35

a) This study, b) Filoso*et al.* (1999), c) Forti and Moreira-Nordemann (1991), d) Tobon*et al.* (2004)

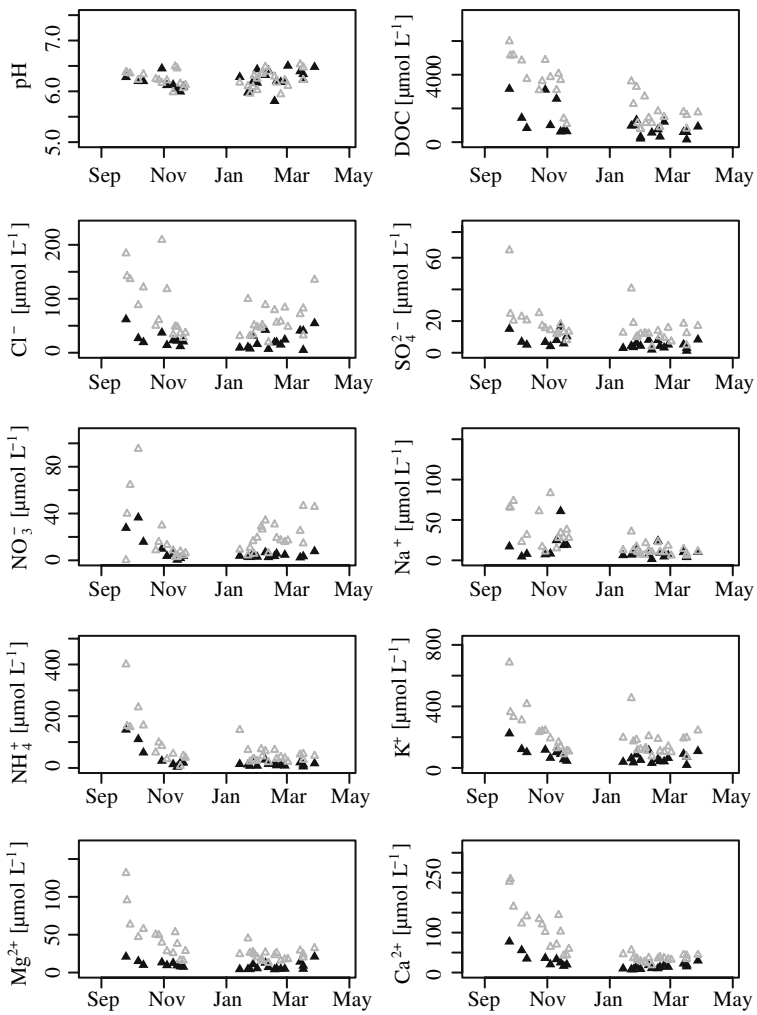

Fig. 6 Temporal dynamics in throughfall solute concentrations of different event stages. Solute concentrations of the first 2.5 mm per event (*open triangles*) and of a later event stage represented by the event interval from 7.5 to 10 mm of throughfall (*solid triangles*) are plotted over the study period

periods (Fig. 8). Throughfall fluxes of Cl^-, Na^+ and Ca^{2+} were higher in the WS than in the TDWS.

The same four solutes (DOC, Ca^{2+}, K^+, Cl^-) had the highest total annual fluxes in both rainfall and throughfall. In rainfall the relative magnitude of fluxes was $DOC > Ca^{2+} > K^+ = Cl^-$, while in throughfall: $DOC > K^+ > Cl^- = Ca^{2+}$ (Table 4). The highest flux enrichment for throughfall compared with rainfall was found for K^+ and it occurred during both sampling periods. In the TDWS the enrichment ratios decrease in the order: $K^+ > Cl^- > Na^+ > Mg^{2+} > NO_3^-$-N$>DOC>$ SO_4^{2-}-S $>$ NH_4^+-N $>$ Ca^{2+} In the WS, the relative enrichments were: $K^+ >$ SO_4^{2-}-S $>$DOC$>$ Mg^{2+} $>$ NO_3^--N $>$ NH_4^+-N $>$ Cl^- $>$ Na^+ $>$ Ca^{2+}. The flux enrichments were statistical significant for all solutes except for NH_4^+-N in the TDWS and for Na^+ and Ca^{2+} in the WS (Table 4). Very low fluxes in rainfall for SO_4^{2-}-S, NO_3^--N, NH_4^+-N and Mg^{2+} within the WS led to relative high enrichment ratios.

