Near-surface hydrology and hydrochemistry under contrasting land-cover

Dissertation

for the degree of
„doctor rerum naturalium“ (Dr. rer. nat.)
from the Faculty of Mathematics and Natural Sciences at the
University of Potsdam, Germany

submitted by
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Potsdam, 17 March 2008
Institute of Geoecology

Rain Forest Land

by Ivar Kalleberg

The cattle may graze Where once was jungle maze
Where panthers and monkeys did roam
We will see them no more On new pastures galore
Have beef cattle and gauchos their home
Oh Rain Forest Land You have lost to the progress of Man
Your wildlife and woods Are low profit goods
But grasslands bring cash in like sand

The trees have been burned Nature's way overturned
Precious topsoil eroded away Some discouraging word
Can often be heard 'Cause black smoke covers sky all the day
Oh new desert land Global warming will soon be at hand
We better take heed Exploitation and greed
Soon may cause the extinction of Man

The climate will change Way back home on the range
Many floods will cause problems galore
The once fertile land will be barren sand
Heavy rainstorms will fall more and more
Oh Rain Forest Son All your birthrights are virtually gone
Since you moved to the town do you often feel down?
When you see that your forests are gone?

There still might be hope If we manage to cope
And replenish those vanishing trees
If our forests may live We can pray God will give
All Mankind on His earth a new lease
Oh Rainforest Land Your herbs might give new cures to Man
Before its too late We must reinstate
All that bounty we had from God's hand

Acknowledgements

I am full of appreciation for the afforded chance to experience the beauty of the tropical rain forest around Rancho Grande. It was the most exciting realization to become increasingly aware of the discerning capabilities of one's aural sense within this particular environment.

This study is one of the outcomes of a wonderful collaborative American-Brazilian-German research project and would have never been realized without the help and support of a numerous persons. In particular, I would like to thank

Prof. Helmut Elsenbeer and **Dr. Christopher Neill** for their unfailing support throughout my candidature,

Dr. Alex V. Krusche and **Dr. Jorge M. Moraes** for a most pleasant co-operation and their much appreciated help with organizational issues in Brazil,

Lisa Werther, **Sergio Neto Gouveia**, **Tobias Vetter**, **Shelby Hayhoe** and **Sonia Remington** for assisting in the field be it night or day,

Dr. Theresa Blume, Dr. Beate Zimmermann and **Dr. Joaquin Chaves** for their keen interest in my study and evolving most constructive scientific discussions,

Dr. Boris Schröder for stimulating discussions on statistics,

Hauke Sattler for technical support whenever in need,

Family Schmitz for keeping me in best spirits by preparing my favorite food and for giving me the feeling that they truly appreciated my presence at Rancho Grande.

And last but not least, **my own family**.

Summary

Human transformation of the Earth's land surface has far-reaching and important consequences for the functioning of hydrological and hydrochemical processes in catchment areas. Land-use change is now a major issue, particularly in the tropics where deforestation has increased dramatically during recent decades. The Amazon Basin of Brazil is currently a global deforestation hotspot. Areas within the "arc of deforestation", which extends from its southern to its eastern edge, are particularly affected. A prerequisite to the assessment of the environmental consequences of further deforestation is a detailed description of the hydrological and hydrochemical processes and their alterations. An in-depth understanding of these processes is furthermore the basis for developing sustainable socio-environmental certification systems with the aim of minimizing environmental damage from agriculture. Since an end of deforestation is not in view, but at the same time demand for certified agricultural products increases, it is becoming evermore important to understand the effect of land-use change on hydrological and hydrochemical processes in all detail.

The impact of land-use change on hydrology was inferred from physical soil characteristics in some Amazonian studies, but direct evidences remains scarce. A change to more rapid flow paths as the result of land-use change can not only provoke changes in the catchment's water yield, but also induce changes on solute exports and thereby provoke an imbalance of the catchment's nutrient budget and foster land degradation. The general objectives of this study were to track the impact of changing land-use from undisturbed forest to pasture on the principal hydrological pathways along which rainfall reaches streams, and to quantify the relationship between input and output water and nutrient fluxes. Hydrochemical differences within the catchments are further linked to differences in the relative importance of specific flowpaths.

The study was conducted in the southwestern part of the Brazilian Amazon basin. A similar hydrological and hydrochemical sampling and monitoring network was set up in adjacent forest and pasture catchments. The forest vegetation is terra firme undisturbed open tropical rainforest (Floresta Ombrófila Aberta) with a large

number of palm trees. We measured rainfall, throughfall, stemflow, and stormflow water fluxes and monitored the occurrence of overland flow and perched water table development. We also sampled rainfall, throughfall, stormflow, soil solution, overland flow and groundwater for chemical analysis.

It was found that the hydrology was altered by land-use change in many ways: Rainfall was strongly redistributed in the forest canopy, resulting in very high local throughfall water fluxes, while other areas were shaded from rainfall. This intense rainfall redistribution was attributed to the abundance of palms, which were very effective in funneling the water. Land-use change from forest to pasture is known to result in soil compaction and a pronounced reduction of the macroporosity. As a consequence, in our study a perched water table above an impeding layer could develop more frequently and persist for longer periods in the pasture than under forest canopy. In addition and as a result, the volume and frequency of overland flow that developed due to rain falling on saturated soil increased from forest to pasture. Return flow was observed in both catchments, but the underlying mechanisms differed. While soil water in the forest returned quickly to the surface through macropores, upward soil water flow from the perched water table resulted in slow return flow in the pasture.

The chemistry of water fluxes also was modified as a result of land-use changes. The burning of biomass affected rainfall and throughfall chemistry during the transition from dry to wet season. Solute exports were particularly linked to the increased volume of overland flow that resulted from the land-use change, and also to the effect of land management practices on overland flow chemistry. While the forest was characterized by tight nutrient cycles with minimal nutrient losses, land-use conversion to pasture resulted in significant losses of total potassium, magnesium and chloride.

This study highlights the close relationship of land-use change to hydrology and hydrochemistry. We must examine changes to hydrological processes and their effects on solute fluxes in order to comprehend the complete impact of deforestation and pasture installation on the ecosystem. While hydrology is the basis for understanding the impact, the hydrochemistry quantifies the significance of the effects on the ecosystem’s nutrient balance.

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1.
Introduction

1.1. Background

Land-use change is currently a major issue, particularly in the tropics where deforestation has increased dramatically during recent decades. The principal reason for deforestation in the Brazilian Amazon is cattle ranching and the annual variations in deforestation rates might be largely explained by economic motivation (Fearnside, 2006). Tax incentives were the most significant drivers for deforestation for almost 20 years, beginning in the early 1970s, (Mahar, 1979). During the 1990s the variations in deforestation rates can be explained as reactions to the state of the national economy (Fearnside, 2006). A second primary driver of deforestation resulted from growth in soy cultivation in the Amazon since the late 1990s (Fearnside, 2001). Currently the expansion of Amazonian beef and soybean industries is mainly driven by international market demand, in particular that of the EU and China (Nepstad et al., 2006). Nepstad et al. (2006) brought attention to the fact that the threat of the beef and soybean industries on the Amazonian environment also increases the potential for large-scale conservation through socioenvironmental certification systems. The combination of increasing deforestation and development of certification systems demands an in-depth understanding of the Amazonian ecosystem. In order to assess the environmental consequences of further deforestation or for the development of socioenvironmental certification systems with the aim of minimizing environmental damage a detailed understanding of the consequences of land-use change and management on the hydrological and biogeochemical functions of these ecosystems is becoming increasingly important. This need was partly expressed by McClain (2001): “Both sustainable development and preservation of the region’s unique ecosystems depend on our understanding of fundamental processes such as the balance of nutrients in land and aquatic ecosystems […]”. Because nutrient fluxes are closely linked to the hydrology of a catchment, I would like to add to McClain’s words that the understanding of fundamental hydrological processes is equally important.

1.2. The Amazonian hydrological cycle and land-use effects

The primary origin of water vapor in the Amazon is the Atlantic Ocean (Biswas, 1999). Precipitation recycling that is the contribution of evaporation of one region to precipitation of the same region was estimated to amount to at least 25% for the Amazon basin (Costa and Foley, 1999; Eltahir and Bras, 1994). In contrast to pasture land, incident rainfall is divided into three flowpaths before reaching the ground in the forest:

(1) A generally small portion of water that flows down the tree trunks as stemflow,

(2) A small fraction of direct throughfall that does not contact with the leaves or stems before reaching the forest floor; and

(3) The remaining water that makes contact with the canopy before reaching the forest floor without evaporating.

Generally the term throughfall combines the latter two flowpaths as they can not be measured separately.

If the intensity of rainfall or throughfall/stemflow exceeds the infiltration capacity of the soil, then 'Hortonian overland flow' is generated. If rainfall or throughfall/stemflow infiltrates the soil, it might be available for plant uptake and later be returned to the atmosphere by transpiration. The remaining water flows trough the soil, but the prevailing flowpaths are site specific (Elsenbeer, 2001). The activation of flowpaths and hence the speed of water flowing to the stream network depends on topography, rainfall (or throughfall/stemflow) intensity and volume and soil characteristics as for example the initial soil moisture and hydrologic conductivity, or the existence of preferential flow lines within the soil. Although lateral subsurface stormflow might occur under unsaturated soil conditions, it is faster under saturated conditions. Rainfall (or throughfall/stemflow) that hits saturated soil generates saturation overland flow while the small portion of rainfall that falls directly on the stream surface is called direct runoff. Overland flow is the fastest type of flowpath to reach streams and drain catchments, followed by saturated subsurface stormflow. The remaining soil water drains slowly, either laterally as throughflow towards the stream or under gravity towards the groundwater body. Groundwater can sustain the baseflow of streams during periods of dry weather.

Land-use change from forest to pasture is known to provoke soil compaction (e.g. Martínez and Zinck, 2004) and hence reduce the hydraulic conductivity of soils.

Previous studies that compared the hydrologic conductivity of soils with rainfall characteristics have concluded that land-use change from forest to pasture alters the hydrologic flowpaths, producing an increase in fast flow (Ziegler et al., 2004; Zimmermann et al., 2006). Hortonian overland flow is rare in undisturbed tropical forest due to the high conductivity of the topsoil, and where it is present it persists only briefly (Johnson et al., 2006), with the exception of some sites that have particularly clayey soils (Bell, 1973). Overland flow is of greater importance on pasture land due to soil compaction (Moraes et al., 2006). Although hydrologic conductivity studies have concluded that an increase of saturation overland flow is due to land-use change, direct evidence is scarce (Moraes et al., 2006). Faster flowpaths after land-use change can, however, not only provoke changes in the catchment water yield but might also induce changes of solute exports (Bruijnzeel, 2004; Neill et al., 2006) and hence cause imbalance to the catchment's solute budget and lead to land degradation.

1.3. Solute fluxes in Amazonia and land-use effects

Solute inputs and outputs need to be quantified in order to calculate solute budgets. Nutrient inputs can be subdivided into the wet and dry deposition of the atmosphere. While wet deposition (rainfall) is the same for all land-cover types, dry deposition can be elevated for forested land due to the greater surface area compared to open land (Lindberg and Lovett, 1985). Therefore rainfall chemistry can be modified during the passage through the canopy as a result of dry deposition removal and solution and, hence the solute input to the forest floor is different to that of adjacent pastures. Other effects of the canopy, such as leaching, might modify rainfall chemistry, but this is part of the internal nutrient cycle and does not change solute inputs. The presence or absence of the forest canopy is one local reason for changes in solute inputs due to land-use change. Particulate emission due to burning of forest or pastures is very high in some Amazonian regions (Artaxo et al., 1988). Particulate emission and dust generation from roads and agricultural areas might modify solute inputs by wet and dry deposition over extended areas.

Solutes are exported from catchments through stream flow and additionally through groundwater in the case of leaky catchments. The chemical composition of exported water depends mainly on the contact material and contact time. For catchments under contrasting land-uses but with the same lithology and soil, the relatively small differences between the contact material 'soil' arise due to interactions of the soil and the soil water with vegetation and microorganisms. The 'contact time' factor depends on the flowpaths along which the water reaches the stream channel (see section 1.2). Therefore the knowledge of the underlying hydrological processes within a catchments appears to be essential for sound understanding of the differences of solute dynamics under contrasting land-uses.

Although tropical forests on strongly weathered soils are generally characterized as having relatively conservative nutrient cycles, only a few studies of catchment-scale solute budgets for forest sites in Amazonia exist (Brinkmann, 1985; Franken and Leopoldo, 1984; Jordan, 1982; Lesack and Melack, 1996) and even fewer studies have examined pastures (Biggs et al., 2006). I am unaware of any nutrient balance study that compared tropical undisturbed forest with pasture and no study simultaneously researched underlying hydrologic processes and established solute budgets in detail with the aim of assessing the respective changes following the transformation of undisturbed forest to pasture.

I propose that modifications in the hydrologic processes due to land-use change directly affect solute exports and hence solute budgets. Furthermore land degradation could be caused by resultant negative solute budgets.

1.4. General objective of this study

The general objective of this study was twofold; firstly, to describe and quantify the main hydrological processes (interception, throughfall, stemflow and runoff generation) in an undisturbed tropical forest catchment and a pasture catchment based on a paired catchment approach. This was carried out with the aim of identifying the relative importance of the activated flowpaths under the contrasting land-uses. The second objective was to describe and quantify the hydrochemical differences between undisturbed forest site and pasture. Because the export of solutes from catchments depends on the time that water is in contact with the soil, and contact time is dependant on which flowpath is activated, I aimed to highlight the links between the hydrochemical variations of the catchments with variations in the relative importance of flowpaths.

1.5. Thesis outline

This thesis consists of a series of four closely related papers. Because field observations suggested that the canopy structure had a major influence on rainfall redistribution, which might effect other hydrological processes in the forest catchment, this process deserves its own chapter. Chapter 2 includes the description of observed temporal trends of rainfall distribution, the quantification of throughfall during the study period and the influence of palms on throughfall variations over time illustrated by interception modeling. Chapter 3 addresses seasonal differences of rainfall and throughfall chemistry. This approach provides evidence of the changes to rainfall chemistry as rainfall washes the canopy.. Dry deposition onto the canopy increases solute inputs and land-use change related activities such as biomass burning and dust generation increasing aerosol concentrations, as highlighted in section 1.3. Therefore this chapter describes the deforestation effect by rainfall on solute fluxes, which is relevant for a large area of Amazonia and the effect of the forest canopy in collecting dry deposition. Water and solute fluxes were quantified and compared for both catchments in chapter 4. Solute budgets were compared between catchments and a regional comparison of solute budgets was performed using previously published results. Chapter 5 addresses the variations in runoff generation between the catchments., This chapter also compared physical and chemical based methods for identifying processes of stormflow generation, regarding their suitability for flowpath identification and conclusions about the geochemical relevance of the different flowpaths. Finally, chapter 6 summarizes the results and discusses their implications for future research work.

2.

Throughfall and temporal trends of rainfall redistribution in an open tropical rainforest, south-western Amazonia (Rondônia, Brazil)

Abstract

Throughfall volumes and incident rainfall were measured between 23 August and 2 December 2004 as well as from 6 January to 15 April 2005 for individual rain events of differing intensities and magnitudes in an open tropical rainforest in Rondônia, Brazil. Temporal patterns of throughfall spatial variability were examined. Estimated interception was compared to modeled interception obtained by applying the revised Gash model in order to identify sources of throughfall variability in open tropical rainforests. Gross precipitation of 97 events amounted to 1309 mm, 89±5.6% (S.E.) of which reached the forest floor as throughfall. The redistribution of water within the canopy was highly variable in time, which we attribute to the high density of babassu palms (*Orbignya phalerata*), their seasonal leaf growth, and their conducive morphology. We identified a 10-min rainfall intensity threshold of 30 mm h^{-1} above which interception was highly variable. This variability is amplified by funneling and shading effects of palms. This interaction between a rainfall variable and vegetation characteristics is relevant for understanding the hydrology of all tropical rainforests with a high palm density.

With Elsenbeer, H. and Moraes, J.M published in *Hydrology and Earth System Sciences,* 10, 383-393, 2006

2.1. Introduction

Interception of rainwater accounts for that amount of rainfall intercepted by the canopy, which is evaporated during events or after rainfall ceased. The remaining rainfall reaches the forest floor either as throughfall or stemflow. As intercepted water does no longer participate in near-surface hydrological processes (Savenije, 2004), precise knowledge of its magnitude is essential for our understanding and modeling of these processes. Interception studies were conducted in different climatic regions and forest types, such as temperate broad-leaf (Liu et al., 2003; Xiao et al., 2000) and conifer forests (Huber and Iroume, 2001; Link et al., 2004), lowland tropical rainforests (Dykes, 1997; Schellekens et al., 1999), and tropical montane forests (Holder, 2004; Munishi and Shear, 2005). Interception is estimated by applying a variety of empirical, physically-based, and analytical models. The physically based Rutter model (Rutter et al., 1971) and the analytical Gash model (Gash, 1979; Gash et al., 1995) are two of the most widely used interception models. Estimates of interception in tropical forests are influenced by a high spatial variability of throughfall (Jackson, 1971; Lloyd and Marques, 1988). This variability seems to be caused by canopy features such as leaf or woody frame properties (Herwitz, 1987). Hall (2003) showed that there is a positive correlation between LAI (leaf area index) and interception, but that interception can vary broadly due to different leaf properties for canopies with the same LAI. Other studies focused on the effect of differing percentage of canopy cover, but found only a weak relationship between throughfall and canopy cover (Loescher et al., 2002; Tobón Marin et al., 2000). Others investigated throughfall amount as a function of distance to tree trunks (Beier et al., 1993; Ford and Deans, 1978; Schroth et al., 1999), but found this distance to be a poor predictor (Keim et al., 2005). Herwitz and Slye (1992) found that neighboring canopy tree crowns can receive different depths of gross rainfall, resulting in a variable pattern of throughfall due to inclined rainfall and shading effects of nearby trees.

Keim et al. (2005) investigated the temporal persistence of spatial patterns of throughfall and found them to be stable for three forest stands with different canopy complexities in the Pacific Northwest, USA. Details of canopy interception, in particular within the tropics, are still not well understood. To our knowledge temporal variability of spatial patterns of throughfall in tropical rainforests has not been studied before. The results of such a study, however, are expected to lead to a better understanding of the interception process within these environments, in particular for event based studies conducted over several months. Our objectives were a) to quantify throughfall in an open tropical rainforest with high palm density, b) to identify any temporal patterns of throughfall spatial variability, and c) to determine the conditions under which this variability complicates the estimation of interception.

2.2. Material and methods

2.2.1. Site and climate

The study site Rancho Grande is located about 50 km south of Ariquemes (10°180' S, 62°520' W, 143 m a.s.l.) in the Brazilian state of Rondônia, which is situated in the southwestern part of the Amazon basin.

The area is part of a morphostructural unit known as “Southern Amazon Dissected Highlands” (Planalto Dissecado Sul da Amazônia, Peixoto de Melo et al., 1978), which is characterized by a very pronounced topography with an altitudinal differential of up to 150 m: remnant ridges of Precambrian basement rock, made up of gneisses and granites of the Xingu (Leal et al., 1978) or Jamari Complex (Isotta et al., 1978), are separated by flat valley floors of varying width. Soil orders associated with this morphostructural unit are Ultisols, Oxisols, and Inceptisols and Entisols (Soil Survey Staff, 1999) on steep slopes and along streams, respectively.

The vegetation at this terra firme study site consists of 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). It is characterized by a discontinuous upper canopy of up to 35 m height with emergent trees up to 45 m tall, permitting the sun light to reach the understory and thereby facilitating a dense undergrowth. Roberts et al. (1996) determined a LAI of 4.6 for an open tropical rainforest at the ecological reserve “Reserva Jaru” about 100 m east of Rancho Grande, compared to a LAI of 6.1 for a dense tropical rainforest measured 60 km north from Manaus. For trees with DBH (diameter at breast height) >5 cm, the tree density is 813 ha^{-1} including 108 palms, and 520 ha^{-1} for DBH>10 cm, including 81 palms. Among the 94 species with DBH>5 cm (89 species with DBH>10 cm) the most abundant are Pama verdadeira (*Brosimum gaudichaudii* Trecul.*, Moraceae*) and Breu rosa (*Protium sp., Burseraceae*). The most common palm species in this region are Paxiuba bariguda (*Iriartea deltoidea*

Ruiz & Pav.), followed by the babassu palm (*Orbignya phalerata* Mart., local name: babaçu) with a density of 36 full-grown and 115 young individuals per hectare.

The climate of Rondônia is tropical wet and dry (Köppen's Aw). The mean annual temperature is about 27°C. Variations in mean monthly temperature maxima and minima are on average 12.4°C, ranging from 10.6°C in March to 15.7°C in August. Mean annual precipitation is 2300 mm with a marked dry period from July through September. On average, 144 days with rainfall are registered per year, 133 of which fall into the rainy season lasting from October to June. On average, 20 rain days per month occur during the peak of the rainy season, from December through March. The seasonal variation in average daily relative humidity levels ranges from 65% in July to 80% in December (averages of the years 1984–2003, Schmitz, personal communication).

2.2.2. Experimental design and data analysis

Throughfall and gross rainfall were measured on event basis between 23 August and 2 December 2004 as well as from 6 January to 15 April 2005, whilst stemflow was measured from 27 January up to 20 March 2005.