Discussion

Rainfall solute concentrations and dynamics

Our results provide the strongest evidence to date that the concentrations of most solutes in rainfall from a lowland moist forest location within the Amazon Basin declined both seasonally (from the early wet season to the late wet season) and within individual rainfall events. Similar declines in rainfall solute concentrations from the early to late wet season have been observed for forest in other Amazon locations,

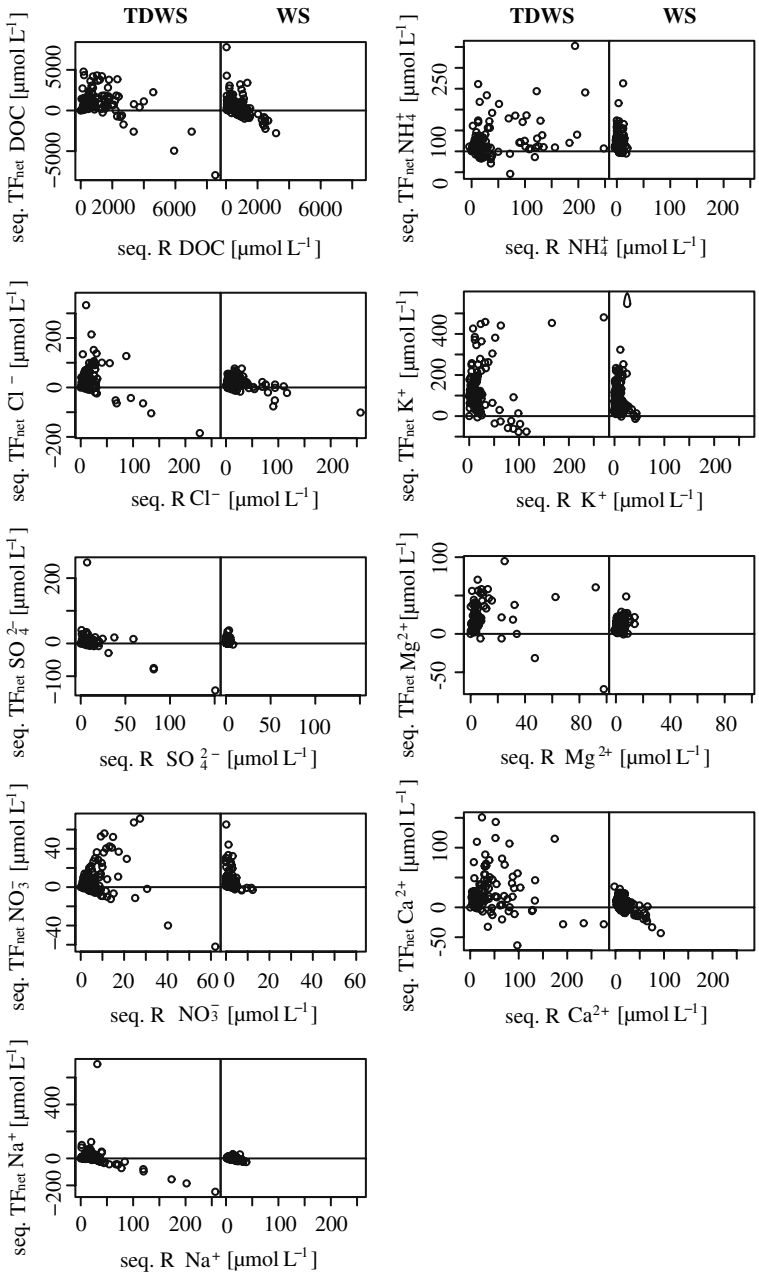

Fig. 7 Sequential net throughfall (seq. TF_{net}) deposition plotted over sequential rainfall (seq. *R*) for TDWS concentrations and WS concentrations. Each point represents a pair of rainfall and net throughfall samples for a single rainfall depth interval per event

but seasonal differences were not significant or no information on the confidence levels of their data was available (Filoso et al. 1999; Forti and Moreira-Nordemann 1991; Williams et al. 1997). Seasonal declines in the solute concentrations in rainfall have been reported for other tropical regions, including central America (Clark et al. 1998; Eklund et al. 1997; Hendry et al. 1984), central Africa (Chuyong et al. 2004; Muoghalu and Johnson 2000) Asia (Bruijnzeel 1989) and Australia (Edwards 1982). Seasonal declines in rainfall solute concentrations have also been documented from a savanna region in the northeastern portion of the Amazon Basin (Forti et al. 2000). There are few reports of within-event variability of solute concentration in tropical rainfall. Stallard and Edmond (1981) sampled three WS rainfall events sequentially at different sites within the Amazon, but clear concentration declines were

Table 3 Models applied for predicting solute concentrations in rainfall and throughfall with the predictor variables event size (R [mm]), event duration (D [h]), event antecedent dry period (ADP [h]) and the mean rainfall intensity per event in (I [mm h^{-1}])

Solute	Rainfall TDWS	Rainfall WS	Throughfall TDWS	Throughfall WS
H^+	$R^{-1\,*} + D^{***}$	–	$R^{-1***} + ADP^{\circ}$	–
DOC	–	$R^{-1\,*} + ADP^{**}$	–	—
Cl^-	$R^{-1\,***} + D^{*}$	–	$R^{-1\,***} + ADP^{***}$	$I^{-1\,***}$
SO_4^{2-}	–	–	–	–
NO_3^-	–	$I^{-1\,\circ}$	–	–
Na^+	–	–	$ADP^{**} + D^{*}$	–
NH_4^+	–	–	D^{*}	–
K^+	–	–	$R^{-1}* + ADP^{\circ}$	$I^{-1\,***}$
Mg^{2+}	–	–	D°	$I^{-1\,***}$
Ca^{2+}	–	–	$R^{-1\,**} + ADP^{**}$	$D^{*} + I^{-1\,***}$

The level of significance per predictor is indicated by either $^{\circ}$ $p < 0.1$, $^{*}p < 0.05$, $^{**}p < 0.01$, or $^{***}p < 0.001$

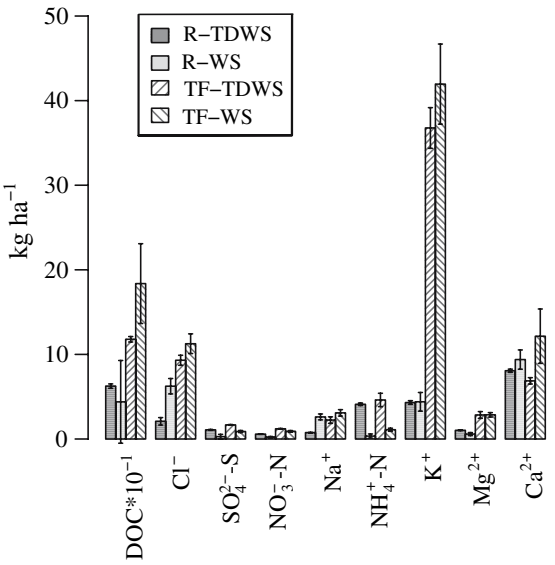

Fig. 8 Seasonal totals of solute fluxes in rainfall (R) and throughfall (TF) plotted separately for the TDWS (01 Aug 2004–23 Nov 2004) and the WS (24 Nov 2004–31 Jul 2005). The error bars indicate the 95% confidence intervals

not described. Radojevic and Lim (1995) reported within-event decreases of rainfall solute concentrations in Brunei. Because of the low number of sampled events, these studies did not yield possible seasonal changes in within-event concentration dynamics.