<u>Gross rainfall</u>

A tipping bucket rain gauge (Hydrological Services P/L, Liverpool Australia) with a resolution of 0.254 mm and a Campbell logger recorded 5-min rainfall intensity values on a pasture about 400 m from the forest. In order to characterize events, we selected for each event the contiguous 10 and 60 min with the highest rainfall intensities to calculate the maximum 10 min intensities (I_{10}max) and maximum 60 min intensities (I_{60}max) in mm h^{-1}. We did not include events with a duration of less than 10 and 60 min, respectively. In addition, incident rainfall was measured with three trough-type collectors. One was read manually and the other two were connected to one single tipping bucket logged by a Hobo Event Logger (Onset) with a resolution of 0.51 mm. The collectors, installed on support 1 m above ground, were made out of 150 mm diameter PVC pipes, which were connected via flexible tubes to 20 L plastic canisters. The total collecting area per collector was 980 cm^2 (7 cm * 140 cm). To avoid splash losses a orifice with a width (70 mm) smaller than the diameter was cut out of the PVC pipes. The rainfall quantity data of the trough-type collectors was only used to calibrate the trough collector volumes with volumes measured by the automatic weather station (calibration factor: 1.1, R^2=0.99).

In order to qualify for an event, at least 0.5 mm of rainfall must have been recorded in half an hour. Events are separated by at least two hours without rain.

Throughfall

Throughfall quantities per event were measured manually with 20 collectors (10 collectors between 26 August and 1 September 2004) as described above, which were leveled and cleaned of litter after each event. The measured throughfall was corrected by the calibration factor described previously. The collectors were distributed throughout a heavily instrumented catchment with a maximum distance of 170 m between collectors. Their sites were chosen at random, but with a view towards minimizing disturbance instead of a strictly random distribution with random relocation of collectors (Lloyd and Marques, 1988); Helvey and Patric (1965) recommended such a random relocation, but only for interception studies on a weekly or monthly basis but not on an event basis as in our case. Even so, we attempted to cover the small-scale variability in vegetation. Two hours after every event or alternatively the next morning for events which ended after 9:00 pm, we emptied the collectors and quantified the throughfall with graduated cylinders of three different sizes. For events with less or equal to 5 mm, between 5 and 15 mm and events bigger or equal to 15 mm graduated cylinders of 100 ml, 500 ml and 1000 ml were used, respectively. Throughfall values per event were tested for normality using the Shapiro-Wilk-Test (Shapiro and Wilk, 1965). As throughfall was not normally distributed for 24% of the events, the median of all collectors was used to estimate throughfall per event. To determine whether high or low throughfall areas persist between events, Keim et al. (2005) used the standardized throughfall, $\tilde{T}_{i,j}$, for each sample point i:

$$T_{i,j} = \frac{T_{i,j} - \overline{T}_j}{s_{T_j}} \tag{2.1}$$

where $T_{i,j}$ is the throughfall at sampling point i of event j, $\overline{T}_j$ is the mean throughfall for a given event j, and s_{T_j} its standard deviation. We used the same equation, but with the median and its MAD (median of the absolute deviations from the median) instead of the mean and its standard deviation.

Stemflow

Stemflow or the rainfall diverted to trunk, p_t, was collected along the catchment perimeter, which resulted in a maximum distance between sample trees of 300 m. Aluminum collectors with an inner diameter of 3–4 cm were fitted around trunks at breast height (1.3 m above the forest floor) in a downward spiral. Polythene inlays were sealed to the trunks, and flexible tubes diverted the water to canisters standing on the forest floor. Stemflow was measured for 24 randomly selected trees in three different DBH classes (5–10 cm, 10–20 cm and >20 cm) and for one palm class with 8 large aborescent babassu palms. The stemflow, S_j, per class j in mm for individual storms n was determined using the equation applied by Hanchi and Rapp (1997):

$$[S_j]_n = [v_j]_n * F_j * 10^{-4} \tag{2.2}$$

where v_j is the median stemflow in liter per class j and event n and F_j is the number of trees per hectare and class j. The stemflow percentage of incident rainfall was then calculated for each class and each storm. The median stemflow percentages per class were summed up, to obtain median stemflow for our study site. The instrumentation and measurement procedure of stemflow is described in more detail in a parallel work (Werther, 2007). For our study, we used an average value for stemflow of 8.0% of incident rainfall for all events.

2.2.3. The revised Gash model

Model description

In cases of low data availability a simple regression equation is often used to describe interception:

$$I = aP_G + b\,, \tag{2.3}$$

where I is the interception in mm of incident rain, P_G is the gross rainfall and a and b are the regression coefficients. Unlike the regression equation, the original Gash model (Gash, 1979) is based on a simple but realistic approach to describe the interception process, and yet is characterized by a low data requirement. The revised Gash model (Gash et al., 1995) is an adaptation of the original model to account for stands with sparse canopies.

The original and the revised Gash model assume that the two major factors which control the evaporation of intercepted rainfall are 1) the duration of evaporation from the saturated canopy per event plus the associated evaporation rate and 2) the canopy saturation capacity as well as the number of times the saturated canopy is dried out completely after an event.

The amount of rainfall needed to completely saturate the canopy, P'_G, is expressed by Gash et al. (1995) as

$$P_G' = \frac{-\overline{R}S_c}{\overline{E}_c} \ln\left[1 - \frac{\overline{E}_c}{\overline{R}}\right], \qquad (2.4)$$

where R is the mean rainfall rate and $\overline{E}_c$ is the mean evaporation rate from the canopy. The canopy capacity per unit area of cover, $S_c = S/c$, is the amount of water remaining on the saturated canopy after rainfall and throughfall ceased.

To get an estimate for the mean rainfall rate falling onto the saturated canopy, R is calculated for all hours exceeding a certain threshold of hourly rainfall. We adopted a value of 0.5 mm h^{-1} in accordance to Gash (1979), Lloyd et al. (1988) and Schellekens et al. (1999).

Interception is calculated in several steps by dividing the rainfall events into three phases. The first considers the stage before the canopy is saturated, with $P_G < P_G'$, the second covers the part of the rainfall event when the canopy is saturated, and the last stage refers to the evaporation after the rain ceased. This trichotomy leads towards the five equations summarized in Table 2.1. Total interception is calculated as the sum of these different components. According to Gash (1979) and Lloyd et al. (1988), we calculated mean rainfall intensity for all hours with P_G greater 0.5 mm h^{-1}; however, the difference to all hours of rainfall is not great due to the short and intense rainfall events typical for this climate.

Gash (1979) suggested to determine $\overline{E}_c$ by regressing interception on gross rainfall, as the regression coefficient provides $\overline{E}_c / \overline{R}$. Due to the high variability of throughfall, $\overline{E}_c$ could not be determined by this method in our study. Instead we adopted the value of 0.21 mm h^{-1} found by Lloyd et al. (1988) for central Amazonia, which appears to be typical for tropical forests (Hall, 2003).

Table 2.1 The components of the revised interception model according to Gash (1995).

Component of interception	Formulation of components
For m small storms, insufficient to saturate the canopy	$c\sum_{j=1}^{m} P_{G,j}$
Wetting up the canopy, for n storms $> P'_G$ which saturate the canopy	$ncP'_G - ncS_c$
Evaporation from saturation until rainfall ceases	$\frac{c\overline{E}_c}{\overline{R}}\sum_{j=1}^{n}(P_{G,j} - P'_G)$
Evaporation after rainfall ceases	ncS_c
Evaporation from trunks, for q storms $> S_t / p_t$, which saturate the trunks and for $n-q$ storms, which do not	$qS_c + p_t\sum_{j=1}^{n-q} P_{G,j}$

Forest parameters

Canopy interception parameters are usually estimated by gross rainfall and throughfall data collected on an event or weekly basis (Gash and Morton, 1978; Jetten, 1996; Leyton et al., 1967; Rowe, 1983), compensating short-term variability. The canopy capacity is often determined by the method of Leyton et al. (1967), where in a plot of throughfall versus rainfall a line with a slope of one is drawn passing through events with maximum throughfall. The intercept with the gross rainfall axis is interpreted as the value for canopy storage.

This method however, is not suitable for forests with a high spatial variability of throughfall. Instead, we employed a slightly modified version of the method of Lloyd et al. (1988). For each collector, we regressed throughfall on gross precipitation for events with 1.5 ≤ P_G ≤ 15.0 mm. Because of outliers and high-leverage points, we used a robust regression method based on Tukey's beweight (Hoaglin et al., 2000). To ensure the drying out of the canopy, only events separated by dry periods of at least 6 h were considered in these calculations. It is assumed that for the small events used for this approach evaporation can be ignored. Stemflow, however, can't be neglected for this kind of forest (Werther, 2007). In contrast to Lloyd et al. (1988), we defined for each collector a regression of throughfall over the difference of gross rainfall and the stemflow proportion

$$T = a(P_G - p_t * P_G) + b, \quad (2.5)$$

with a as the slope of the regression and b the intercept. The canopy capacity per ground area, S, is determined as the mean intercept of the regression lines with the x-axis. The standard deviation of S was calculated using the mean standard deviation of b for all collectors.

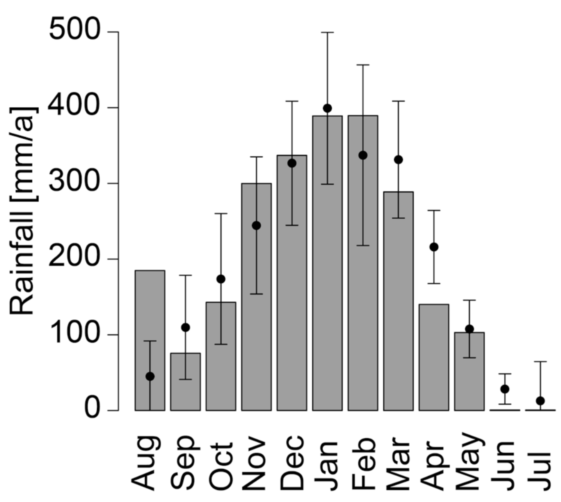
We estimated the free throughfall coefficient, p, with digital photographs taken on January 15, 2005. At each of three equidistant points in the catchment, we laid out two 10-m long transects normal to each other, along which we took black-and-white pictures of the canopy, with a camera mounted on a level, in one meter intervals, resulting in a total of 60 pictures. An image editing program was used to find the center of the images to verify if the center was covered by the canopy or not, which yielded a proportion of canopy coverage, c, and hence the free throughfall coefficient $p = 1 - c$.

2.3. Results and discussion

2.3.1. Gross rainfall

The total incident rainfall at Rancho Grande from August 2004 to July 2005 was 2286 mm a^{-1}, being in line with the mean annual rainfall amount of the previous 20 years of 2300 mm a^{-1}. The month of August, however, was far wetter than the average (Figure 2.1), due to an early start of the rainy season. In addition, April and June were much drier than the respective 20-year average.

Figure 2.1 Monthly rainfall data from August 2004 to July 2005. The solid circles and the vertical lines are the mean and standard error, respectively for the period 1984–2003.



We collected 97 events over the two monitoring periods (Aug–Dec and Jan–Apr), with a total of gross precipitation of 1309 mm. Rainfall intensity for all measured events and all hours with intensities >0.5 mm h^{-1} averaged 6.66 mm h^{-1}. The highest values for I_{10}max and I_{60}max were 100.61 mm h^{-1} and 57.91 mm h^{-1}, respectively. Durations shorter than 1 h were found for 44% of the events.

2.3.2. Throughfall

All throughfall results are summarized in Table 2.2. A sample size n of less than 20 (less than 10 for events between 26 August and 1 September 2004) implies loss of data for individual collectors. The total measured throughfall volume of the whole study period was 1175 mm or 89.8±5.6% (S.E.) of incident rainfall. This percentage is in line with results of other studies. Ubarana (1996) reported 87% of observed total throughfall for Reserva Jarú site within about 100 km of our site. These values fall within the range of throughfall values reported for rainforests in the Amazon basin with 78–91% (Elsenbeer et al., 1994; Filoso et al., 1999; Lloyd and Marques, 1988; Tobón Marin et al., 2000), in Asia of about 80% (Dykes, 1997; Sinun et al., 1992) or Africa with 92–97% (Chuyong et al., 2004).

For 18 events throughfall volumes of more than 100% of P_G were measured and throughfall plus the proportional stemflow volumes of the incident rainfall exceeded rainfall volumes in 25 cases, resulting in negative values for interception. Despite two cases in August negative values did occur more frequently from November onwards. Since negative values for average interception per event can only be expected for some special forest types, e.g. mountain cloud forests (Holder, 2004), there is either an underestimation of rainfall or an overestimation of throughfall quantities for these events. Our own manual rainfall measurements next to the automatic rain gauge, however, preclude the former possibility. Therefore, these negative values are likely to result from an effect induced by not only the spatial variability of throughfall, but also the temporal variability of throughfall in individual collectors as discussed hereafter.

Table 2.2 Summary of events, P_G : observed gross precipitation; $\overline{T}$: median throughfall of n collectors; S : estimated stemflow; I : interception; n : number of collectors.

Event	Date	P_G [mm]	$\overline{T}$ [mm]	$\overline{T}$ in % of P_G	S [mm]	I [mm]	n
1	26/08/2004	12.44	7.07	56.83	0.97	4.40	10
2	26/08/2004	1.77	2.12	119.77	0.14	-0.49	10
3	28/08/2004	19.81	21.23	107.17	1.55	-2.97	9
4	29/08/2004	4.82	3.44	71.37	0.38	1.00	10
5	30/08/2004	1.01	0.07	6.93	0.08	0.86	10
6	01/09/2004	6.09	3.67	60.26	0.48	1.94	10
7	16/09/2004	21.33	14.91	69.90	1.66	4.76	19
8	25/09/2004	27.17	22.76	83.77	2.12	2.29	19
9	28/09/2004	2.28	0.22	9.65	0.18	1.88	20
10	29/09/2004	7.87	2.46	31.26	0.61	4.80	20
11	04/10/2004	2.03	1.41	69.46	0.16	0.46	19
12	07/10/2004	25.65	18.97	73.96	2.00	4.68	20
13	12/10/2004	31.24	27.28	87.32	2.44	1.52	20
14	14/10/2004	3.81	0.94	24.67	0.30	2.57	20
15	15/10/2004	3.81	1.56	40.94	0.30	1.95	20
16	19/10/2004	0.76	0.24	31.58	0.06	0.46	20
17	21/10/2004	33.27	24.48	73.58	2.60	6.19	20
18	24/10/2004	10.41	8.89	85.40	0.81	0.71	20
19	27/10/2004	4.31	2.72	63.11	0.34	1.25	20
20	30/10/2004	19.81	17.30	87.33	1.55	0.96	20
21	31/10/2004	3.04	2.42	79.61	0.24	0.38	20
22	02/11/2004	3.81	2.49	65.35	0.30	1.02	20
23	03/11/2004	0.50	0.08	16.00	0.04	0.38	20
24	04/11/2004	45.46	43.45	95.58	3.55	-1.54	20
25	10/11/2004	30.98	36.07	116.43	2.42	-7.51	20
26	11/11/2004	6.35	4.59	72.28	0.50	1.26	20
27	14/11/2004	63.75	70.46	110.53	4.97	-11.68	19
28	17/11/2004	23.62	29.81	126.21	1.84	-8.03	20
29	18/11/2004	7.87	7.38	93.77	0.61	-0.12	20
30	20/11/2004	30.98	39.61	127.86	2.42	-11.05	20
31	20/11/2004	0.50	0.23	46.00	0.04	0.23	20
32	22/11/2004	10.41	7.41	71.18	0.81	2.19	20
33	24/11/2004	5.32	4.25	79.89	0.41	0.66	20
34	25/11/2004	0.50	0.32	64.00	0.04	0.14	20
35	26/11/2004	0.50	0.55	110.00	0.04	-0.09	20
36	28/11/2004	5.84	4.33	74.14	0.46	1.05	20
37	30/11/2004	1.52	0.61	40.13	0.12	0.79	20
38	11/01/2005	35.30	35.82	101.47	2.75	-3.27	20
39	14/01/2005	17.52	15.90	90.75	1.37	0.25	19
40	14/01/2005	6.85	6.89	100.58	0.53	-0.57	20
41	16/01/2005	0.50	0.19	38.00	0.04	0.27	20
42	18/01/2005	1.01	0.69	68.32	0.08	0.24	20
43	22/01/2005	78.23	75.02	95.90	6.10	-2.89	20
44	24/01/2005	23.11	18.83	81.48	1.80	2.48	20
45	25/01/2005	0.76	0.00	0.00	0.06	0.70	20
46	26/01/2005	1.01	0.29	28.71	0.08	0.64	20
47	27/01/2005	24.88	24.75	99.48	1.94	-1.81	19
48	28/01/2005	6.09	6.37	104.60	0.48	-0.76	20

Table 2.2 continued

Event	Date	P_G [mm]	$\bar{T}$ [mm]	$\bar{T}$ in % of P_G	S [mm]	I [mm]	n
49	29/01/2005	11.43	10.07	88.10	0.89	0.47	20
50	30/01/2005	4.57	4.58	100.22	0.36	-0.37	20
51	30/01/2005	1.01	0.51	50.50	0.08	0.42	20
52	31/01/2005	29.46	20.14	68.36	2.30	7.02	20
53	31/01/2005	42.91	40.92	95.36	3.35	-1.36	20
54	04/02/2005	15.24	4.75	31.17	1.19	9.30	20
55	05/02/2005	8.89	5.44	61.19	0.69	2.76	20
56	06/02/2005	1.27	0.52	40.94	0.10	0.65	20
57	08/02/2005	43.43	38.62	88.92	3.39	1.42	20
58	09/02/2005	14.73	13.77	93.48	1.15	-0.19	20
59	11/02/2005	37.84	24.34	64.32	2.95	10.55	20
60	13/02/2005	2.54	1.93	75.98	0.20	0.41	20
61	15/02/2005	2.03	1.54	75.86	0.16	0.33	20
62	17/02/2005	30.22	27.24	90.14	2.36	0.62	20
63	17/02/2005	4.57	3.66	80.09	0.36	0.55	20
64	18/02/2005	2.28	1.31	57.46	0.18	0.79	20
65	19/02/2005	30.48	24.07	78.97	2.38	4.03	20
66	21/02/2005	0.76	0.66	64.71	0.08	0.28	20
67	21/02/2005	23.36	24.03	102.87	1.82	-2.49	20
68	23/02/2005	33.27	50.50	151.79	2.60	-19.83	19
69	24/02/2005	3.04	0.57	18.75	0.24	2.23	20
70	26/02/2005	1.52	0.82	53.95	0.12	0.58	20
71	27/02/2005	31.75	24.39	76.82	2.48	4.88	20
72	28/02/2005	17.27	18.52	107.24	1.35	-2.60	20
73	01/03/2005	8.12	5.74	70.69	0.63	1.75	20
74	02/03/2005	11.68	13.86	118.66	0.91	-3.09	20
75	04/03/2005	6.09	4.02	66.01	0.48	1.59	20
76	05/03/2005	57.66	61.56	106.76	4.50	-8.40	20
77	07/03/2005	6.09	1.67	27.42	0.48	3.94	20
78	07/03/2005	3.04	1.65	54.28	0.24	1.15	20
79	10/03/2005	6.09	4.43	72.74	0.48	1.18	19
80	11/03/2005	2.79	1.72	61.65	0.22	0.85	20
81	13/03/2005	1.77	1.61	90.96	0.14	0.02	20
82	14/03/2005	21.84	20.37	93.27	1.70	-0.23	20
83	16/03/2005	16.75	14.41	86.03	1.31	1.03	20
84	17/03/2005	10.66	12.65	118.67	0.83	-2.82	20
85	18/03/2005	8.38	6.82	81.38	0.65	0.91	20
86	20/03/2005	2.03	2.71	133.50	0.16	-0.84	20
87	20/03/2005	4.57	3.57	78.12	0.36	0.64	20
88	21/03/2005	1.01	0.72	71.29	0.08	0.21	20
89	23/03/2005	3.04	0.61	20.07	0.24	2.19	20
90	28/03/2005	33.52	30.21	90.13	2.61	0.70	20
91	01/04/2005	1.77	1.22	68.93	0.14	0.41	20
92	02/04/2005	14.47	12.06	83.34	1.13	1.28	20
93	03/04/2005	4.82	3.48	72.20	0.38	0.96	20
94	04/04/2005	2.54	1.31	51.57	0.20	1.03	20
95	05/04/2005	4.57	2.53	55.36	0.36	1.68	19
96	06/04/2005	0.76	0.25	32.89	0.06	0.45	20
97	10/04/2005	4.57	2.73	59.74	0.36	1.48	20
Total:		**1307.90**	**1175.36**		**102.20**	**31.10**	

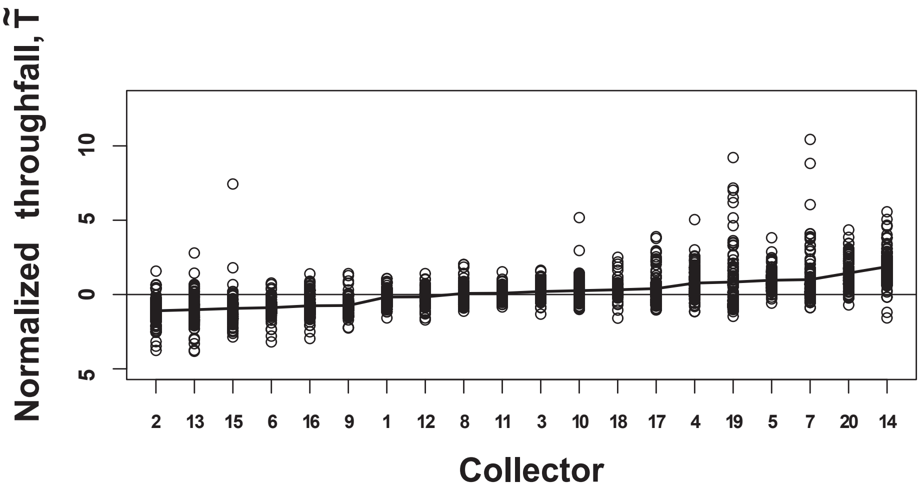
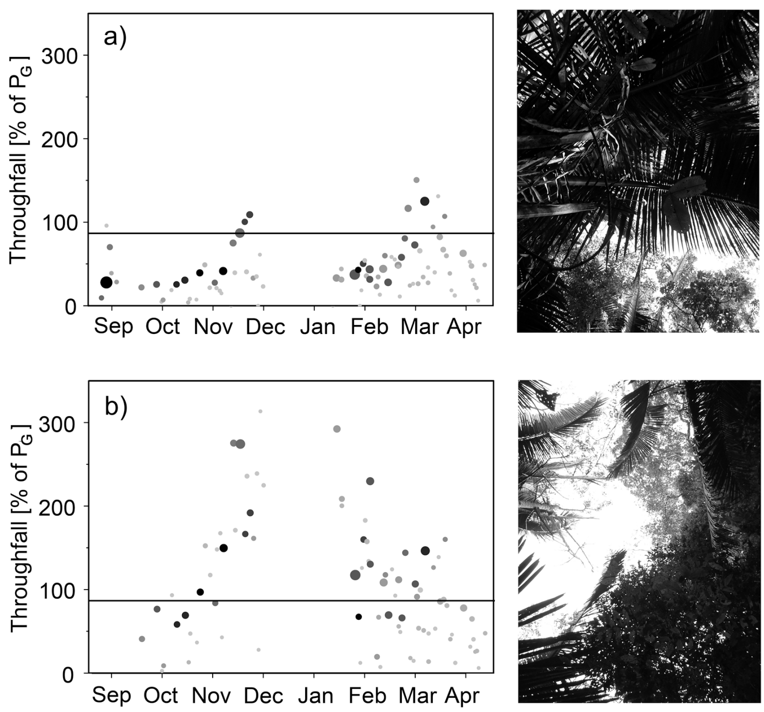


Figure 2.2 Plot of normalized throughfall, $\tilde{T}$, for the whole period. Each circle represents the event throughfall volume at a single collector, normalized to zero median and unit variance for that event. The collectors are plotted on the horizontal axis and ranked by their means, $\tilde{T}$, which are connected by the black curve.