Several lines of evidence suggest that high regional aerosol concentrations and seasonal patterns of aerosol concentrations caused by land use and biomass burning in Rondônia play an important role in controlling these patterns. Aerosol concentrations in Rondônia undergo pronounced seasonal changes, with the highest concentrations occurring at the end of the dry season, when biomass burning is most widespread (Artaxo et al. 2002). In 2004, September had the highest density of forest and pasture fires within Rondônia (Embrapa 2005). This was also the time of peak rainfall concentrations reported in this study. Biomass burning is implicated as an important source of DOC, NO_3^+, NH_4^+, SO_4^{2-} and K^+ in aerosols in the Amazon (Andreae et al. 1988a; Guyon et al. 2003; Maenhaut et al. 1996). With the exception of K^+, we found rainfall to be most enriched in these solutes in the TDWS compared with the WS, suggesting a link between atmospheric aerosol load and rainfall solute concentrations. The seasonal concentration decrease of K^+ may have been less pronounced because of biogenic emissions of K^+ can be high during the WS (Guyon et al. 2003). We also found strong correlations of NO_3^+, NH_4^+ and SO_4^{2-} in rainfall only during the TDWS and lower overall concentrations during the WS, suggesting that higher concentrations of these solutes during the TWDS were linked to biomass burning and that this source was less important in the WS.

The processes of the transfer of aerosols to rainfall are also potentially linked to both seasonal and within-event dynamics of solute concentrations. This transfer process is two-fold. The initial stages of rain events are dominated by aerosol transfer to falling raindrops (washout), while later stages are dominated

Table 4 Annual totals of solute fluxes [kg ha^{-1} year^{-1}] rainfall (R), throughfall (TF) and net throughfall (TF_{net}) (01 Aug 2004–31 Jul 2005)

		DOC	Cl^-	SO_4^{2-}-S	NO_3^--N	Na^+	NH_4^+-N	K^+	Mg^{2+}	Ca^{2+}
Our study	R	106.45 (51.48)	83.30 (13.40)	1.36 (0.32)	0.80 (0.10)	3.37 (0.37)	4.46 (0.40)	8.71 (1.32)	1.61 (0.21)	17.46 (1.33)
	TF	301.59 (50.39)	205.70 (17.60)	2.55 (0.21)	2.11 (0.14)	5.33 (0.77)	5.71 (0.97)	78.72 (7.14)	5.70 (0.66)	19.03 (3.59)
	TF_{net}	195.14	122.40	1.19	1.31	1.96	1.25	70.01	4.09	1.57
Filoso et al. (1999)	R	–	1.56	1.04	0.78	2.44	0.68	0.73	0.37	2.46
	TF	–	5.38	1.71	0.62	3.83	0.54	27.70	2.70	5.54
	TF_{net}	–	3.82	0.67	–0.16	1.39	0.13	26.97	2.33	3.08

The numbers put in parentheses are 1/2 95% confidence intervals

– no data provided

by aerosol incorporation into cloud droplets during cloud formation and subsequent rainfall (rainout). Changes to solute concentrations over time within events, as well as seasonal changes to initial or late-event stage solute concentrations are likely to be a function of not only the total mass of aerosols incorporated in wet deposition but also the relative fraction of fine to coarse aerosols. The fine aerosol fraction (<5 μm) is predominant within clouds and responsible for rainout, while the coarse fraction of aerosols, which is subject to gravitational deposition, is more important in washout (Saha and Moorthy 2004; Seinfeld and Pandis 1998). Relatively higher coarse aerosol fractions are implicated when higher initial solute concentrations within events require a greater amount of rainfall to reach low constant and when differences between initial and constant concentrations are large. In our study, within-event sampling showed Ca^{2+}, NH_4^+ and NO_3^+ required greater rainfall to reach constant, low concentrations in TWDS events compared with WS events, suggesting that the coarse aerosol fraction is an important source of these solutes. This is also consistent with evidence that Ca^{2+} and NO_3^+ are abundant in coarse aerosols (Allen and Miguel 1995; Guyon et al. 2003; Roberts et al. 2002).