Figure 2.3 Temporal patterns of throughfall percentages of incident rainfall for two collectors standing only 5 m apart from each other. Each event is represented by a dot whose diameter is proportional to rainfall amount. Varying colors from light grey to black illustrate low and high rainfall intensity (I_{10}max) values, respectively. The photographs on the right site show the vegetation above these two collectors.



Throughfall amounts vary highly among collectors due to drip points and caps above the collectors (Loescher et al., 2002). The plot of normalized throughfall, $\tilde{T}$ (Figure 2.2) is ranked by mean $\tilde{T}$ per collector. Since each dot represents one throughfall observation at a single collector, the plot shows the temporal variability of throughfall for each collector. Several collectors registered frequently more (e.g. collectors 14 or 20) or less (e.g. collectors 2 or 13) than the median throughfall per event, as indicated by the deviation from the horizontal axis. None of the collectors deviated, however, persistently in either direction. The temporal variability in some of our collectors was up to three times as high as in others (e.g. collectors 7 and 19). In contrast to our results, Keim et al. (2005) found a much lower temporal variability for coniferous and deciduous stands in the Pacific Northwest, USA, which we attribute to the differences in homogeneity of the two forest types.

Figure 2.2 does not show whether the variability of single collectors is temporally stable. By plotting throughfall per event as a percentage of P_G over time for each collector separately, a temporal trend in some of the collectors becomes evident. Figure 2.3 shows two impressive examples of this temporal variability of throughfall proportions, for two collectors, 2 and 19. For the latter, maximum throughfall percentages of over 300% were registered. In both cases, throughfall rises sharply from early October towards December. During the second study period (Jan–Apr), the same trend can be observed for collector no. 2 and a decreasing trend for collector no. 19. For both periods, collector no. 2 (Figure 2.3a) shows a pattern only for large, high intensity events, while collector no. 19 (Figure 2.3b) shows a pattern regardless of event size or intensity. The photographs in Figure 2.3 were taken upright from the middle of the collectors, showing the canopy structures at the respective site. Eleven out of twenty collectors showed temporal trends (collector no. 2,3, 5, 7, 8, 10, 12, 15, 17, 19 and 20) in throughfall proportions. Among the nine remaining collectors without any temporal trends, five collectors (no. 6, 9, 11, 13 and 18) did not have palm leaves above them. Only one collector (no. 12) without palm tree parts above it showed a slight temporal effect in the beginning of the first study period. Nevertheless, the results show that strong temporal patterns of throughfall volumes were observed beneath palms. Individual palm leaves can act as a natural gutter thanks to the typical, convex form of the petioles, which enables them to collect more water than some trees of the understory. The water is either diverted to the stems or is funneled towards drip points. As babassu palm leaves grow, they do not just increase in size, but move vertically and horizontally within the canopy due to their own weight gain. If the palm leaves move, the associated drip points move as well and collectors at fixed positions may record a temporal pattern of throughfall percentages. As the growing season of babassu palms falls within the rainy season (Anderson, 1983), these temporal patterns start in October and become more obvious with the beginning of November.

These observations suggest a significant redistribution of water within the canopy and a temporal pattern of this redistribution. Because this redistribution is linked to babassu palms, our findings are pertinent to the understanding of the hydrology of palm-dominated tropical rainforests. Such forests are wide-spread from the eastern to southwestern region of the Amazon basin (Kahn and Granville, 1992). In some regions, this invasive plant forms pure populations in regenerating forest gaps or in abandoned pastures (Lorenzi, 2002). Regional forest surveys do not include subterraneanstemmed palms, whose leaves may reach a length of 9 m. Several authors (Jordan, 1978; Lloyd and Marques, 1988; Manfroi et al., 2004) found that small trees growing in the understory of forests often produce more stemflow than emergent trees with a greater DBH. Consequently, the juvenile palm leaves may be at least as important as leaves from adult palms concerning the redistribution and uneven input of rainfall to the forest floor. A high density of juvenile palms in the understory as we found for an open tropical rainforest has been reported from other authors for dense rainforests, with individuals reaching heights of 2-4 m in Colombian Amazonia (Tobón Marin et al., 2000) or 4-5 m in Central Brazilian Amazonia (Lloyd and Marques, 1988). More research with an appropriate sampling design is required to evaluate the importance of small palms in redistributing water and producing locally high inputs of throughfall to the forest floor.

2.3.3. *The revised Gash model*

Table 2.3 summarizes the meteorological and canopy input parameters for the interception modeling. Beside canopy cover, the most sensitive parameter in the original and revised Gash model is the canopy capacity per unit cover area, S_c. The value of 0.74±0.44 mm (S.E.) for S_c for our site does not differs from the 1.03 mm reported for the Reserva Jarú, Rondônia (Ubarana, 1996) or from the 1.15 mm found by Schellekens et al. (1999) for a lowland tropical rainforest in Puerto Rico. But it is lower than the 1.25 mm and 1.16–1.55 mm reported for other sites in Amazonia (Tobón Marin et al., 2000, respectively; Ubarana, 1996).

Table 2.3 Canopy parameters used for interception modeling.

Parameter	Value
S_c (canopy capacity per unit cover area) [mm]	0.72 +/- 0.44
c (canopy cover)	0.97
P_G' (P_G needed to saturate the canopy) [mm]	0.74
$\overline{E}_c$ (mean evaporation rate) [mm h^{-1}]	0.21
$\overline{R}$ (mean rainfall rate) [mm h^{-1}]	6.66
p_t (rainfall diverted to trunk)	0.08
S_t (trunk storage capacity) [mm]	0.22

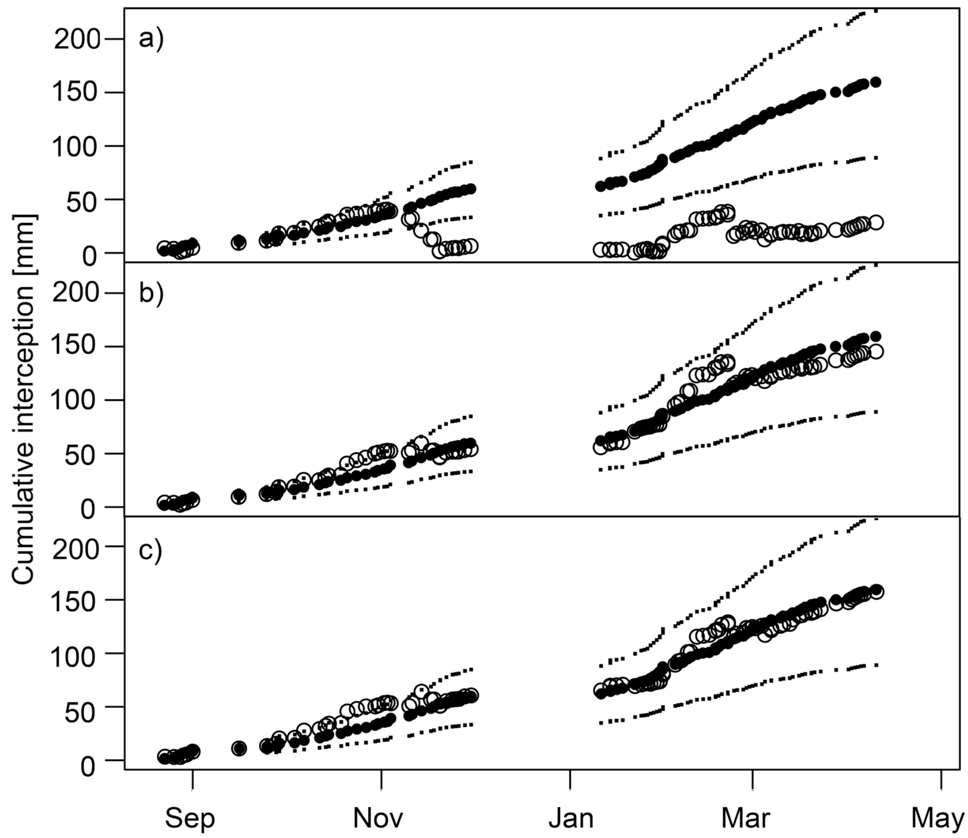


Figure 2.4 Cumulative totals of calculated (open circles) and estimated (solid circles) interception for **(a)** all collectors (n=20), **(b)** collectors not showing temporal patterns of throughfall percentages (n=9) and for **(c)** collectors without obvious influence of the palm species *Orbignya phalerata* (n=6). The dots indicate the uncertainty of the modeled interception resulting from the uncertainty in S_c.

It should be kept in mind that any discrepancy between modeled and actual interception derives from the uncertainty not only of S_C, but also of mean evaporation. Schellekens et al. (1999), using the original Gash model, reported good predictability of cumulated throughfall for a maritime dense tropical rainforest in Puerto Rico as long as the value of $E_w/\overline{R}$ was derived from the regression of interception and event rainfall. Although some of their events exceeded our 10-min rainfall intensity threshold (Schellekens, private communication), the authors did not report high negative interception values for single events. Lloyd et al. (1988) stated that the original Gash model performed adequately for a dense tropical rainforest in Central Amazonia, although they did get negative values for interception, which they attributed to the low number of collectors and high spatial variability. It would be interesting to know if the negative interception values found by Lloyd et al. (1988) were associated to maximum 10-min intensities greater than 30 mm h^{-1}.

We found a free throughfall coefficient, p, of 0.03, which is in line with the range of values (0.03 to 0.08) obtained by photographic techniques (Lloyd et al., 1988; Ubarana, 1996). These values differ clearly from those determined by more subjective methods (Leyton et al., 1967), which range from 0.23 to 0.32 (Elsenbeer et al., 1994; Jackson, 1975; Schellekens et al., 1999). According to the definition of free throughfall as the amount of water falling through the canopy without striking it, the photographic techniques seem to estimate this proportion better than the other methods, that are influenced by that part of throughfall striking the canopy but reaching the forest floor before the canopy is saturated.

Figure 2.4 shows the modeled cumulative interception and that calculated from median throughfall (further referred to as “calculated interception”) for all events. As discussed in the previous section, negative interception was observed due to the occasional overestimation of average throughfall. Beside this overestimation, it is clear from Figure 2.4a that the curves of modeled and calculated interception values show a similar increase up to the beginning of November, when the number of events with negative interception increased and the growing season of the babassu palm started. If the assumption is true that the redistribution of rainfall water within the canopy due to the babassu palms is responsible for the difference of the curves of modeled and calculated values, then these differences should not be observed for throughfall medians from collectors with no obvious palm influence or for all collectors which do not show any temporal trends. Figure 2.4b and c show a better agreement between calculated and modeled values, due to higher calculated interception from mid-November on. The modeled interception does not change within Figure 2.4, as the forest parameters used in the model are mean values for our study site. The better fit for collectors without temporal patterns (Figure 2.4b) is plausible because the excluded collectors tend towards higher throughfall which is most obvious for collectors 7, 17 and 19 (Figure 2.2). In addition, the increase of calculated cumulative interception is greater if fewer collectors with palm influence (14, 4, 0 in Figure 2.4a, b and c, respectively) are used for the calculations. But the crucial point is that the curves in Figure 2.4b and c still show the same trends of calculated interception. Hence, this pattern is unlikely to be induced, but rather amplified, by the presence or absence of drip points associated with palms.

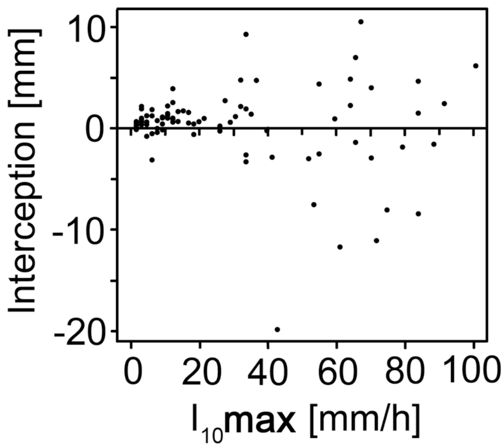


Figure 2.5 The relationship between calculated interception and maximum 10min rainfall intensity (I_{10}max).

In order to identify causes for the trends in calculated interception, we examined the dependency of interception on rainfall intensity. I_{10}max instead of I_{60}max was used for this purpose, to include the maximum possible number of events. The relationship of calculated interception and I_{10}max (Figure 2.5) reveals a rainfall intensity threshold of about 30 mm h^{-1}, beyond which interception values show considerable scatter. When cumulative calculated and modeled interception are plotted separately for events with rainfall intensities below and above this threshold (Figure 2.6a and b, respectively), the calculated cumulative curve for low intensities shows a uniform trend and falls within the limits of uncertainty of the estimated values. In contrast, the calculated interception for high intensity events shows a variable trend and exceeds the uncertainty limits of the modeled values. As the calculated interception is inferred from the throughfall median, we conclude that for high intensity events it is not adequate to estimate the average throughfall from randomly distributed collectors. Instead, the spatial pattern of drip points and hence of throughfall must be known to estimate a weighted throughfall mean. Such a weighted throughfall mean might improve the estimation of interception also at low rainfall intensities.

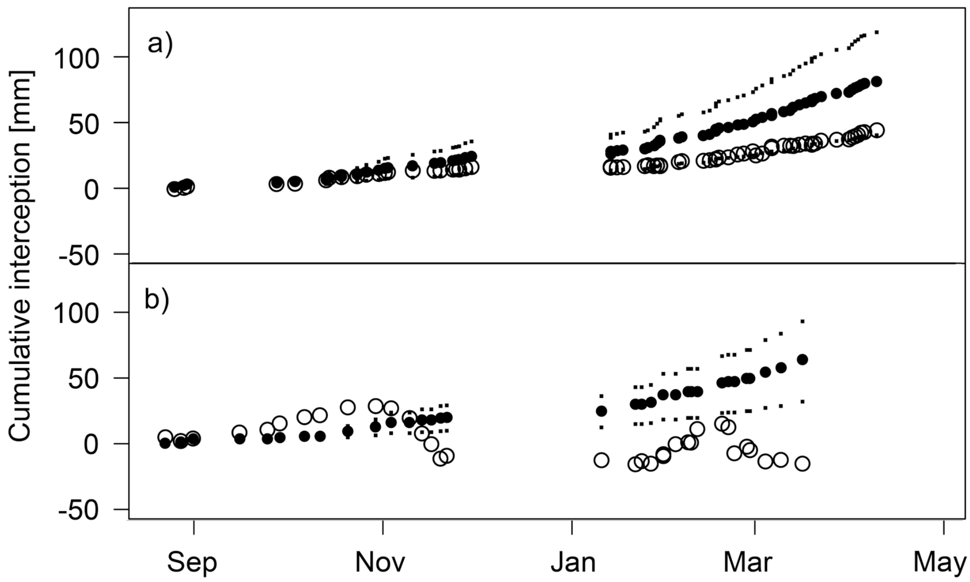


Figure 2.6 Cumulative totals of calculated (open circles) and estimated (solid circles) interception for maximum 10min rainfall intensities **(a)** $I_{10}max \leq 30$ mm h^{-1} and **(b)** $I_{10}max > 30$ mm h^{-1} including all collectors (n=20). The dots indicate the uncertainty of the modeled interception resulting from the uncertainty in S_c .

2.4. Conclusions

Tropical rainforest is the most difficult forest type in which to measure throughfall, stemflow and consequently to determine interception. We calculated a total measured throughfall volume of 89.8±5.6% of incident rainfall.

The results of our experiment suggest furthermore that in open tropical rainforests with high palm densities, the palms play an important role in generating dynamic spatial variability of throughfall. At our study site, the babassu palm (*Orbignya phalerata*) is the most important species responsible for high redistribution of rainfall within the canopy due to their conducive morphology and their high stem density. The spatial pattern of water input to the forest floor shows temporal patterns, which appear to be controlled by babassu palms and their leaf growth. Furthermore, the relationship of 10-min rainfall intensity and interception revealed a threshold of

30 mm h^{-1} above which the calculated interception is highly variable. A comparison of calculated and modeled interception showed that this variability can be greatly amplified by funneling and shading effects of palms (Figure 2.4). We conclude that for high intensity events it is not possible to estimate interception from median throughfall. If the spatial pattern of throughfall is known, a weighted mean throughfall might yield better results.

As the babassu palm is common throughout the Amazon basin (Kahn and Granville, 1992) in upland as well as in seasonal swamp forests, the role of pronounced redistribution of rainfall within the canopy due to these palms should be considered in future research. As the high intensity events responsible for the large variability in throughfall tend to be of high magnitude as well, our results are relevant for the hydrology not only of open tropical rainforest dominated by palms, but perhaps as well for dense tropical rainforest with a high density of juvenile palms in the understory.

3.

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

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 Amazonia, 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.

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3.1. 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 (Davidson 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 Amazonia 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.

3.2. Study area and methods

3.2.1. 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, chapter 2, 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, chapter 2).

3.2.2. 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 liter 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 x 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 (Figure 3.1) 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 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 9:00 pm (Germer et al., 2006, chapter 2). Rainfall and throughfall samples of up to 1 liter 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.

Figure 3.1 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.

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 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.

3.2.3. 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

$$VWM_E = \left(\sum_{n=1}^{i} C_{i,E} V_{i,E} \right) \left(\sum_{n=1}^{i} V_{i,E} \right)^{-1} \qquad (3.1)$$

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 3.1 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).

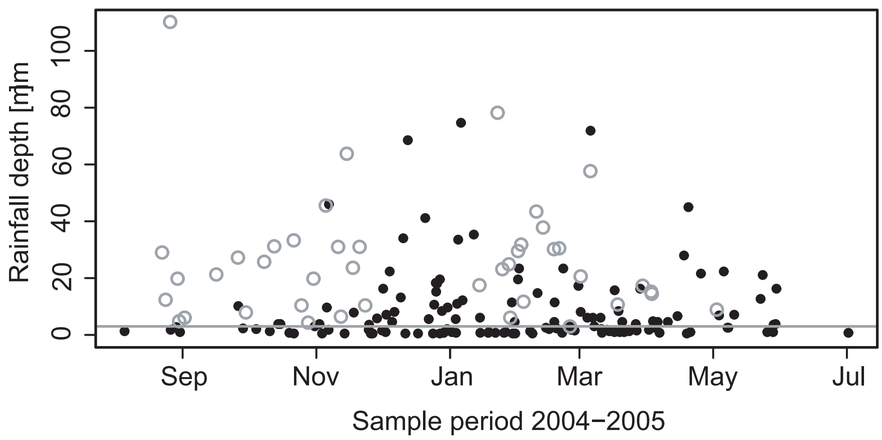


Figure 3.2 Overview of all events from August 2004 to July 2005 grouped into those sampled on event basis (grey open circles) and the remaining not-sampled events (black solid circles). The grey line at 3 mm rainfall depth represents the minimum sample size.

3.3. 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 (Figure 3.2).

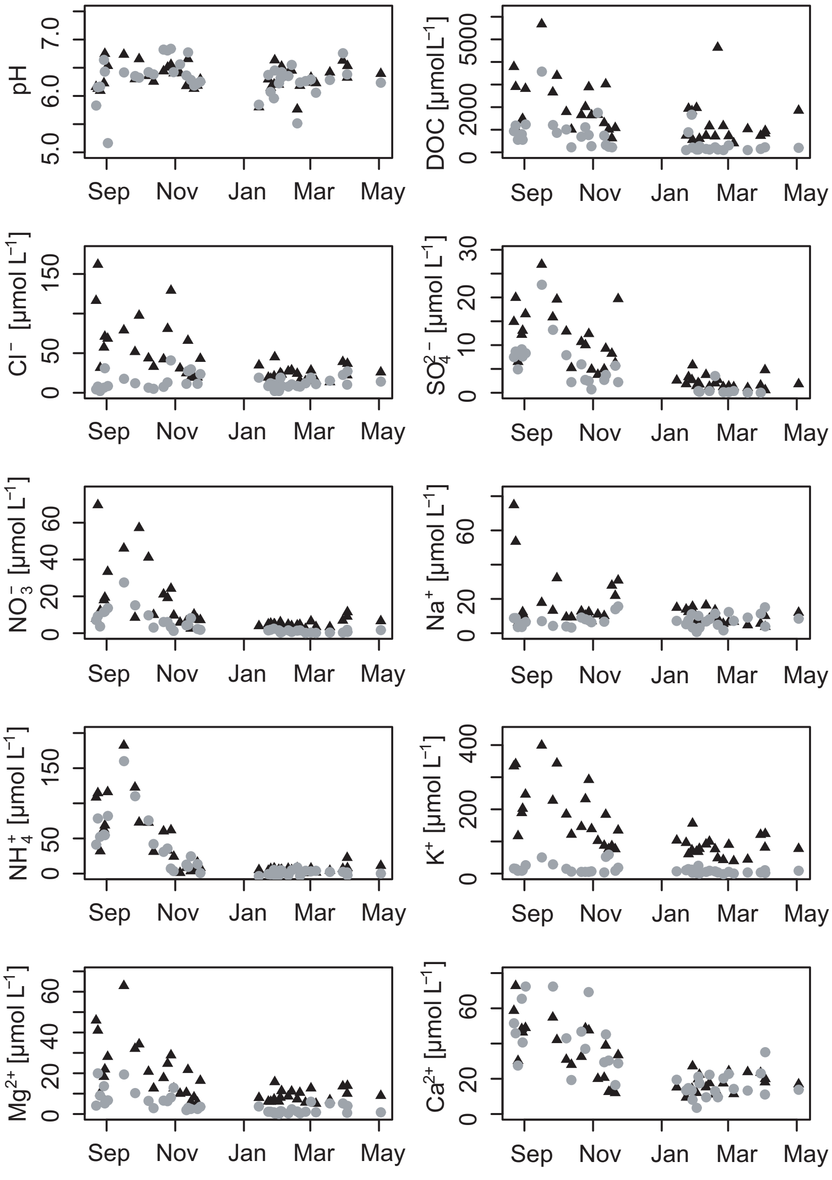


Figure 3.3 Rainfall (grey solid circles) and throughfall VWM_E (black solid triangles) solute concentrations plotted over time for all events sampled on event basis.

3.3.1. *Seasonal patterns of rainfall solute concentrations*

In rainfall, VWM_S solute concentrations followed the pattern $DOC >> Ca^{2+} = NH_4^+ > K^+ = Cl^- > Na^+ = SO_4^{2-} = Mg^{2+} = NO_3^-$, (with $Na^+ > Mg^{2+}$ and NO_3^-) (Table 3.1). In the TDWS, the pattern was $DOC >> NH_4^+ = Ca^{2+} > K^+ = Cl^- = Mg^{2+} = NO_3^- = SO_4^{2-} = Na^+$ (with $K^+ > Mg^{2+}$ and $Cl^- > Na^+$), and in the WS the pattern was DOC >> Ca^{2+} = Cl^{-} = Na^{+} = K^{+} > Mg^{2+} = NH_4^{+} = NO_3^{-} = SO_4^{2-}, with (Ca^{2+} > Na^{+} and K^{+}) (Table 3.1). 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 (Figure 3.3). 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^{+}.

Table 3.1 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. Where available, results are listed separately for the dry season (DS) or the transition from dry to wet season (TDWS) and the wet

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	375.0	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	14.0	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	1081.0	20	11.3	8.0	14.6	18	6.5	4.6	8.4	18	7.1	5.1	9.0	19
previous studies																						
Amazonia (central) [b)]	all events	5.0	---	---	---	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	13.0	---	---	18	18.0	---	---	18
Amazonia (central) [c)]	all events	4.7	---	---	---	95	---	---	---	---	4.6	---	---	95	4.0	---	---	95	12.6	---	---	95
Amazonia (central) [c)]	WS	5.0	---	---	---	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	5.0	---	---	---	13	68	---	---	13	4.0	---	---	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	-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	---	---	---	---	289.0	---	---	1	29.9	---	---	1	---	---	---	---
Amazonia (central) [g)]		4.8	4.7-4.9	---	---	1*)	---	---	---	---	27.3	---	---	1*)	7.9	---	---	1*)	3.0	---	---	1*)
Amazonia (cent.-W) [g)]		5.3	---	---	---	1	---	---	---	---	8.4	---	---	1	5.7	---	---	1	4.3	---	---	1
Amazonia (W) [g)]		5.7	---	---	---	1	---	---	---	---	3.4	---	---	1	1.9	---	---	1	---	---	---	---
Amazonia (NW) [h)]	all events	5.0	---	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	5.0	7.8	35

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
our study																					
Amazonia (SW) [a)]	all events	7.0	5.9	8.1	37	24.0	13.0	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	6.0	9.0	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	59.0	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	3.0	---	---	30	11.8	---	---	30
Amazonia (central) [b)]	WS	3.6	---	---	12	0.5	---	---	12	0.6	---	---	12	1.6	---	---	12	7.0	---	---	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	3.0	---	---	95	0.8	---	---	95	1.8	---	---	95	4.8	---	---	95
Amazonia (central) [c)]	WS	2.1	---	---	72	1.2	---	---	72	0.7	---	---	72	2.0	---	---	72	4.8	---	---	72
Amazonia (central) [c)]	DS	3.4	---	---	23	7.4	---	---	23	1.2	---	---	23	1.2	---	---	23	4.8	---	---	23
Amazonia (central) [d)]	WS	4.4	---	---	13	4.7	---	---	13	1.8	---	---	13	---	---	---	---	---	---	---	---
Amazonia (central) [e)]	all events **)	17.0	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) [h)]	all events	20.0	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	6.0	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

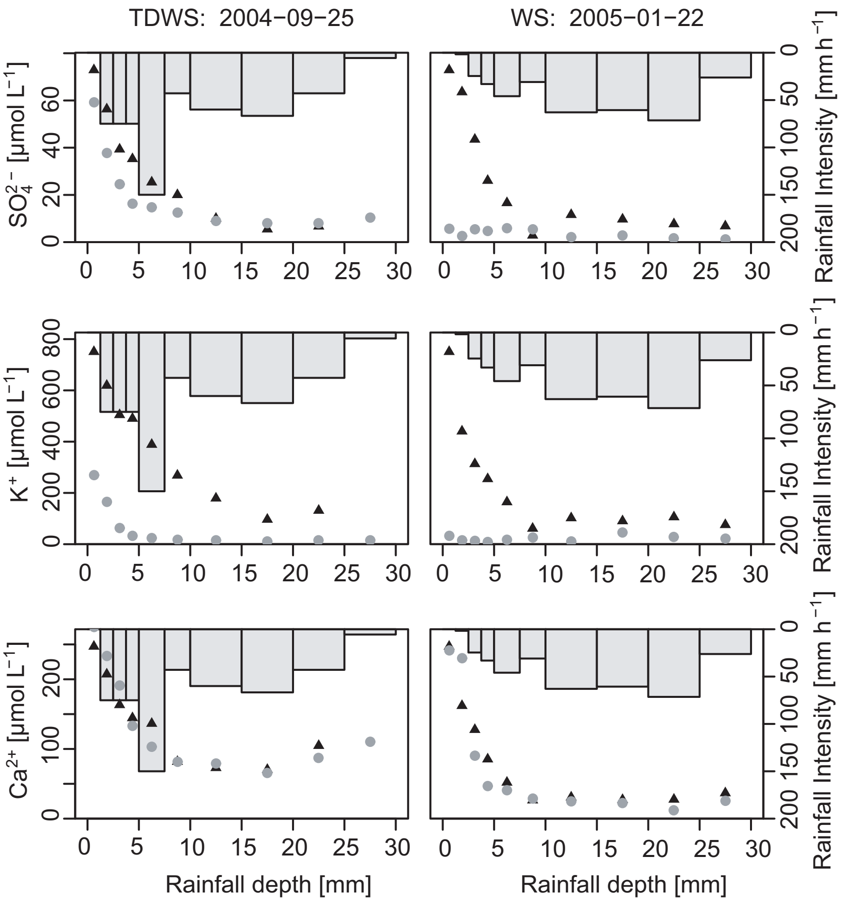


Figure 3.4 Typical within-event solute concentration dynamics in rainfall (grey solid circles) and throughfall (black solid triangles) for sulfate, potassium and calcium. The bars illustrate the rainfall intensity.

3.3.2. 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 3.4 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^+. 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 to 19th) with trends corresponding to those of the early season.

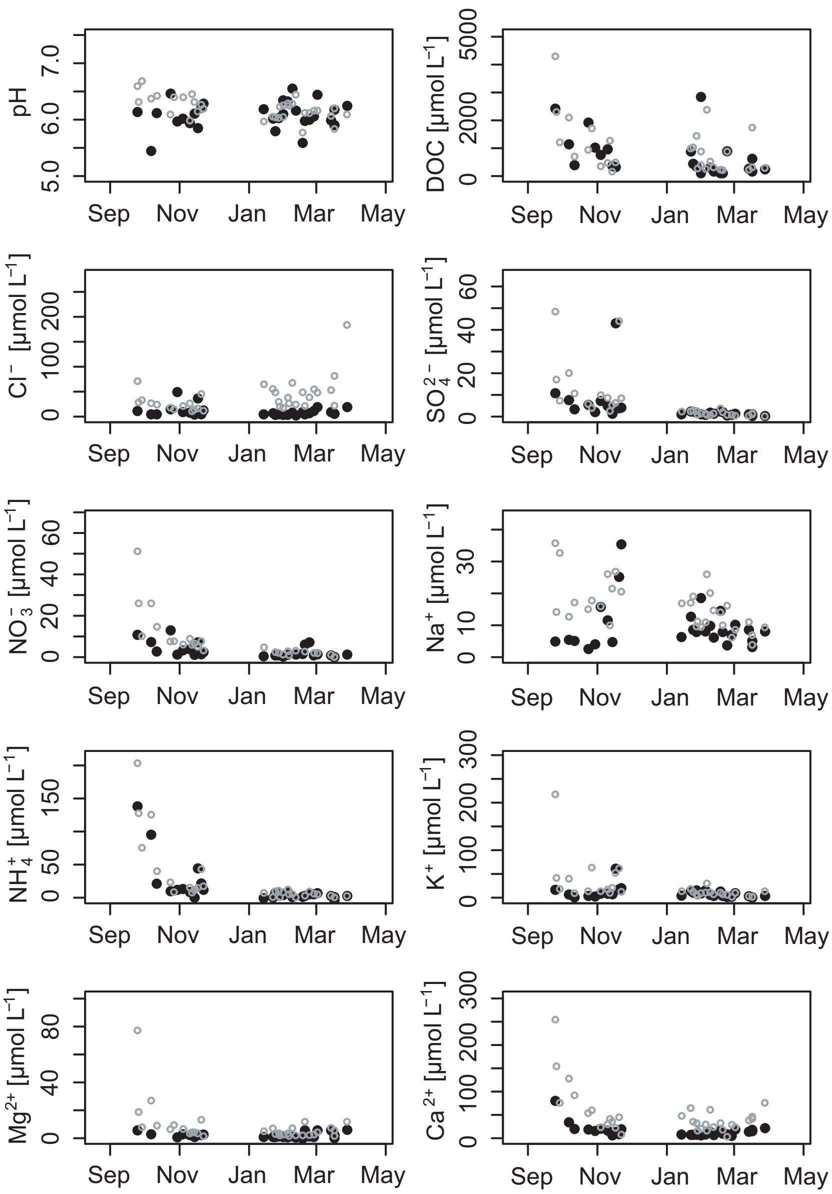


Figure 3.5 Temporal dynamics in rainfall solute concentrations of different event stages. Solute concentrations of the first 2.5 mm per event (open circles) and of a later event stage represented by the event interval from 7.5 to 10 mm of rainfall (solid circles) are plotted over the study period.

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 mm to 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 (Figure 3.5). 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.

3.3.3. Seasonal patterns of throughfall solute concentrations

In throughfall, VWM$_S$ solute concentrations over the entire year decreased in the pattern $DOC >> K^+ > Cl^- = NH_4^+ = Ca^{2+} > Na^+ = Mg^{2+} = NO_3^- = SO_4^{2-}$ (with $Mg^{2+} > SO_4^{2-}$) (Table 3.2). In the TDWS, the pattern was $DOC >> K^+ > Cl^- = NH_4^+ = Ca^{2+} > Na^+ = Mg^{2+} = NO_3^- = SO_4^{2-}$ (with $Mg^{2+} > SO_4^{2-}$), and in the WS the pattern was $DOC >> K^+ > Cl^- > Ca^{2+} > Na^+ = Mg^{2+} > NH_4^+ = NO_3^- > SO_4^{2-}$ (Table 3.2). 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 abundance of K^+ and Cl^- increased. VWMS concentrations in throughfall samples were significantly higher in the TDWS than in the WS for all solutes except DOC. The VWMS of pH was higher in the WS. The VWME's of bulk throughfall samples decreased for all solutes during the TDWS, but did not show temporal trends during the WS (Figure 3.3). The VWME 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.

Table 3.2 VWM_S throughfall solute concentrations and lower (lwr) and upper (upr) confidence limits (where provided by the authors) in µM per liter measured for different rainforests. Where available, results are listed separately for the dry season (DS) or the transition from dry to wet season (TDWS)

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	4.5-7.1	6.2	6.3	42	1354	1031	1678	40	31.4	24.2	38.5	41	5.3	3.7	7.0	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	2.0	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	---	---	---	---	---	---	---	---	---	21.0	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	59.0	52.1	66.0	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	62.0	93.0	35	16.6	11.3	22.0	35
Amazonia (NW) [d)]	low terrace	5.3	---	5.3	5.3	35	558.1	525.6	590.6	35	35.6	32.2	39.0	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	39.0	17.9	60,2	35

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
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)

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-} ($R^2=0.82$). 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 Ca^{2+} as well as between c and Ca^{2+} ($R^2<0.55$, $p\geq0.05$).

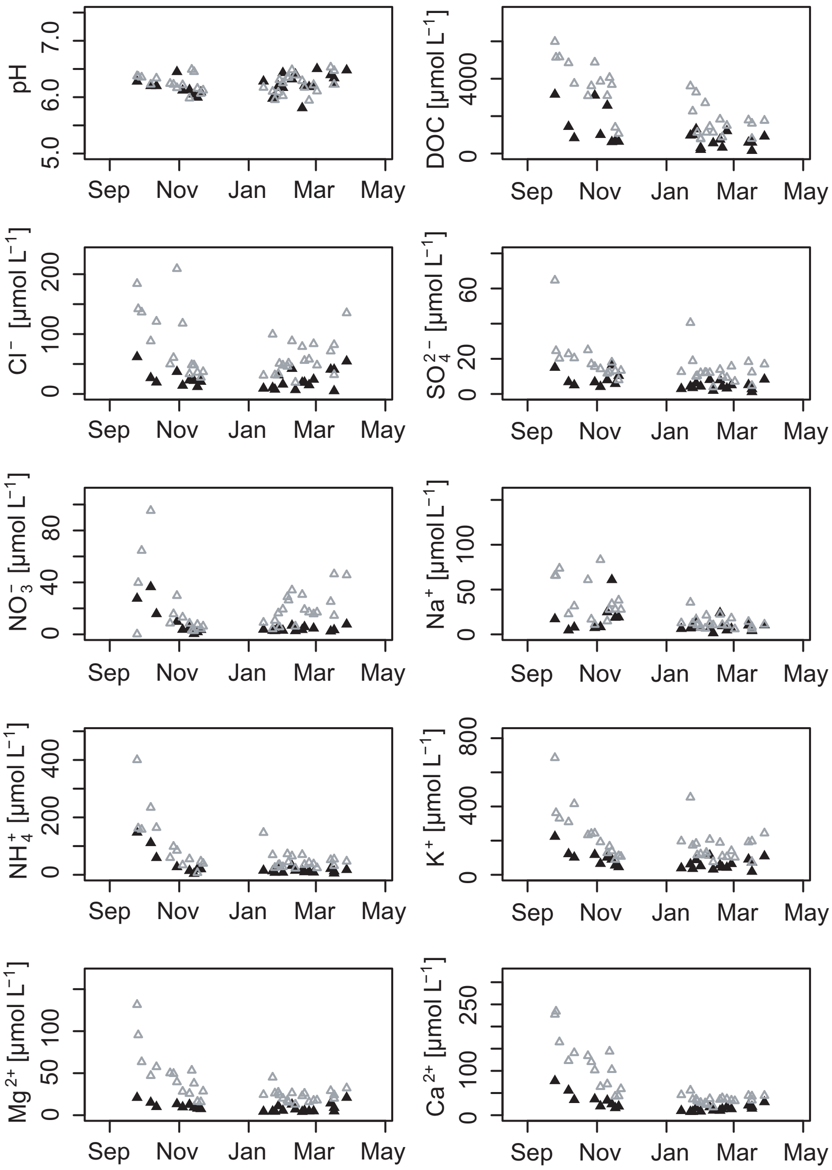


Figure 3.6 Temporal dynamics in throughfall solute concentrations of different event stages. Solute concentrations of the first 2.5 mm per event (open triangles) and of a later event stage represented by the event interval from 7.5 to 10 mm of throughfall (solid triangles) are plotted over the study period.

3.3.4. Within-event patterns of throughfall concentrations

Throughfall solute concentrations decreased after the onset of rains for all solutes over the whole study period. Figure 3.4 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. 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 (Figure 3.7). 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.

3.3.5. Modeling and annual solute fluxes

For rainfall, step-wise regression resulted in relatively few models capable of predicting solute concentrations (Table 3.3). 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.

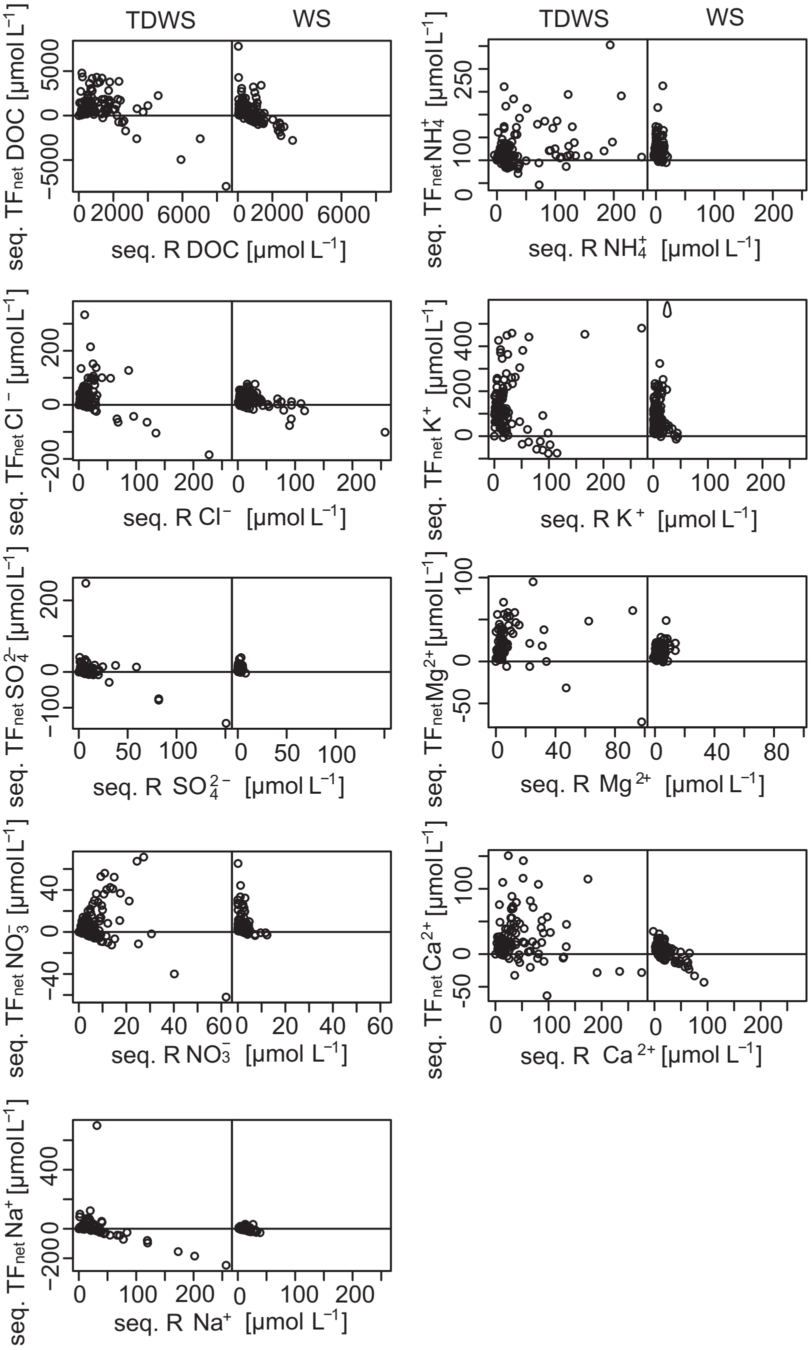


Figure 3.7 Sequential net throughfall (seq. TF_{net}) deposition plotted over sequential rainfall (seq. R) for TDWS concentrations and WS concentrations. Each point represents a pair of rainfall and net throughfall samples for a single rainfall depth interval per event.

For throughfall, models with varying levels of significance were found for 7 of 10 solutes (Table 3.3). 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+}.