Throughfall solute concentrations and dynamics

All of the solutes we measured in bulk throughfall from our Rondônia forest, except for DOC, showed significant seasonal and within-event declines in concentrations. Similar patterns have been observed in the few other Amazon locations (Table 2) and other forest locations where seasonal throughfall solute concentrations have been measured, suggesting that this pattern is widespread. Forti and Moreira-Nordemann (1991) reported a similar result (with the exception of NH_4^+) from the central Amazon. Filoso et al. (1999) reported a similar pattern from another central Amazon location, but without information on whether these difference were statistically significant. For a secondary forest and fallow vegetation in the northeastern Amazon Basin, Hölscher et al. (1998) also found that throughfall solute concentration increased toward the end of the dry season. Outside Amazonia, seasonal dynamics of forest throughfall solute concentrations have been reported for other

tropical regions, including central Africa (Chuyong et al. 2004; Laclau et al. 2003) and Australia (Edwards 1982), as well as from temperate regions of Europe (Beier et al. 1993; Herrmann et al. 2005; Kindlmann and Stadler 2004; Moffat et al. 2002) and North America (Henderson et al. 1977; Lichter et al. 2000).

We are aware of no other example of changes in throughfall solute concentrations within individual rainfall events in tropical forest that can be compared with our results. In temperate regions, throughfall solute concentrations at the initiation of events are often high, but constant concentrations late in natural events are not typically reported (Crockford et al. 1996; Hambuckers and Remacle 1993; Hansen et al. 1994). We assume that constant concentration levels are reached after the complete removal of dry deposition, which requires a critical amount of water (Neary and Gizyn 1994). Therefore tropical rainfall with greater total amount of water and greater intensity might explain the differing patterns. Rapid flushing of leaf surfaces has been shown to transfer dry deposition on leaves to throughfall (Lindberg and Lovett 1985; Rodrigo and Ávila 2002).

Dry deposition and canopy exchange are largely responsible for controlling solute concentrations in throughfall (Parker 1983). Because dry deposition is strongly influenced by the aerosol content of the atmosphere, the temporal dynamics of many solutes are similar to those in rainfall. Canopy exchange differs, however, among solutes and is strongly influenced by nutrient stoichiometry (Veneklass 1990). We measured an annual net enrichment of throughfall over rainfall for all solutes, but we observed canopy uptake of Ca^{2+}, Na^{+}, NO_3^- and NH_4^+ in some events. Reports showing forest canopy uptake of Ca^{2+} and Na^{+} are rare (Jordan et al. 1980; Langusch et al. 2003), but reports of canopy uptake of NO_3^- and NH_4^+ are far more common and these solutes can be either leached from or retained by the canopy (e.g. Draaijers and Erisman 1995; Filoso et al. 1999; Forti and Moreira-Nordermann 1991; Franken et al. 1985; Laclau et al. 2003; Liu et al. 2002; Lovett and Lindberg 1984; Maraues and Ranger 1997; Parker 1983; Rodrigo et al. 2003; Zeng et al. 2005).

By analyzing rainfall events sequentially, we also found negative net throughfall, indicating canopy uptake furthermore for DOC and K^{+} for some periods during events (Fig. 7). These effects might be obscured by periods of leaching during the same events, if sampling is only performed on event basis. While the TDWS is more influenced by dry deposition indicated by positive correlations of net throughfall and rainfall concentrations, leaching (positive TF_{net}) was dominant in the WS and occurred for those event periods, when rainfall concentration is low. Canopy uptake of solutes was favored when solute concentrations in rainfall were high during both seasons. The dependence of leaching and canopy uptake on rainfall concentrations indicated canopy exchange of solutes by diffusion.