Table 3.3 Models applied for predicting solute concentrations [µmol l-1] 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 ° p<0.1, * p<0.05, ** p<0.01, or *** p<0.001

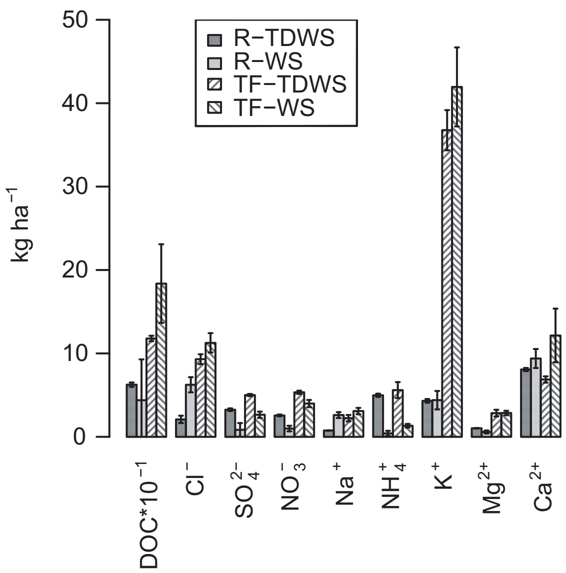


Figure 3.8 Seasonal totals of solute fluxes in rainfall (R) and throughfall (TF) plotted separately for the TDWS (01. Aug. 2004 – 23. Nov. 2004) and the WS (24. Nov. 2004 – 31. Jul. 2005). The error bars indicate the 95% confidence intervals.

In rainfall, fluxes of SO_4^{2-}, NO_3^-, NH_4^+ and Mg^{2+} were significantly higher in the TDWS than in the WS (Figure 3.8). 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-}, NO_3^- and NH_4^+ were also higher in the TDWS than in the WS, but fluxes of Mg^{2+} were similar between sampling periods (Figure 3.8). Throughfall fluxes of DOC, Cl^-, Na^+ and Ca^{2+} were higher in the WS than in the TDWS.

Table 3.4 Annual totals of solute fluxes [kg ha^{-1} yr^{-1}] in rainfall (R), throughfall (TF) and net throughfall (TF_{net}) (01. Aug. 2004 – 31. Jul. 2005). The numbers put in parentheses are ½ 95% confidence intervals

	DOC	Cl^-	SO_4^{2-}	NO_3^-	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
our study									
R	106.45 (51.48)	8.33 (1.34)	4.09 (0.97)	3.55 (0.44)	3.37 (0.37)	5.41 (0.49)	8.71 (1.32)	1.61 (0.21)	17.46 (1.33)
TF	301.59 (50.39)	20.57 (1.76)	7.65 (0.51)	9.33 (0.63)	5.33 (0.77)	6.93 (1.18)	78.72 (7.14)	5.70 (0.66)	19.03 (3.59)
TF_{net}	195.14	12.24	3.56	5.78	1.96	1.52	70.01	4.09	1.57
Filoso et al. (1999)									
R	---	1.56	3.13	3.45	2.44	0.82	0.73	0.37	2.46
TF	---	5.38	5.13	2.74	3.83	0.66	27.70	2.70	5.54
TF_{net}	---	3.82	2.00	-0.71	1.39	-016	26.97	2.33	3.08

--- no data provided

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 3.4). 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: $K^+ > Cl^- > Na^+ > Mg^{2+} > NO_3^- > DOC > SO_4^{2-} > NH_4^+ > Ca^{2+}$. In the WS, the relative enrichments were: $K^+ > SO_4^{2-} > DOC > Mg^{2+} > NO_3^- > NH_4^+ > Cl^- > Na^+ > Ca^{2+}$. The flux enrichments were statistical significant for all solutes except for NH_4^+ in the TDWS and for Na^+ and Ca^{2+} in the WS (Table 3.4). Very low fluxes in rainfall for SO_4^{2-}, NO_3^-, NH_4^+ and Mg^{2+} within the WS led to relative high enrichment ratios.

3.4. Discussion

3.4.1. 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, 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 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 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 (< 5μm) 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., 2002b).

3.4.2. 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 3.2) 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 the forest floor (Lindberg and Lovett, 1985; Rodrigo and Àvila, 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 (Veneklaas, 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-Nordemann, 1991; Franken et al., 1985; Laclau et al., 2003; Liu et al., 2002; Lovett and Lindberg, 1984; Marques 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 (Figure 3.7). 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.

3.4.3. 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 3.1). 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 3.1), 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 3.1). 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 3.1). 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, 2004a). 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 x 10^{6} kg a^{-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 3.2). 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 3.2), despite higher Ca^{2+} rainfall concentration in Rondônia. Throughfall DOC VWM concentrations over all events were higher for our study compared 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 3.4). 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 Rondônia 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.

3.5. Conclusion

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.

4.

Implications of long-term land-use change for the hydrology and solute budgets of small catchments in Amazonia*

Abstract

The replacement of undisturbed tropical forest with cattle pasture has the potential to greatly modify the hydrology of small watersheds and the fluxes of solutes. We examined the fluxes of water, Cl^{-}, $NO_3^{-}-N$, $SO_4^{2-}-S$, $NH_4^{+}-N$, Na^{+}, K^{+}, Mg^{2+} and Ca^{2+} in different flowpaths in ~1 ha catchments of undisturbed open tropical rainforest and established pasture in the southwestern Brazilian Amazon state of Rondônia. Stormflow discharge was 18% of incident rainfall in pasture, but only 1% in forest. Quickflow predominated over baseflow in both catchments and in both wet and dry seasons. In the pasture, groundwater and quickflow were important flowpaths for the export of all solutes. In the forest, quickflow was important for $NO_3^{-}-N$ export, but all other solutes were exported primarily by groundwater outflow. Both catchments were sinks for $SO_4^{2-}-S$ and Ca^{2+}, and sources of Na^{+}. The pasture also lost K^{+} and Mg^{2+} because of higher overland flow frequency and volume and to cattle excrement. These results show that forest clearing dramatically influences small watershed hydrology by increasing quickflow and water export to streams. They also indicate that tropical forest watersheds are highly conservative of most solutes but that pastures continue to lose important cations even decades after deforestation and pasture establishment.

* With Neill, C., Vetter, T., Chaves, J., Krusche, A.V. and Elsenbeer, H. submitted to *Journal of Hydrology*

4.1. Introduction

Human transformation of the Earth’s land surface has far-reaching and important consequences for the functioning of hydrological and hydrochemical processes in watersheds. The effects of altered vegetation cover and land use on these processes deserve increasing attention (DeFries and Eshleman, 2004). Deforestation is a globally important change that has the potential to alter water infiltration, the balance between surface and groundwater runoff, solute concentrations and budgets of watersheds. The Amazon Basin of Brazil is today a global deforestation hotspot (Achard et al., 2002). Since the early 1970s large areas of tropical forest in the Brazilian Amazon have been cleared, especially in the “arc of deforestation” that extends from the southern to the eastern edge (Fearnside, 2006). By 2004 the total area of deforestation within the Legal Brazilian Amazon reached 674×10^3 km^2 or 17% of the 4×10^6 km^2 of the Basin’s originally forested area (Fearnside, 2006; INPE, 2006). Despite abandonment of pastures or transformations of pastures to row crops in some areas (Serrão and Toledo, 1991), most of them persist over decades and cattle ranching is the main use of deforested land.

Much of our current understanding of land-use effects on hydrology and hydrochemistry in forested tropical regions derives from controlled experimental manipulations of small watersheds. These results generally show a consistent picture of increasing stream discharge after forest conversion to crop land, plantations and pastures caused by lower evapotranspiration and a diminished capacity of plants in these land covers to extract water from deeper soil layers during periods of drought (Bruijnzeel, 2004). Recent studies show that forest clearing for pasture leads to an increase of overland flow caused by lower soil hydraulic conductivity and soil water contents near saturation in pastures (Moraes et al., 2006). Because different hydrological flowpaths have distinct chemical fingerprints (Elsenbeer et al., 1995; Hensel and Elsenbeer, 1997), shifts in the proportional contribution of single flowpaths to watershed discharge has the potential to result in large changes to total solute export.

Tropical forests on strongly weathered soils are generally characterized as having relatively conservative nutrient cycles that result in low losses of solutes to streams or groundwater (Brinkmann, 1985; Herrera et al., 1978). Despite the large extent of cattle ranching in Amazonia, the long-term consequences of land-use conversion from undisturbed forest to pasture for watershed nutrient budgets are largely unquantified. Few studies of watershed-scale solute budgets for forest sites exist in Amazonia (Brinkmann, 1985; Franken and Leopoldo, 1984; Jordan, 1982; Lesack and Melack, 1996). Even fewer studies have examined pastures (Biggs et al., 2006) and we are unaware of any nutrient balance study that compares tropical undisturbed forest and pastures.

We quantified annual total discharge and solute fluxes of headwater catchments under undisturbed forest and well established pasture in the southwestern Brazilian Amazon state of Rondônia. Because land conversion to pasture increases the proportion of overland flow (Chaves et al., 2007) and could influence solute exports and consequently solute budgets, we evaluated the relative importance of quickflow, baseflow and groundwater flow in the watersheds. We also analyzed hydrographs and chemographs to gain insight into solute transport processes that might influence annual totals of solute exports. Our goal was to evaluate in the two catchments: 1) differences in hydrologic fluxes, 2) the solute transport processes, 3) the implications of the hydrologic fluxes on solute output, and 4) the characterization of the catchments as sinks or sources for solutes over a water year.

4.2. Study area and methods

4.2.1. Study area

The study site, Rancho Grande, is located about 50 km south of Ariquemes (10˚18′S, 62˚52′W, 143 m a.s.l.) in the Brazilian state of Rondônia, in the southwestern Amazon Basin of Brazil. The area is part of a morphostructural unit known as “Southern Amazon Dissected Highlands” (Planalto Dissecado Sul da Amazônia, Peixoto de Melo et al., 1978), which is characterized by pronounced topography with an altitudinal differential of up to 150 m. Remnant ridges of Precambrian basement rock, made up of gneisses and granites of the Xingu (Leal et al., 1978) or Jamari Complex (Isotta et al., 1978), are separated by flat valley floors of varying width. The climate is tropical wet and dry (Köppen’s Aw). From 1984-2003 mean annual temperature was 27°C and mean annual precipitation was 2 300 mm a^{-1} with a marked dry period from July through September (Germer et al., 2006, chapter 2).

We selected adjacent forest (1.37 ha) and pasture (0.73 ha) catchments approximately 400 m apart. Both catchments are drained by 0-order ephemeral streams. The soils of both catchments were classified as Kandiudults (Zimmermann et al., 2006). The forest vegetation at Rancho Grande is predominantly terra firme undisturbed 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 southern Amazon (IBGE, 2004b). The pasture was cleared and burned twice in 1980 and 1981. Since 1984 the pasture has been grazed by one head of cattle per hectare, tilled once in 1993 and planted with *Brachiaria humidicola* (Rendle) Schweick. (Zimmermann et al., 2006). More details about soils, vegetation and climate at Rancho Grande can be found in Soberaj et al. (2002) and Germer et al. (2006, chapter 2).

4.2.2. Field measurements

A similar hydrological and hydrochemical sampling and monitoring network (Figure 4.1) was set up in August 2004 in both catchments. A tipping bucket rain gauge (Hydrological Services P/L, Liverpool Australia) with a resolution of 0.254 mm and a Campbell logger recorded five-minute rainfall intensity adjacent to the pasture catchment. Incident rainfall and throughfall were collected on an event basis with trough-type collectors for chemical analysis. The collectors, installed on supports 1 m above ground, were made from 150 mm diameter PVC pipes, which were connected by flexible tubes to 20 liter plastic canisters. Funnels with a thin-mesh nylon net pre-leached with deionized water (DIW) were installed between collector pipe and tubes and prevented coarse material entering the canisters. The total collecting area per collector was 980 cm² (7 cm * 140 cm). Throughfall was collected with 20 collectors, which were cleaned of litter after each event. The samplers collected dry plus wet deposition. To minimize dry deposition from August through November, the rainfall collector was rinsed with deionized water on days with no precipitation. For the remaining year dry deposition was expected to be low. In order to qualify for an event, at least 0.5 mm of rainfall must have been recorded in half an hour. Events were separated by at least two hours without rain.

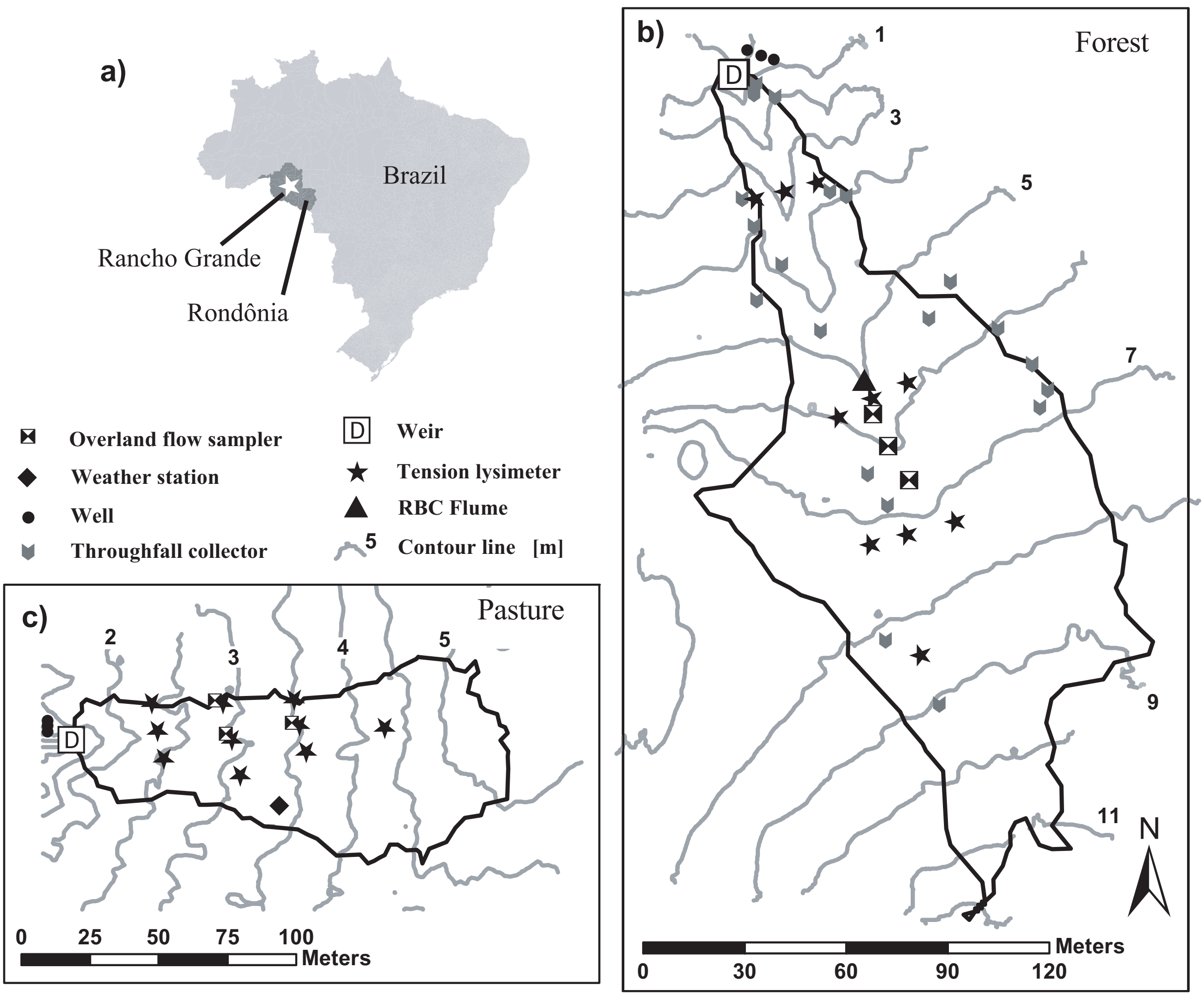


Figure 4.1 Map of the study site (a) and detailed maps for the forest (b) and pasture (c) catchments, showing instrumentation sites and contour lines (meter).

Stemflow was collected along the catchment perimeter, which resulted in a maximum distance between sample trees of 300 m. Aluminum collectors with an inner diameter of 3–4 cm were fitted around trunks at breast height (1.3 m above the forest floor) in a downward spiral. Acid washed polythene inlays were sealed to the trunks, and flexible tubes diverted the water to canisters standing on the forest floor. Stemflow volume was measured on event basis for 24 randomly selected trees in three different DBH classes (5–10 cm, 10–20 cm and >20 cm) and for one palm class with 8 large aborescent babassu palms (*Orbignya phalerata*, local name: babaçu). Stemflow was sampled from all 24 trees and from 4 of the babassu palms. Throughfall and stemflow samples were collected two hours after every event or alternatively the next morning for events that ended after 9:00 pm.

Both catchments were equipped with 1.0 ft H-flume-type weirs (Blaisdell, 1976; Gwinn and Parsons, 1976) and water levels were recorded with TruTrack loggers every 5 minutes from September through November 2004 as well as from January to mid April, and every 15 minutes in December 2004 and from mid April to July 2005. Stage-triggered Teledyne-ISCO samplers were installed at the weirs for stormflow sampling. Samples were collected every five minutes during the first 80 min of stormflow and every 20 min for the following 160 min. Due to limited accuracy of low flow in the H-flumes, only events with a maximal discharge height greater than 1 cm were considered as stormflow discharge events.

To sample overland flow we installed a large version of those collectors first used by Kirkby et al. (1976) in the upper part of the catchments (Figure 4.1), and equipped them with acid-washed polyethylene bags. One and three overland flow collectors per catchment were operating before and after December 2004, respectively. In the forest, overland flow was sampled sequentially in the upper part of the catchment (Figure 4.1) for four events (2004-11-20, 2005-01-22, 2005-02-19 and 2005-02-23). A stage-triggered Teledyne-ISCO sampler sampled overland flow every 5 minutes at the outlet of a V-shaped flume (13.17.02 RBC Flume, Eijkelkamp). Soil solution was sampled every ten days with tension lysimeters at ten locations and two depths (20 and 100 cm) in each catchment. Groundwater was sampled weekly from three wells per catchment situated near the outlets.

Rainfall and water level were monitored from August 2004 to July 2005. All sampling was conducted from September 2004 to April 2005 (excluding December 2004), except stemflow, which was sampled from January to March 2005.

4.2.3. Laboratory analyses

Rainfall and quickflow samples of up to one liter were collected in Nalgene polyethylene bottles that were prewashed with dilute (5%) *HCl* then thoroughly rinsed with nanopure dionized water. All samples were transported to a field laboratory about 500 m from the catchments 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 pre-ashed 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. The frozen cation/anion samples were shipped in Styrofoam coolers to CENA in Piracicaba. The samples were maintained frozen 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). 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 was 0.99 or higher. 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 and Ca^{2+} = 1.25. Analytical variability of solute concentrations was always less than 10%. Sample blanks of DIW and DIW passed through PVC collectors were below detection limits.

4.2.4. Hydrograph separation and hydrological flux calculation

Event hydrographs were divided into quickflow and baseflow following the method of Hewlett and Hibbert (1967) for small catchments in humid temperate areas. This method was chosen due to its simplicity and to ensure comparability with other tropical hydrological flux studies (Johnson et al., 2006; Lesack and Melack, 1996). Stormflow was defined as the beginning of flow response to event precipitation and to end with the start of the following stormflow. Quickflow was separated from baseflow with a straight line starting with the onset of stormflow and with a slope of 0.546×10^{-3} m³ s^{-1} km^{-2} × A [km^2], where A corresponded to the catchment area. The time when the straight line and the hydrograph intersected determined the end of quickflow. Baseflow is often associated with groundwater flow, but because hydrograph separation techniques provide no information about the sources of baseflow (Blume et al., 2006; Dingman, 2002), we assumed no such association. The stormflow response factor, R, was calculated as the proportion of quickflow to rainfall per event. We used the term streamflow for annual observations.

To estimate quickflow when there was a gap in the stage record for one event on August 26, 2004 for the pasture, we used linear regression of water flux on rainfall size for the first 6 measured discharge events. Baseflow was assumed to be zero for the event on August 26, 2004 in the forest because the first 6 discharge events did not generate enough baseflow for linear regression estimation. We assumed that the same event did not generate quickflow in the forest because stormflow was first recorded in the beginning of November (between August and November we recorded 5 rain events of similar or greater rainfall total and intensity that did not generate stormflow).

The net groundwater flux (Q_{GW}) was estimated as a residual of the other annual water balance components, assuming minimal changes in total groundwater storage for the hydrological year 2004-2005. For the pasture we applied the equation:

$$Q_{GW} = Q_R - Q_{StF} - Q_{SS} - Q_{ET} \tag{4.1}$$

where Q_R, Q_{StF}, Q_{SS} and Q_{ET} are rainfall, stormflow (quick- plus baseflow), subsurface flow and evapotranspiration, respectively. Q_{SS} was assumed to be zero, as it is minimal even where impeding layers exist (Moraes et al., 2006).

Evapotranspiration values were estimated as 1 024 mm yr^{-1} (2.8 mm d^{-1}) for the pasture and 1 387 mm yr^{-1} (3.7 mm d^{-1}) for the forest as reported by Kabat et al. (1997) for an palm rich open tropical rainforest at the Reserva Jarú research site and a *Bracharia brizantha* pasture at the Ranch Nossa Senhora, both in Rondônia. These values (henceforth referred as ET_{dry}) match the lower end of evapotranspiration values from other studies (Hodnett et al., 1996; Jipp et al., 1998; Moraes et al., 2006) because they represented conditions during a relatively dry year. To evaluate the sensitivity of our flux calculations to the range of evapotranspiration estimates reported in the literature, we also used upper end evapotranspiration estimates from eastern Amazonia (henceforth referred to as ET_{wet}) of 1 419 mm yr^{-1} (3.9 mm d^{-1}) for the pasture and 1 629 mm yr^{-1} (4.5 mm d^{-1}) for the forest reported by Moraes et al. (2006). We then calculated total solute fluxes based on both water budgets.

4.2.5. Flux calculations

For seasonal comparisons and for flux calculations the dataset was divided into a transition from dry to wet season (TDWS), and a wet season (WS). The TDWS incorporated all samples from August to November, 2004 and the WS all samples from January to April, 2005.

Quickflow solute fluxes (F_{QF}) for each sampled event were calculated by:

$$F_{QF} = \sum_{i=1}^{n} C_{QF(i)} \times Q_{QF(i)} \quad (4.2)$$

where $C_{QF(i)}$ and $Q_{QF(i)}$ were the solute concentration and the water flux per event interval i for the number of event intervals n. The solute fluxes of the remaining events were estimated by robust linear regression of C_{QF} per sampled event over the total water flux per event. The annual quickflow flux was then the sum of all calculated and estimated event quickflow fluxes. The uncertainty of annual fluxes was expressed by 95% confidence intervals. They were calculated from the prediction uncertainty of all estimated event fluxes. Flux estimates and confidence intervals were calculated using the language and environment of *R* (Version 2.2.1). Annual baseflow and groundwater fluxes were calculated by multiplying annual mean solute concentrations by the respective water fluxes. Annual rainfall fluxes were taken from Germer et al. (2007, chapter 3).

4.3. Results

4.3.1. Hydrological fluxes

The total incident rainfall at Rancho Grande from August 2004 to July 2005 was 2 286 mm, similar to the mean annual rainfall from 1984 to 2003 of 2 300 mm. Of 176 rainfall events that occurred from August 2004 to July 2005, 70 events generated stormflow in the pasture, but only 37 events did so in the forest catchment (Table 4.1). Annual streamflow was 18% of incident rainfall in the pasture and 1% in the forest. Forest stream discharge was only 6 % of pasture stream discharge.

On an event basis, the quickflow response ranged from 0 to 54% of incident rainfall in the pasture, and from 0 to 14% in the forest. Quickflow was greater than baseflow in both catchments and in both seasons (Table 4.1). In the pasture, 12 discharge events took place during the TDWS and generated a total of 48.0 mm of quickflow and < 1 mm of baseflow; during the WS, the remaining 58 events generated a total of 359 mm of quickflow and 9 mm of baseflow. In the forest, 6 events generated a total of < 1 mm of quickflow during the TDWS and no baseflow (Table 4.2). In the same catchment, 31 events generated stormflow during the WS, with a total of 22 mm as quickflow and < 1 mm as baseflow, respectively. Of those events that generated stormflow, we sampled 16 in the forest and 24 in the pasture

(Table 4.1). Quickflow in sampled events accounted for 34% of the total stormflow in the pasture and 17% of the total stormflow in the forest.

Table 4.1 Summary of discharge events, P: observed precipitation, P: pasture, F: forest, dura: quickflow duration, QF: quickflow depth, BF: baseflow, R: quickflow response factor.

Event #	P [mm]	Start of quickflow in pasture	P dura [min]	P QF [mm]	P BF [mm]	P R	F dura [min]	F QF [mm]	F BF [mm]	F R
1	110.23	2004-08-26 [*)]		1.16	0.00	0.01	---	---	---	- --
2	27.17	2004-09-25 16:10	35	0.13	0.00	0.00	---	---	---	---
3 [P)]	25.65	2004-10-07 17:35	30	0.02	0.00	0.00	---	---	---	---
4 [P)]	31.24	2004-10-12 15:45	50	0.32	0.00	0.01	---	---	---	---
5	33.27	2004-10-21 13:46	80	1.02	0.00	0.03	---	---	---	---
6 [P)]	19.81	2004-10-30 14:46	35	0.05	0.00	0.00	---	---	---	---
7 [P) F)]	45.46	2004-11-04 17:01	130	2.35	0.01	0.05	40	0.01	0.00	0.00
8	45.97	2004-11-06 19:31	165	16.44	0.01	0.36	85	0.28	0.00	0.01
9 [P) F)]	30.98	2004-11-10 16:36	120	0.99	0.01	0.03	65	0.03	0.00	0.00
10 [P) F)]	63.75	2004-11-14 05:46	285	14.38	0.02	0.23	190	0.18	0.00	0.00
11 [P) F)]	23.62	2004-11-17 13:16	125	3.73	0.00	0.16	45	0.15	0.00	0.01
12 [P) F)]	30.98	2004-11-20 14:06	140	7.38	0.00	0.24	60	0.23	0.00	0.01
13	16.25	2004-12-01 11:34	30	0.01	0.00	0.00	---	---	---	---
14	22.35	2004-12-04 10:24	150	2.80	0.01	0.13	---	---	---	---
15	34.04	2004-12-10 15:24	170	12.21	0.01	0.36	70	0.22	0.00	0.01
16	68.57	2004-12-12 17:34	210	30.89	0.01	0.45	120	0.97	0.00	0.01
17	41.14	2004-12-20 17:34	240	2.76	0.01	0.07	---	---	---	---
18	18.28	2004-12-25 12:04	180	2.83	0.01	0.15	70	0.01	0.00	0.00
19	15.24	2004-12-25 15:44	220	2.14	0.02	0.14	130	0.04	0.00	0.00
20	18.03	2004-12-26 02:34	360	0.35	0.03	0.02	---	---	---	---
21	19.55	2004-12-27 14:34	230	1.49	0.04	0.08	---	---	---	---
22	10.92	2005-01-04 06:04	90	0.04	0.01	0.00	---	---	---	---
23	33.52	2005-01-04 16:14	270	11.40	0.05	0.34	100	0.09	0.00	0.00
24	74.67	2005-01-05 23:44	360	39.82	0.06	0.53	250	1.37	0.01	0.02
25	12.19	2005-01-06 17:44	140	0.07	0.20	0.01	---	---	---	---
26	35.30	2005-01-11 20:10	295	3.37	0.13	0.10	---	---	---	---
27 [P) F)]	17.52	2005-01-14 04:45	195	1.60	0.46	0.09	23	0.02	0.00	0.00
28 [F)]	78.23	2005-01-22 11:30	290	33.14	0.11	0.42	170	0.97	0.00	0.01
29 [P) F)]	23.11	2005-01-24 14:40	180	6.28	0.12	0.27	56	0.11	0.00	0.00
30	24.88	2005-01-27 17:50	185	6.38	0.03	0.26	56	0.14	0.00	0.01
31	11.43	2005-01-29 07:55	125	0.16	0.12	0.01	---	---	---	---
32 [P) F)]	29.46	2005-01-31 19:10	195	9.21	0.03	0.31	91	0.13	0.00	0.00
33	19.55	2005-02-01 00:30	290	2.83	0.12	0.14	194	0.26	0.01	0.01
34	23.36	2005-02-01 11:55	250	7.77	0.12	0.33	100	0.27	0.00	0.01
35 [P)]	15.24	2005-02-04 15:35	160	0.76	0.04	0.05	---	---	---	---
36	8.89	2005-02-05 13:50	120	0.21	0.17	0.02	---	---	---	---
37 [P) F)]	43.43	2005-02-09 02:20	340	10.58	0.09	0.24	112	0.19	0.00	0.00
38 [F)]	14.73	2005-02-09 21:50	250	2.97	0.22	0.20	60	0.12	0.00	0.01

Table 4.1 continued

Event #	P [mm]	Start of quickflow in pasture	P dura [min]	P QF [mm]	P BF [mm]	P R	F dura [min]	F QF [mm]	F BF [mm]	F R
39 P)	37.84	2005-02-11 16:45	615	5.96	0.36	0.16	---	---	---	---
40 P)	30.22	2005-02-17 03:39	260	7.34	0.03	0.24	119	0.21	0.00	0.01
41	4.57	2005-02-17 13:09	95	0.13	0.01	0.03	---	---	---	---
42	11.43	2005-02-17 16:04	270	2.20	0.10	0.19	71	0.13	0.00	0.01
43 P) F)	30.48	2005-02-19 12:39	295	14.58	0.23	0.48	95	0.29	0.00	0.01
44	23.36	2005-02-21 16:09	315	4.71	0.20	0.20	55	0.12	0.00	0.01
45 P) F)	33.27	2005-02-23 15:09	370	11.11	0.48	0.33	144	1.17	0.00	0.04
46 P) F)	31.75	2005-02-27 20:49	275	9.73	0.08	0.31	100	0.22	0.00	0.01
47	17.27	2005-02-28 12:04	320	4.40	0.20	0.25	100	0.30	0.00	0.02
48	8.12	2005-03-01 13:14	205	0.59	0.09	0.07	---	---	---	---
49	11.68	2005-03-02 03:44	385	0.87	0.37	0.07	---	---	---	---
50	6.09	2005-03-04 14:24	55	0.09	0.13	0.01	---	---	---	---
51 P)	57.66	2005-03-05 16:19	275	29.67	0.08	0.51	174	3.47	0.01	0.06
52	71.88	2005-03-06 02:34	580	39.17	0.25	0.54	1727	10.19	0.64	0.14
53	6.09	2005-03-07 02:19	325	0.60	0.17	0.10	---	---	---	---
54	3.04	2005-03-07 17:24	115	0.20	0.49	0.07	113	0.27	0.17	0.09
55	6.09	2005-03-10 15:24	55	0.11	0.58	0.02	---	---	---	---
56 P)	20.57	2005-03-14 07:34	355	1.44	0.27	0.07	---	---	---	---
57	15.74	2005-03-17 04:18	240	0.86	0.06	0.05	---	---	---	---
58 P) F)	10.66	2005-03-17 18:03	240	2.35	0.27	0.22	62	0.17	0.00	0.02
59	4.57	2005-03-20 13:23	70	0.12	0.71	0.03	---	---	---	---
60 P)	16.25	2005-03-28 23:43	120	0.40	0.04	0.02	---	---	---	---
61	17.27	2005-03-29 03:58	465	2.61	0.57	0.15	---	---	---	---
62 P)	14.47	2005-04-03 01:58	155	0.46	0.84	0.03	---	---	---	---
63	6.60	2005-04-14 17:43	40	0.04	0.00	0.01	---	---	---	---
64	27.94	2005-04-17 17:53	150	2.44	0.00	0.09	110	0.04	0.00	0.00
65	44.95	2005-04-19 17:33	210	21.94	0.01	0.49	110	0.85	0.00	0.02
66	21.59	2005-04-25 11:13	140	0.97	0.00	0.04	80	0.03	0.01	0.00
67	22.35	2005-05-05 22:03	150	0.82	0.00	0.04	---	---	---	---
68	12.70	2005-05-22 18:23	30	0.05	0.00	0.00	---	---	---	---
69	21.08	2005-05-23 14:33	80	1.18	0.00	0.06	80	0.03	0.01	0.00
70	16.25	2005-05-29 20:33	70	0.27	0.00	0.02	110	0.05	0.02	0.00
Sum:	**1 881.84**		**234**	**407.45**	**8.89**		**89**	**23.33**	**0.88**	

Table 4.2 Summary of quickflow (QF), baseflow (BF) and total stream discharge [mm] in forest and pasture for the transition from dry to wet season (TDWS) and the wet season (WS).

	Pasture	Forest
QF_{TDWS}	47.97	0.88
BF_{TDWS}	0.05	0.00
$Total_{TDWS}$	**48.02**	**0.88**
QF_{WS}	359.48	22.45
BF_{WS}	8.84	0.88
$Total_{WS}$	**368.32**	**23.33**
TOTAL year	**416.34**	**24.21**

While sufficient discharge to qualify for a discharge event was first recorded by the end of September in the pasture, the first forest discharge was not recorded until the beginning of November. Baseflow depth exceeding 0.05 mm per catchment and event was recorded for almost all events from the beginning of January to the beginning of April in the pasture but it was recorded only twice during March in the forest catchment (Table 4.1). Therefore, during the wet season, quickflow could develop in the pasture for small rainfall events (< 10 mm), but not in the forest except for one event (# 54, Table 4.1) with very wet antecedent conditions.

The estimated annual groundwater flux was similar for pasture (845 mm yr^{-1}) and forest (875 mm yr^{-1}) when we used ET_{dry} values (pasture: 2.8 mm d^{-1}, forest 3.8 mm d^{-1}). Estimated groundwater flux was lower in the pasture (451 mm yr^{-1}) than in the forest (633 mm yr^{-1}) for ET_{wet} values (pasture: 3.9 mm d^{-1}, forest: 4.5 mm d^{-1}).

4.3.2. Hydro- versus Chemographs

The pattern of stormflow chemistry during events allowed us to distinguish two types of solute behavior. For type I solutes (K^+, Mg^{2+} and Ca^{2+}) a sharp and short-term initial concentration decrease was observed for most of the events in the pasture catchment. This response was seen only for TDWS events in the forest (Figure 4.2). In both forest and pasture catchments type I solute concentrations increased rapidly shortly after the onset of stormflow up a point where they either reached a steady state or they showed only slow increases or decreases in concentrations (Figures 4.2, 4.3). In the pasture, stormflow concentrations rose shortly after the onset of stormflow from rainfall concentration levels to overland flow concentrations at the chemographs' steady states. In the forest a similar concentration increase was observed starting from concentrations between rainfall and throughfall and raising towards overland flow concentrations but not reaching them. Pasture overland flow had the highest concentrations of Mg^{2+} and K^{+} compared to the other flowpaths, but for pasture Ca^{2+} and forest K^{+}, Mg^{2+} and Ca^{2+} soil solution concentrations were higher than overland flow concentrations (Figure 4.2, 4.3).

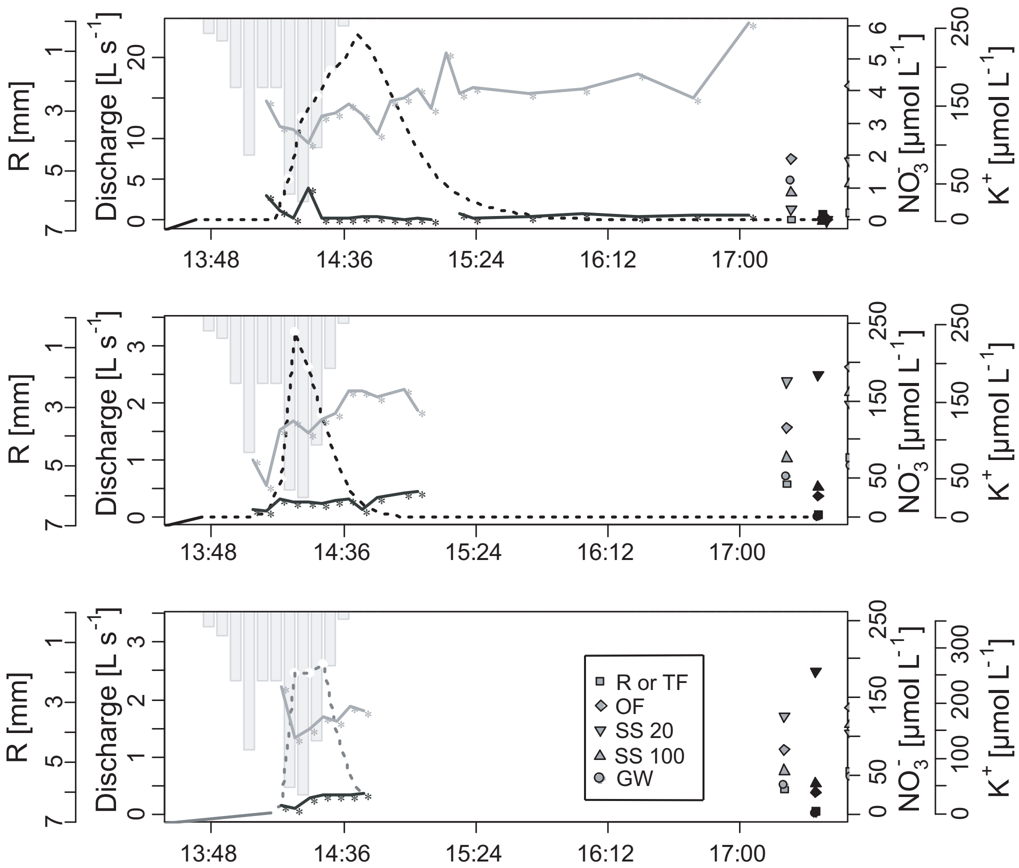


Figure 4.2 Pasture (top panel) and forest stormflow (middle panel), and forest overland flow (bottom panel) hydrographs (dotted line) and chemographs of NO_3^- (solid black line) and K^+ (solid grey line) for the rainfall event on November 20, 2004. Concentrations of rainfall (R in pasture), event volume weighted throughfall (TF in forest), event mean overland flow from bulk sampler (OF), pre-event mean soil solution in 20 cm (SS 20) and 100 cm (SS 100) depth and pre-event mean groundwater (GW) are shown for NO_3^- (black symbols) and K^+ (grey symbols). The bars indicate 5-minute rainfall total.

Type II solute (Cl^-, SO_4^{2-}, NH_4^+ and Na^+) concentrations in both forest and pasture catchments showed no dependence on discharge. On an event basis, there were no great differences between rainfall or throughfall and overland flow concentrations, except for pasture Cl^-. In the pasture stormflow Cl^- concentrations were similar to overland flow concentrations throughout events. NO_3^- behaved like a type II solute in the pasture (Figures 4.2, 4.3), but as a type I solute in the forest catchment, with steadily increasing NO_3^- concentration during stormflow (Figures 4.2, 4.3). The forest NO_3^- quickflow concentration during the February 23, 2005 event increased more than fivefold from an already high initial concentration, quite in contrast to the pasture. NO_3^- initial stormflow concentrations of the November 20, 2004 event were lower and increased only threefold during that event.

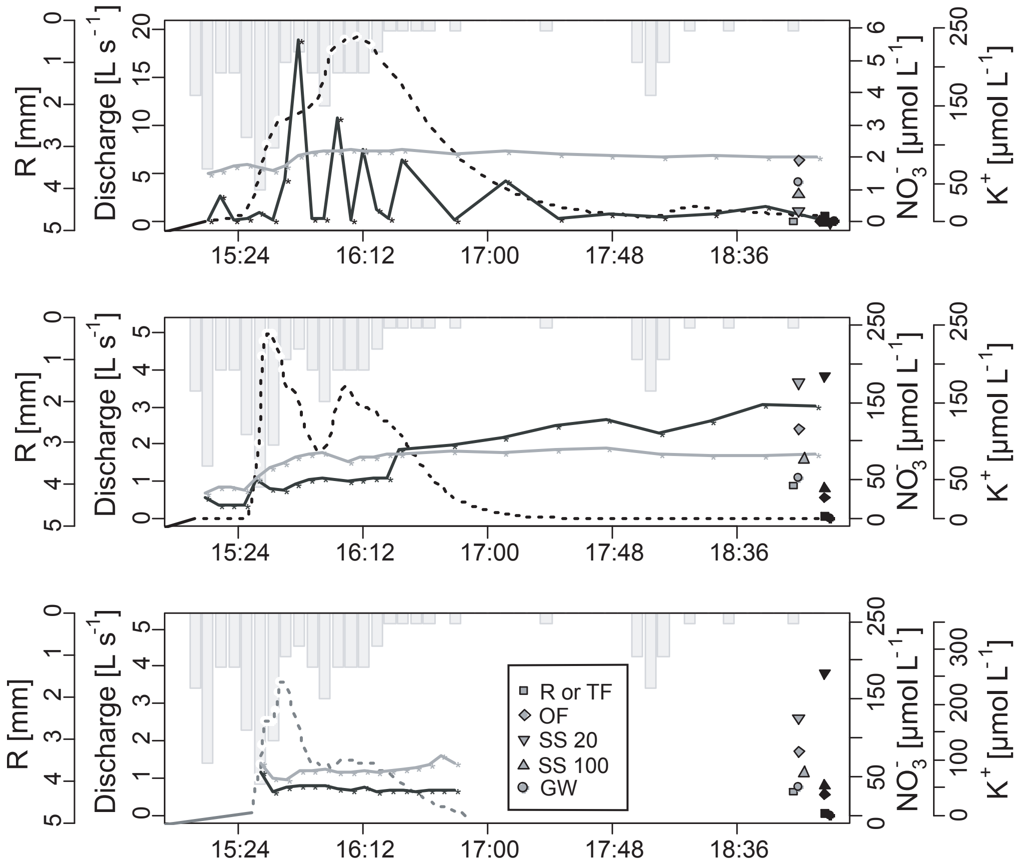


Figure 4.3 Pasture (top panel) and forest stormflow (middle panel), and forest overland flow (bottom panel) hydrographs (dotted line) and chemographs of NO_3^- (solid black line) and K^+ (solid grey line) for the rainfall event on February 23, 2005. Concentrations of rainfall (R in pasture), event volume-weighted throughfall (TF in forest), event mean overland flow from bulk sampler (OF), pre-event mean soil solution in 20 cm (SS 20) and 100 cm (SS 100) depth and pre-event mean groundwater (GW) are shown for NO_3^- (black symbols) and K^+ (grey symbols). The bars indicate 5-minute rainfall total.

Independent of hydrograph shape and particularly during low-discharge periods, chemographs tended to recede with increases in short-term rainfall intensity. Solute concentrations of samples taken during the rising and falling limbs of hydrographs showed concentration-discharge hysteresis with opposite signs for the two catchments. While in the pasture high K^+, Mg^{2+} and Ca^{2+} (and NO_3^- for some events) initial concentrations were diluted during the rising limb and not reached again on the falling limb, the low K^+, Mg^{2+}, Ca^{2+} and NO_3^- initial concentrations were always topped by higher concentrations at the end of quickflow events in the forest.