The influence of dry deposition in the TDWS and the dominance of leaching during the WS were further supported by good correlations of most of the solutes during the TDWS in bulk throughfall compared to the WS. Leaching, which is controlled by nutrient mobility within plants (Hambuckers and Remacle 1993), differed between solutes. In our study, better WS correlation for Mg^{2+} than for Ca^{2+} with Cl^- and K^+ in throughfall might be explained by faster uptake by roots and transportation within plants for Mg^{2+} than for Ca^{2+} (Kozlowski and Pallardy 1997).

A seasonal decline in the importance of dry deposition wash off and an increase in the importance of canopy leaching from TDWS to WS is also supported by our throughfall concentration modeling results. For throughfall concentrations on an event basis, the antecedent dry period (ADP) was an important predictor in the TDWS, while the relevance of the reciprocal rainfall intensity (I^{-1}) was greater in the WS. Usually the ADP is related to aerosol mass and hence dry deposition (Filoso et al. 1999; Lovett and Lindberg 1984). Lower nutrient availability and higher rainfall amount and frequency are assumed to be responsible for the low significance of the ADP as predictor during the WS. ADP and rainfall size have been found to influence throughfall solute concentrations in temperate forests (Aboal et al. 2002; Crockford et al. 1996). Our study suggests that, in particular during the WS, rainfall intensity is also an important control of throughfall solute concentration in tropical forests.

Regional comparisons

We compared our measured solute concentrations in rainfall and throughfall with previous measurements

of solute concentrations from Amazon locations that differ in the length of the dry season. For central Amazonia, where regional deforestation and biomass fire are less significant, the dry and the wet season Ca^{2+} and K^+ concentrations in rainfall tended to be lower than at our site, but SO_4^{2-} and NO_3^- concentrations in rainfall were higher or similar (Table 1). This result was largely driven by the very low concentrations of SO_4^{2-} and NO_3^- that we observed in Rondônia during the WS.

In contrast, the central and NW Amazon had generally higher Na^+ concentrations (Franken and Leopoldo 1984; Tobon et al. 2004). Our Rondônia site might not have shown higher concentrations of Cl^-, Na^+ and SO_4^{2-} concentrations in contrast to all other solutes because of the high concentrations of these solutes in marine air masses (Mello 2001; Stallard and Edmond 1981) affecting more central or northwestern Amazonian sites.

Although not statistically significant, dry season VWM_S DOC concentrations were higher at our site than in the central Amazon (Table 1), consistent with the high concentration of DOC in aerosols resulting from biomass burning (Andreae et al. 1988a).

The VWM_S of pH in rainfall was higher in Rondônia than at any other site (Table 1). Ranging from 5.2 to 6.8 with a mean of 6.3 (compared to the equilibrium pH of atmospheric CO_2 of 5.6), acid rain is rather negligible at our study site, while rainfall of central Amazonia (range of means: 4.3–5.2) was typically acid (Table 1). An increase in pH from the central Amazon towards western Amazonia was also observed by Stallard and Edmond (1981). In remote areas of central Amazonia, organic acids (mainly formic and acetic acid) were largely responsible for the acidity of rain (Andreae et al. 1988b; Andreae et al. 1990; Williams et al. 1997). Central Amazonian air masses are transported to Rondônia by prevailing northeasterly winds. A decrease of acidity may result from neutralization of organic acids by alkaline mineral aerosols as has been reported for other regions (Galy-Lacaux and Modi 1998; Hoffmann et al. 1997). It is tempting to try to explain higher pH and cation concentrations in rainfall in Rondônia as a function of aerosol input from the Andes or from central Brazil, but low concentrations of Ca^{2+} in rainfall in these source areas (Lilienfein and Wilcke 2004; Wilcke et al. 2001) do not support this assumption.