Type I solute concentrations of sequentially sampled overland flow were slightly diluted during peak discharge and increased again during the falling hydrograph limb on November 20, 2004 and February 23, 2005. No temporal patterns existed for overland flow solute concentrations during the events on January 22, 2005 and February 19, 2004. Chemograph shapes were similar for each solute in forest stormflow and overland flow except for NO_3^- during the WS. In contrast to the striking increase of NO_3^- in stormflow, overland flow NO_3^- concentrations did not change substantially during wet season events, except of slight concentration dilution during peak discharge (Figures 4.3).

4.3.3. Solute fluxes

Relationships of quickflow fluxes and event discharge varied among solutes and land use. For $SO_4^{2-}-S$, NH_4^+-N and Ca^{2+}, a single linear model explained fluxes of these solutes in both forest and pasture (Table 4.3). In the pasture, the flux-discharge relationship differed among seasons for Na^+ and K^+ but not for Cl^-, $SO_4^{2-}-S$, NO_3^--N, NH_4^+-N, Mg^{2+} or Ca^{2+} (Table 4.3). For Na^+ and K^+, the TDWS event fluxes increased linearly with increasing discharge but WS event fluxes increased logarithmically with increasing discharge. This implied that pasture discharge events > 5 mm had greater Na^+ and K^+ event fluxes in the TDWS than in the WS.

In the forest, no corresponding seasonal differences were observed because of the relatively late stormflow onset in November. With increasing discharge, forest Cl^-, Na^+, K^+ and Mg^{2+} fluxes increased less than pasture fluxes. The most conspicuous differences of solute flux increases with increasing discharge was found for NO_3^--N with a regression slope of 2.87 in the forest compared with a slope of 0.09 in the pasture, resulting in much higher NO_3^--N from the forest for similar discharge volumes in both catchments (Table 4.3).

Table 4.3 Best fit functions and coefficients used for quickflow solute flux estimation (α=0.05) derived by robust linear regression of measured quickflow solute fluxes (F_{QF}) against quickflow discharge (Q_{QF}) per event.

	P_{TDWS}	**P_{WS}**	**F**
Cl^-	$F_{QF} = 18.5140 * Q_{QF}^{1/2}$		$F_{QF} = 0.5450 * Q_{QF}$
$SO_4^{2-} - S$	$F_{QF} = 0.9749 * Q_{QF}^{1/2}$		
$NO_3^- - N$	$F_{QF} = 0.0921 * Q_{QF}$		$F_{QF} = 2.8765 * Q_{QF}$
Na^+	$F_{QF} = 1.1983 * Q_{QF}$	$F_{QF} = 0.7091 * Q_{QF} - 0.0010 * Q_{QF}^2$	$F_{QF} = 0.3391 * Q_{QF}$
$NH_4^+ - N$	$F_{QF} = 0.0357 * Q_{QF} + 0.0006 * Q_{QF}^2$		
K^+	$F_{QF} = 7.8060 * Q_{QF}$	$F_{QF} = 4.9894 * Q_{QF} - 0.0090 * Q_{QF}^2$	$F_{QF} = 2.6660 * Q_{QF}$
Mg^{2+}	$F_{QF} = 0.9907 * Q_{QF} - 0.0021 * Q_{QF}^2$		$F_{QF} = 0.3116 * Q_{QF}$
Ca^{2+}	$F_{QF} = 1.3254 * Q_{QF} - 0.0013 * Q_{QF}^2$		

Input fluxes based on ETdry exceeded the total output fluxes (groundwater + baseflow + quickflow) for $SO_4^{2-} - S$, $NO_3^- - N$, $NH_4^+ - N$ and Ca^{2+} (Table 4.4), while total output fluxes exceeded input fluxes for Na^+, K^+ and Mg^{2+} (Figure 4.4). The Cl^- flux balance was negative in the pasture and positive in the forest. For total output fluxes estimated with ET_{wet} values the pattern changed only for pasture Cl^- and for forest K^+ and Mg^{2+}, which had balanced input and output fluxes (within the confidence limits) using ET_{wet}. The relative magnitude of input fluxes by rainfall was Ca^{2+} > K^+ = Cl^- > $NH_4^+ - N$ > Na^+ > $SO_4^{2-} - S$ = Mg^{2+} > $NO_3^- - N$ (Figure 4.4), while in pasture output: K^+ > Cl^- > Na^+ > Ca^{2+} > Mg^{2+} > $SO_4^{2-} - S$ > $NH_4^+ - N$ > $NO_3^- - N$ and in forest output: K^+ > Na^+ > Ca^{2+} > Cl^- = Mg^{2+} > $NO_3^- - N$ = $SO_4^{2-} - S$ = $NH_4^+ - N$. Major differences in solute exports between land uses were found for Cl^-, which had fivefold higher export in pasture than forest, for K^+ and $NH_4^+ - N$, which had twofold higher exports in the pasture than forest, and for $NO_3^- - N$, which had threefold higher export in the forest than in the pasture (Table 4.4).

Table 4.4 Input solute fluxes by rainfall, total output solute fluxes by groundwater plus quickflow plus baseflow for the pasture and forest catchments and the ratio of pasture and forest output solute flux. The numbers put in parentheses are half width 95% confidence intervals.

		Fluxes in kg h^{-1} yr^{-1}							
		Cl^-	$SO_4^{2-}-S$	NO_3^--N	Na^+	NH_4^+-N	K^+	Mg^{2+}	Ca^{2+}
input		8.33 (0.30)	1.36 (0.06)	0.80 (0.02)	3.37 (0.07)	4.46 (0.10)	8.71 (0.23)	1.61 (0.06)	17.46 (0.23)
output pasture	ET_{dry}	10.60 (0.89)	0.36 (0.09)	0.13 (0.03)	9.36 (0.41)	0.57 (0.05)	29.54 (1.24)	3.07 (0.18)	5.28 (0.38)
	ET_{wet}	8.62 (0.71)	0.26 (0.05)	0.10 (0.02)	5.88 (0.26)	0.48 (0.03)	21.61 (0.88)	2.61 (0.14)	4.55 (0.24)
output forest	ET_{dry}	2.11 (0.44)	0.32 (0.06)	0.37 (0.05)	11.19 (0.46)	0.31 (0.04)	13.13 (0.72)	2.04 (0.14)	7.88 (0.85)
	ET_{wet}	1.54 (0.32)	0.23 (0.04)	0.33 (0.04)	7.94 (0.34)	0.23 (0.03)	9.67 (0.53)	1.48 (0.10)	5.69 (0.62)
output ratio pasture/ forest	ET_{dry}	5.0	1.1	0.3	0.8	1.8	2.2	1.5	0.7
	ET_{wet}	5.6	1.1	0.3	0.7	2.1	2.2	1.8	0.8

In the pasture catchment, groundwater and quickflow were important flowpaths for the export of all solutes and baseflow contributed < 4% of total solute fluxes. Annual pasture quickflow fluxes, calculated using ET_{dry}, exceeded groundwater fluxes for Ca^{2+}, Mg^{2+}, NH_4^+-N and Cl^-, while pasture groundwater fluxes exceeded quickflow fluxes for Na^+, $SO_4^{2-}-S$ and K^+. The only substantial difference created by using higher evapotranspiration values (ET_{wet}) was greater K^+ fluxes via quickflow than groundwater (Figure 4.4). In the forest, in contrast, the solute exports were driven predominantly by groundwater outflow for the whole range of ET values. Solute exports via baseflow, calculated using ET_{dry}, did not exceed 1% of total export. Quickflow contribution to solute exports did not exceed 10% (12% for ET_{wet}) of total solute export, except for NO_3^--N, for which quickflow was responsible for 56% of NO_3^--N export (64% for ET_{wet}).

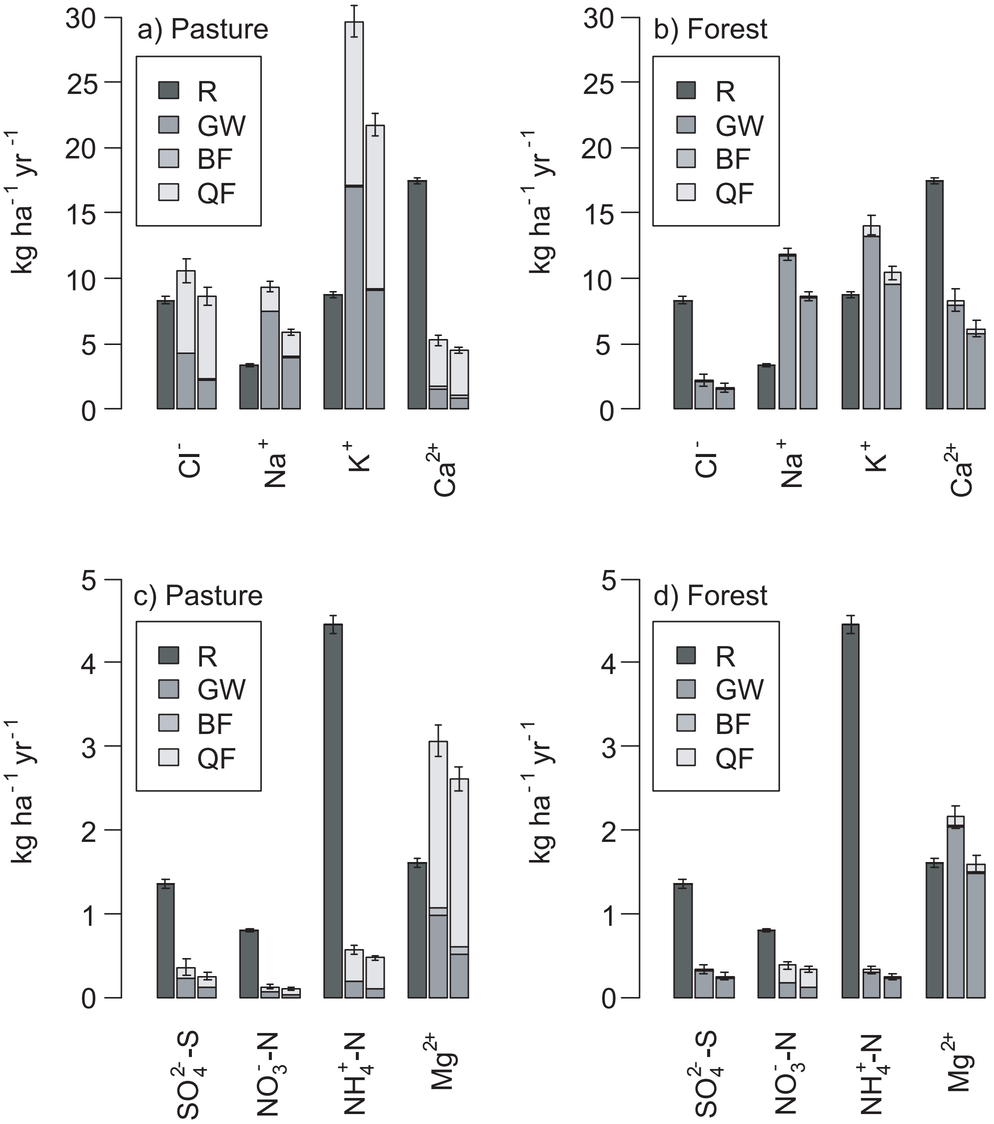


Figure 4.4 Total solute input fluxes (left bars) via rainfall (R) and solute output fluxes (middle bars: estimated with ET_{dry}, right bars: estimated with ET_{wet}) via quickflow (QF), baseflow (BF) and groundwater (GW). The error bars indicate 95% confidence intervals.

Solute outputs in quickflow were higher in the pasture for all solutes, except for $NO_3^- - N$, which was > 3-fold higher in the forest. Despite similar groundwater discharge estimated by ET_{dry}, solute fluxes in groundwater differed significantly between catchments, except for $SO_4^{2-} - S$ (Figure 4.4). Groundwater solute fluxes of Cl^- and K^+ were higher in the pasture than in the forest, while groundwater solute fluxes of Ca^{2+}, $NO_3^- - N$, Mg^{2+}, Na^+ and $NH_4^+ - N$ were higher in the forest than in the pasture (Figure 4.4). Estimates of groundwater solute fluxes in the pasture relative to groundwater solute fluxes in the forest hardly depended on the choice of ET estimation.

4.4. Discussion

4.4.1. Land-use change implications for hydrology

Land-use change from undisturbed forest to pasture dramatically changed the relative proportions of (slow) groundwater flow to (fast) streamflow. The pasture had greatly increased frequency and volume of quickflow as well as quickflow onset earlier in the rainy season. The total annual generation of ephemeral streamflow in the forest was of similar magnitude as observed by Moraes et al. (2006). These authors found a runoff coefficient of 2.7% in a 0.33 ha catchment in eastern Amazonia. In larger forest catchments also form central Amazonia, Lesack (1993) found that perennial streamflow made up 57% of rainfall in a 23 ha catchment, Leopoldo et al. (1995) reported a value of 32% for a 1.3 km² catchment, and Trancoso (2006) reported a value of 15% from a 1.3 km² catchment. Waterloo et al. (2006) found a runoff coefficients of 38% for 2003 and 46% for 2002 in a 6.8 km² catchment near Manaus. Our annual pasture streamflow of 18% was nearly an order of magnitude higher than annual forest streamflow. This was very similar to the 17% reported by Moraes et al. (2006) for a 0.72 ha pasture in eastern Amazonia, but lower than the 35-47% reported by Biggs et al. (2006) from a 3.9 ha pasture in Rondônia or the 32% found by Transcoso (2006) from a 1.2 km² pasture in central Amazonia. These land use and scale comparisons suggest that low runoff coefficients in small undisturbed forest catchments will significantly increase after land use conversion to pasture, but these differences become much less apparent in catchments > 1 km².

Soil compaction and the ensuing decrease of near-surface hydraulic conductivity is the major mechanism that results in elevated overland flow generation in pasture compared with undisturbed forest. Median hydraulic conductivity in 12.5 cm soil depth was 131 mm h^{-1} in undisturbed forest compared to 22 mm h^{-1} in the pasture (Zimmermann et al., 2006), which resulted in the maximum 30-minute rainfall intensity of our study period exceeding the hydraulic conductivity for none of the storms in forest but 27% of storms in pasture. At 20 cm soil depth, the maximum 30-minute rainfall intensity of our study period exceeded the hydraulic conductivity for

27% of the storms in forest (Ksat: 22 mm h^{-1}) and 52% of storms in pasture (Ksat: 6 mm h^{-1}). In the compacted pasture soils, perched water tables result in saturation-excess overland flow when they intersect with the soil surface (Biggs et al., 2006; Moraes et al., 2006).

Our pasture watershed was cleared 24 years ago and has been used as pasture for the past 20 years. This history was similar to large areas of established pasture in the developed regions of the eastern, central and western Amazon where cattle ranching has predominated on cleared forest lands (Fearnside, 2006; Roberts et al., 2002a; Serrão and Toledo, 1991). It was also similar in age and grazing history to other pastures where hydrological studies have been conducted (Biggs et al., 2006; Moraes et al., 2006; Trancoso, 2006). While pasture soil properties can vary with age since clearing, there is good evidence that many soil and physical properties develop in predictable ways under land use as continuous pasture (Neill et al., 1997a) and that these pastures are broadly representative of hydrological responses in pastures over wider areas.

These results have several important implications for understanding the hydrological consequences of deforestation in the Amazon. First, there were large and fairly consistent increases in streamflow in small catchment streams following deforestation for pasture. Second, higher quickflow frequency and volume in pasture catchments compared with forest resulted in groundwater discharge from the pasture that was similar or less than groundwater discharge from forest despite lower evapotranspiration in pasture. Third, streamflow of small pasture and forest catchments was dominated by quickflow (this study and Moraes et al., 2006), while in larger catchments with perennial flow it was dominated by baseflow (Biggs et al., 2006; Lesack, 1993; Waterloo et al., 2006). This may help to explain why despite the large magnitude of changes to runoff generation in small watersheds, changes in the magnitude and timing of flows in larger rivers have been detected in relatively few places, despite large deforested areas (Costa et al., 2003; Marengo et al., 1998).

4.4.2. Solute transport processes inferred from hydro- and chemographs

The hydro- and chemograph comparison revealed similarities and differences of stormflow chemistry in the pasture and forest catchment.

Type I chemographs (K^{+}, Mg^{2+} and Ca^{2+}) were dominated by a rainfall or throughfall signal in the beginning of events, but by an overland flow signal towards the end of events. Rainfall and throughfall solute concentrations were significantly modified upon contact with the soil surface. Because concentrations rose not only during the falling but also during the rising limb, we conclude that the time water was in contact with the soil surface had a positive effect on concentrations. In the beginning of events, when the covered distance by overland flow was short and only the lower part of the catchment contributed to runoff, concentrations resembled that of rainfall, but as runoff distances increased so did concentrations. Potassium behaved different in that concentrations in the forest were already enriched by canopy leaching (Germer et al., 2007, chapter 3), diminishing the effect of contact with soil surface contact on K^{+} concentrations. In the forest stormflow concentrations did not reach overland flow levels. Forest overland flow was collected only in the upper part of the catchment (Figure 4.1), where it was generated less frequently compared with the lower catchment area, possibly leading to higher overland flow concentrations.

Type II chemographs (Cl^{-}, SO_4^{2-}, NH_4^{+} and Na^{+}) did not increase over time and had very similar chemistry to rainfall and overland flow. The exception was for Cl^{-} in the pasture, where Cl^{-} concentrations fluctuated around the overland flow signal during discharge, indicting that processes other than runoff distance must have been important.

In the pasture catchment, a distinct overland flow signal existed for K^{+}, Cl^{-} and Mg^{2+}. The concentrations of these solutes were highest in overland flow compared to other flowpaths and could not be explained as the result of flowpath mixing. Potassium and Cl^{-} are assumed to be abundant at the soil surface and hence in overland flow due to cattle urine, while Mg^{2+} is concentrated in overland flow and soil solution possibly because of cattle dung input (Figure 4.5) (Buschbacher, 1987; Humphreys, 1991). This distinct overland flow signal in the pasture indicated that overland flow was the main flowpath even towards the end of rainfall events.

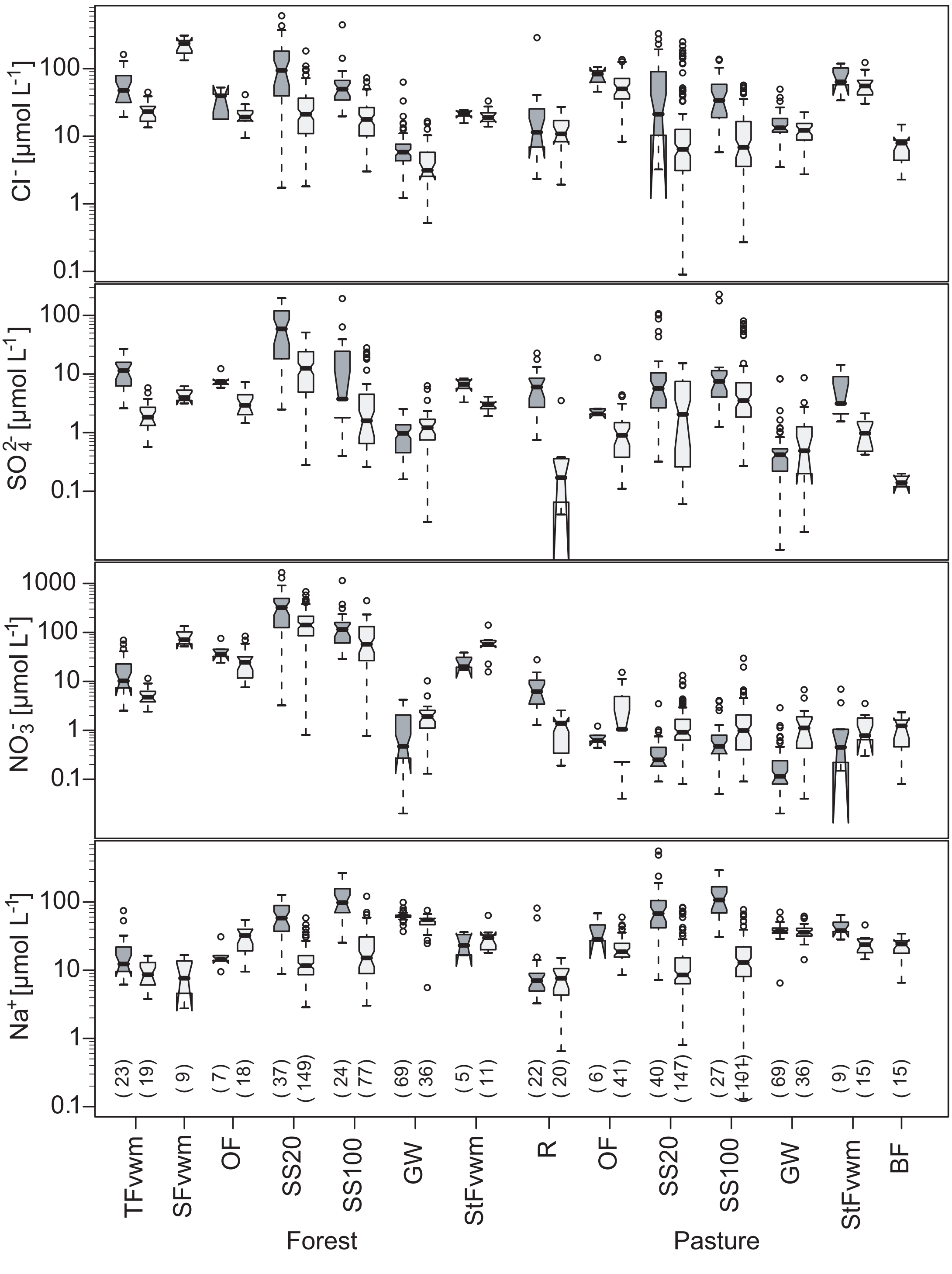


Figure 4.5 Boxplot comparison of NH_4^+, K^+, Mg^{2+} and Ca^{2+} concentrations in different flowpaths for the forest and pasture catchment plotted separately for the TDWS (dark grey boxes) and WS (light grey boxes): TF = throughfall, SF = stemflow, OF = overland flow, SS20 = soil solution at 20 cm depth, SS100 = soil solution at 100 cm depth, GW = ground water, StF = stormflow, R = rainfall and BF = baseflow. For TF, SF and StF volume-weighted event means were used. The numbers in parentheses are the sample sizes. The crossbar within the box shows the median, the length of the box reflects the interquartile range, the fences are marked by the extremes if there are no outliers, or else by the largest and smallest observation that does not qualify for an outlier. Outliers are defined as data points

more than 1.5 times the interquartile range away from the upper or lower quartile. The notches represent the 95% confidence interval for the median, and overlapping notches from two boxes indicate that there is no significant difference between medians. Lower notches are missing if the lower confidence limit is negative, due to the logarithmic y-axis.