Several more local factors in Rondônia could be important influences on rainfall solute concentrations. Soils in the southeastern part of Rondônia overlaying Precambrian basement rock, made up of gneisses and granites of the morphostructural unit "Southern Amazon Dissected Highlands," are less deep and have higher pH and cation concentrations than those on tertiary sediments in the north (Cochrane 1998; Holmes et al. 2000). Furthermore, carbonate shale outcrops occur in the southeastern part of the state (CPRM 2001), suggesting that a natural local soil dust effect might contribute to these regional differences. In addition, Rondônia (0.39 head ha^{-1}) and adjoining Mato Grosso (0.28 head ha^{-1}) have the highest cattle densities in the Amazon (IBGE 2004). The mix of mineral supplement salt for cattle is composed mainly of calcium phosphate, and might explain the most pronounced Ca^{2+} concentrations for our site compared to sites in central Amazonia. Assuming an annual supply of 14 kg cattle salt per head (Knorr et al. 2005 and Harald Schmitz, personal communication) and a total of 9.4 million head for Rondônia in the year 2003, results in a annual cattle salt consumption of 131×10^6 kg ha^{-1} for the whole state. Conclusive links between these regional factors and solute concentrations have not been demonstrated, but Biggs et al. (2002) implicated regional application of cattle salts in higher observed Ca^{2+} concentrations in streamwater in Rondônia.

Few data on throughfall concentration sampled on event basis at other Amazonian sites were available for comparison with our study. Our throughfall concentrations fell within the range of those measured for central and northwestern Amazonia except for K^+, which is consistently higher at our site (Table 2). K^+ was the ion with the highest annual VWM_S concentration for our site and the central Amazon (Filoso et al. 1999). The throughfall VWM_S concentrations for Ca^{2+} in our study were generally similar to those at other Amazon sites (Table 2), despite higher Ca^{2+} rainfall concentration in Rondônia. Throughfall DOC VWM concentrations over all events were higher for our study compared with other Amazonian sites, while WS DOC VWM_S did not differ.

Filoso et al. (1999) was the only other study that reported annual fluxes of cations and anions based on event sampling. They found much lower rainfall fluxes for Cl^-, NH_4^+, K^+, and Ca^{2+}, slightly lower

rainfall fluxes for Na^+ and Mg^{2+} and similar rainfall fluxes for SO_4^{2-} and NO^{3-}. Filoso et al. (1999) found lower throughfall fluxes of all solutes (Table 4). Filoso et al. (1999) did, however, report higher throughfall concentrations for some solute that is likely explained by almost 10% higher annual rainfall at the Rondonia site. In addition, they used annual VWM concentrations to calculate the fluxes, while our study distinguished between seasons.

Differences between our site and other Amazonian sites in duration or intensity of the dry season, annual rainfall amount, total deforested area and nutrient availability in soils may somewhat mask biomass burning and regional agricultural effects when comparing rainfall and throughfall chemistry among locations. Seasonal and within-event dynamics, however, provided evidence for large differences in rainfall and throughfall patterns and concentrations that strongly suggest strong effects of regional land use.

Conclusions

The concentrations of many solutes in rainfall and throughfall measured in Rondônia where highly dynamic both seasonally and within individual rain events. Concentrations declined as the wet season advanced and as more rain fell in individual events. These patterns appeared to be amplified by biomass burning, which was widespread in Rondônia at the end of the dry season and in the transition to the wet season. In addition to biomass burning, soil dust, agricultural additions as fertilizer and cattle salt could possibly impact aerosol loads and composition and hence rainfall and throughfall solute concentrations in this highly agricultural region. Patterns of solute concentrations in rainfall and throughfall and relationships to rainfall amount, intensity, duration and length of antecedent dry period, and differences in behaviour of individual solutes, indicated that throughfall concentrations in the TDWS were dominated by dry deposition, while canopy leaching was more important in generating solutes in throughfall during the WS. Concentrations of Ca^{2+}, K^+ and DOC in rainfall and concentrations of K^+ and DOC in throughfall in Rondônia were higher than in other studies in the central Amazon where biomass burning, deforestation and agricultural activities are less extensive. Solute fluxes in Rondônia were particularly elevated for those solutes originating from pyrogenic emissions. These regional effects and strongly seasonal effects associated with deforestation in Rondônia now appear to be altering the patterns in which solutes are delivered to Rondônia's remaining moist tropical forests.

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