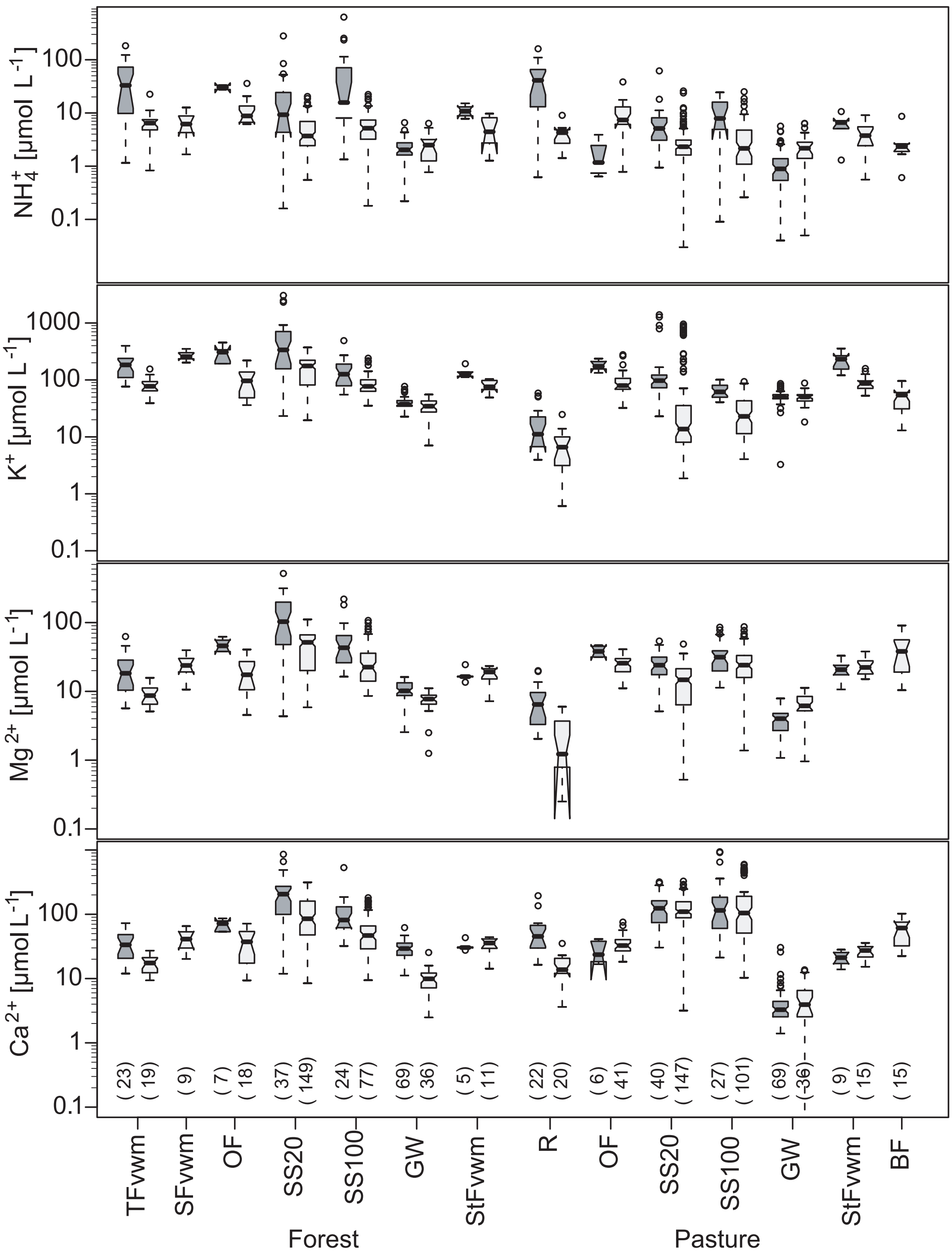


Figure 4.6 Boxplot comparison of Cl^-, SO_4^{2-}, NO_3^- and Na^+ concentrations in different flowpaths for the forest and pasture catchment, plotted separately for the TDWS (dark grey boxes) and WS (light grey boxes). For details see caption of Figure 4.5

No distinct overland flow signal existed in the forest. Overland flow concentrations of all solutes could be explained as a mixture of rainfall or throughfall concentrations and soil solution. A closer look at NO_3^- concentrations provided insight into the contribution of soil solution to total discharge. The relatively small TDWS stormflow events revealed no differences of stormflow and sequentially sampled overland flow NO_3^- concentrations (Figure 4.2). During WS events, however, NO_3^- concentrations in stormflow sampled in the lower part of the forest catchment increased constantly, while sequentially sampled overland flow did not change (Figure 4.3). Initial NO_3^- concentrations in stormflow corresponded to overland flow concentrations and increased to the median value in soil solution at a depth of 20 cm (Figure 4.3) towards the end of storms. We interpret this as indicating increasing soil solution and decreasing overland flow contribution to stormflow, which is in line with results from temperate regions (Britton et al., 1993; Muraoka and Hirata, 1988; Pionke et al., 1988). This interpretation is, however, not strongly supported by an equivalent pattern of K^+ concentrations. Potassium concentrations in stormflow did not increase to the corresponding median soil solution level. Potassium is derived mainly from throughfall (Germer et al., 2007, chapter 3) and is restocked much more slowly to the soil than NO_3^-, which originates mainly from high N mineralization and subsequent nitrification rates within the soil itself (Neill et al., 1997b; Neill et al., 1995). Frequent rainfall events and slower rates of restocking K^+ compared to NO_3^- may explain why stormflow NO_3^- concentrations but not K^+ concentrations did reach soil solution levels at the end of events. Contact with soil also explains patterns of NO_3^- concentrations in forest and pasture (type I in the forest, but type II in the pasture). Nitrate concentrations were increased by contact with the soil in the forest, where soil NO_3^- concentrations were high, but very low NO_3^- concentrations in all flowpaths in the pasture led to fluctuating chemographs.

For type I solutes, differences in initial concentration decreases were found for pasture and forest stormflow chemographs. While initial decreases were obvious in both seasons at the pasture, they were observed only during the TDWS in the forest. Initial concentration decreases can be explained by flushing of solutes from the soil surface during the beginning of events (Avila et al., 1992; Walling and Foster, 1975). In the pasture, cattle likely acted as a source delivering nutrients to the soil surface throughout the year. The litter layer in the forest that was largely decomposed by the end of the TDWS acted as a comparable nutrient source. The differing chemograph hysteresis in pasture and forest probably originated from comparatively higher initial stormflow solute concentrations in the pasture.

4.4.3. Implications of hydrological fluxes on solute fluxes

As pointed out in section 4.1, the land use change had a major impact on the frequency and quantity of overland flow runoff. The increase of overland flow in the pasture is expected to increase total solute outputs in particular for solutes with high concentrations in overland flow compared to groundwater (K^+, Ca^{2+}, Mg^{2+} and Cl^-, Figure 5, 6). This is not true for Ca^{2+} due to its lower concentration in pasture than in forest groundwater. Total K^+, Mg^{2+} and Cl^- pasture output fluxes did increase compared to total forest fluxes. This is, however, not only an effect of increased overland flow in the pasture. As discussed before (section 4.2.), pasture overland flow had a distinct concentration signal for K^+, Mg^{2+} and Cl^-, exceeding the concentration levels of all other flowpaths. Hence land use change from undisturbed forest to pasture increases total K^+, Mg^{2+} and Cl^- output fluxes due to overland flow increase and due to constant nutrient supply from cattle excrement.

The only solute, whose output flux was much higher in the forest than in the pasture was $NO_3^- - N$. Compared to pasture, forest NO_3^- concentrations are slightly higher in groundwater and much higher in overland flow. Therefore, the increase of overland flow in the pasture didn't increase $NO_3^- - N$ output fluxes. It was rather the reduced NO_3^- concentrations in pasture overland flow and groundwater that diminished total $NO_3^- - N$ output fluxes in pasture compared to forest.

4.4.4. Catchments acting as nutrient sinks or sources

Tropical forests on nutrient-poor soils are believed to have developed tight nutrient cycles that minimize nutrient losses (e.g., Brinkmann, 1985; Herrera et al., 1978). Our study supported this general pattern for forest. It also indicated increased losses for some solutes after land-use conversion to pasture. We compared total input and output fluxes to characterize the catchments as nutrient sinks or sources. While the forest K^+ and Mg^{2+} input and output fluxes were balanced, the pasture was a clear source of K^+ and Mg^{2+} (Figure 4.4). Both, the increased frequency and quantity of overland flow and the high K^+ and Mg^{2+} concentrations in overland flow supplied by cattle excrement led to K^+ and Mg^{2+} export from pasture.

Table 4.5 Net solute fluxes (input fluxes minus output fluxes) reported for Amazonia.

		Net fluxes in kg ha^{-1} yr^{-1}							
		Cl^-	$SO_4^{2-}-S$	$NO_3^- - N$	Na^+	$NH_4^+ - N$	K^+	Mg^{2+}	Ca^{2+}
Forest									
Jordan (1982) Northern Amazonia	plot	---	---	---	---	---	8.0	2.8	7.0
Franken & Leopoldo (1984) Central Amazonia	130 ha catchment Barro Branco	17.0	---	---	9.5	5.8	1.7	---	---
	2300 ha catchment Bacia Modelo	5.1	48.7	---	6.3	---	3.9	---	---
Brinkmann (1985) Central Amazonia	several pots and catchments	---	---	---	-2.9	-1.9	---	-0.3	-0.6
Lesack and Melack (1996) Central Amazonia	23 ha catchment	-3.6	0.9	-1.4	-1.2	2.2	0.3	0.1	0.5
this study Southwestern Amazonia	0.7 ha catchment ET_{dry} estimates	6.2	1.1	0.4	-7.7	4.3	-4.5	-0.4	9.6
	0.7 ha catchment ET_{wet} estimates	6.8	1.2	0.5	-4.6	4.4	-1.0	0.1	11.8
Pasture									
Biggs (2006) Southwestern Amazonia	3.9 ha catchment lower estimates	0.0	---	---	-44.0	---	-13.1	---	---
	3.9 ha catchment upper estimates	-3.8	---	---	-80.0	---	-19.5	---	---
this study Southwestern Amazonia	1.7 ha catchment ET_{dry} estimates	-2.3	1.0	0.7	-6.0	4.0	-20.8	-1.4	12.2
	1.7 ha catchment ET_{wet} estimates	-0.3	1.1	0.7	-2.5	4.1	-12.9	-1.0	12.9

Both forest and pasture were sinks for Ca^{2+} and $SO_4^{2-} - S$. Despite increased Ca^{2+} exports in stormflow from the pasture, the Ca^{2+} inputs clearly exceeded outputs in both catchments due to comparatively low concentrations of Ca^{2+} in groundwater compared to rainfall (Figure 4.5). At the same time, the Na^{+} balance in both catchments was negative and Na^{+} groundwater concentration was comparatively high in both catchments. This may have indicated a soil cation exchange of weakly adsorbed Na^{+} in favor of stronger adsorbed Ca^{2+} or from a low content of Ca-bearing mineral in the weathering zone, or both. The fact that both catchments were $SO_4^{2-} - S$ sinks, may be attributed to a permanently high capacity of SO_4^{2-} adsorption by sequioxides, particularly Fe oxides (Johnson et al., 1979; Johnson and Todd, 1984), which are common in Kandiudults. Another solute increasingly exported by the pasture stream is Cl^{-} (Figure 4.4). While the forest was a Cl^{-} sink, inputs and outputs were balanced in the pasture. We found a distinct overland flow signal of very high Cl^{-} concentrations that we attributed to the additional Cl^{-} input from cattle excrement. As this additional Cl^{-} input was not quantified in this study, our Cl^{-} input by rainfall underestimates the actual input.

Both catchments were sinks for $NO_3^{-} - N$ and $NH_4^{+} - N$. But because of gaseous N_2O efflux due to denitrification within the soil and biological N_2 fixation were not quantified, it remains unknown if the catchments were overall N sinks or sources.

4.4.5. Regional comparison

From a global and regional comparisons of solute input-output budgets for tropical forests it has been concluded that the results are highly variable due to differing lithology, soil type and fertility, and climatic conditions (Bruijnzeel, 1991). The few nutrient budgets for the Amazon forest (Table 4.5) also show quite contrasting results. They should, however, be interpreted with caution because some studies are either not catchment-based (Jordan, 1982), apparently ignore solute export per groundwater (Brinkmann, 1985) or ignore concentration changes during stormflow conditions (Franken and Leopoldo, 1984), whose importance has been highlighted elsewhere (Elsenbeer et al., 1996). The only catchment-based study considering several flowpaths was that of Lesack and Melack (1996) in Central

Amazonia. These authors measured slight net outputs for $SO_4^{2-} - S$, TN, K^+, Mg^{2+} and Ca^{2+}. This study was based on a 1 in 10 wet year, which generated more runoff than normal. With this in mind, Lesack and Melack (1996) concluded that for average runoff volumes, the catchment ecosystem was roughly in equilibrium for these solutes. It was, however, a source of Cl^- and Na^+. Our findings were in line with these results for a central Amazonian catchment, except that our site was a clear sink for Cl^-.

For pasture, our results were similar to the only other published study. Biggs et al. (2006) considered several flowpaths in their nutrient budget study for a pasture catchment in Rondônia and reported net exports for K^+ and Na^+, but balanced inputs and outputs for Cl^-. The Na^+ exports reported by Biggs et al. (2006), however, exceed ours by more than a magnitude. Unfortunately the authors not provide information on Ca^{2+} flux, which seemed to explain the Na^+ loss in our pasture.

4.5. Conclusions

In a paired-catchment study we could show that solute output fluxes and the proportional contribution of single flowpaths to watershed discharge differed between forest and pasture. While the forest was a sink for Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, and Ca^{2+}, about balanced for K^+ and Mg^{2+}, and a source of Na^+, the pasture was a sink for NO_3^-, SO_4^{2-}, NH_4^+, and Ca^{2+}, balanced for Cl^-, and a source of Na^+, K^{++}, and Mg^{2+}. These differences in solute balances between forest and pasture resulted from land-use change effects. Pasture cultivation led to decreased permeability, which increased the frequency and volume of quickflow. Increased quickflow resulted in higher output fluxes for solutes with higher concentrations in overland flow than groundwater. This effect was reinforced by some solutes with elevated concentrations in pasture compared to forest, possibly due to cattle excrements. While the land-use change effect on hydrology seems to be dampened in larger catchments the effect of land-use change on solute budgets in larger catchments is still not well known. Further research is needed to understand these scaling effects.

5.
Influence of land use change on near-surface hydrological processes: Undisturbed forest to pasture

Abstract

Conversion of undisturbed forest into pasture is a common type of land-use change in Amazonia. Deforestation and the introduction of pasture are both recognized causes of soil compaction. Compacted soil beneath pasture has lower hydrologic conductivity than soil that supports a forest. As a direct consequence the frequency as well as the volume of overland flow increases. We investigated the effect of land-use change from undisturbed forest to pasture on the frequency of several conditions: perched water table, overland flow and stormflow. We compared the results with the frequency estimated from comparisons of rainfall intensity and soil hydrologic conductivity. In addition, we looked at stormflow generation processes beneath undisturbed forest and pasture and evaluated different approaches to flowpath identification. The frequency of soil saturation was estimated to double as a result of land-use change. This corresponds well to the observed increase in the frequency of stormflow, overland flow and perched water table. The stormflow volume augmented 17 times. This disproportional increase of stormflow resulted from overland flow generation on large pasture areas. In contrast, the overland flow generation along the concentration line in the forest was spatially limited. In both catchments, stormflow was generated by saturation excess because of perched water tables and due to surface-near groundwater levels. Storm-flow was additionally generated in the forest by rapid return flow from macropores and in the pasture by slow return flow from a continuous perched water table. This detailed hydrologic study seemed the most suitable approach to flowpath identification. This basis for the interpretation of results is as essential as more chemical approaches, such as hydrograph-chemograph comparisons or end-member mixing analysis. To assess the biogeochemical significance of hydrologic alterations after land-use change, that is the effect on nutrient budgets, these chemical approaches are, however, indispensable.

* With Neill, C., Krusche, A.V. and Elsenbeer, H. in preparation for submission to *Journal of Hydrology*

5.1. Introduction

Land-use change from undisturbed forest to agricultural land drastically modified the appearance of waste areas in the tropics, as illustrated by satellite images of tropical areas around the world (Achard et al., 2002). While the most apparent modification is the change of vegetation itself, the hydrology and nutrient balance of the ecosystems are also altered. The alteration of stormflow generation is driven by changes to physical characteristics of the soil, which are predominantly caused by compaction during and after the conversion of undisturbed forest to pasture. Soil compaction increases in bulk density and penetration resistance as a result of deforestation and land management practices. With the decrease in porosity, both infiltration rate and hydrologic conductivity are lowered (Alegre and Cassel, 1996; Chauvel et al., 1991; Martínez and Zinck, 2004; McDowell et al., 2003). Deforestation with heavy machinery and the introduction of cattle are reported to reduce macroporosity and hydrologic conductivity (Chauvel et al., 1991; Martínez and Zinck, 2004; McDowell et al., 2003).

In order to assess the soil compaction effect on the catchments' hydrology several authors (e.g. Johnson et al., 2006; Zimmermann et al., 2006) restricted their field methods on the measurement of the infiltrability and the hydraulic conductivity of soils. By comparing the hydraulic conductivity of soils with intensity of rainfall they estimated the frequency of perched water table generation in different soil depths and the generation of saturation or infiltration excess overland flow. Land-use change from undisturbed forest to pasture is known to decrease hydraulic conductivity and consequently increase the frequency and volume of overland flow (Germer et al., submitted; Moraes et al., 2006; Ziegler et al., 2004; Zimmermann et al., 2006). Questions arise from these studies, as follows:

a) Whether or not the estimated frequency corresponds to the observed frequency of perched water tables; and
b) If the frequency of perched water table occurrence is the only hydrologic change that occurs as a consequence of the change in land-use.

Corresponding observed and estimated frequencies of perched water table occurrence might allow the quantifation of the increase in stormflow after land-use change by measurement of the increase of hydrologic conductivity.

The aims of this paper were:

1) To study the relationship between the expected and observed frequency of saturated soil conditions
2) To compare the generation of stormflow in undisturbed forest and pasture, including differences in frequency and duration of saturated conditions; and
3) To compare physical and chemical based methods for identification of stormflow generation processes regarding their suitability for flowpath identification and conclusions about the geochemical relevance of different flowpaths.

5.2. Study area and methods

5.2.1. Study area

Rancho Grande, the study site, is located approximately 50 kilometres south of Ariquemes (10˚18′S, 62˚52′W, 143 m a.s.l.) in the Brazilian state of Rondônia, in the southwestern Amazon Basin of Brazil. The area is part of a morphostructural unit known as “Southern Amazon Dissected Highlands” (Planalto Dissecado Sul da Amazônia, Peixoto de Melo et al., 1978), which is characterized by pronounced topography with an altitudinal differential of up to 150 metres. Remnant ridges of Precambrian basement rock composed of gneisses and granites of the Xingu (Leal et al., 1978) or Jamari Complex (Isotta et al., 1978), are separated by flat valley floors of varying width. The climate is tropical wet and dry (Köppen’s Aw). The mean annual temperature between 1984 and 2003 was 27°C. The mean annual precipitation during the same period was 2 300 mm a^{-1} with a marked dry period from July to September (Germer et al., 2006).

We selected adjacent forest (1.37 ha) and pasture (0.73 ha) catchments approximately 400 m apart. Both catchments are drained by 0-order ephemeral streams and underlain by Kandiudults (Zimmermann et al., 2006). The forest vegetation at Rancho Grande is predominantly terra firme undisturbed open tropical rainforest (Floresta Ombrófila Aberta) with a large number of palm trees. Open tropical rainforest is the predominant vegetation type within the transition zone from dense rainforest to cerrado vegetation (savanna) in the southern Amazon (IBGE, 2004b), and amounts to 55% of the total vegetation area in Rondônia (Pequeno et al., 2002). The pasture was cleared and burned twice, in 1980 and 1981. Since 1984 the pasture has been grazed by one head of cattle per hectare, tilled once, in 1993, and planted with *Brachiaria humidicola* (Zimmermann et al., 2006).

5.2.2. Field measurements

A similar hydrological and hydrochemical sampling design (Figure 5.1) was set up in August 2004 in both catchment areas. The instruments in the pasture were protected against disturbance by cattle with fences.

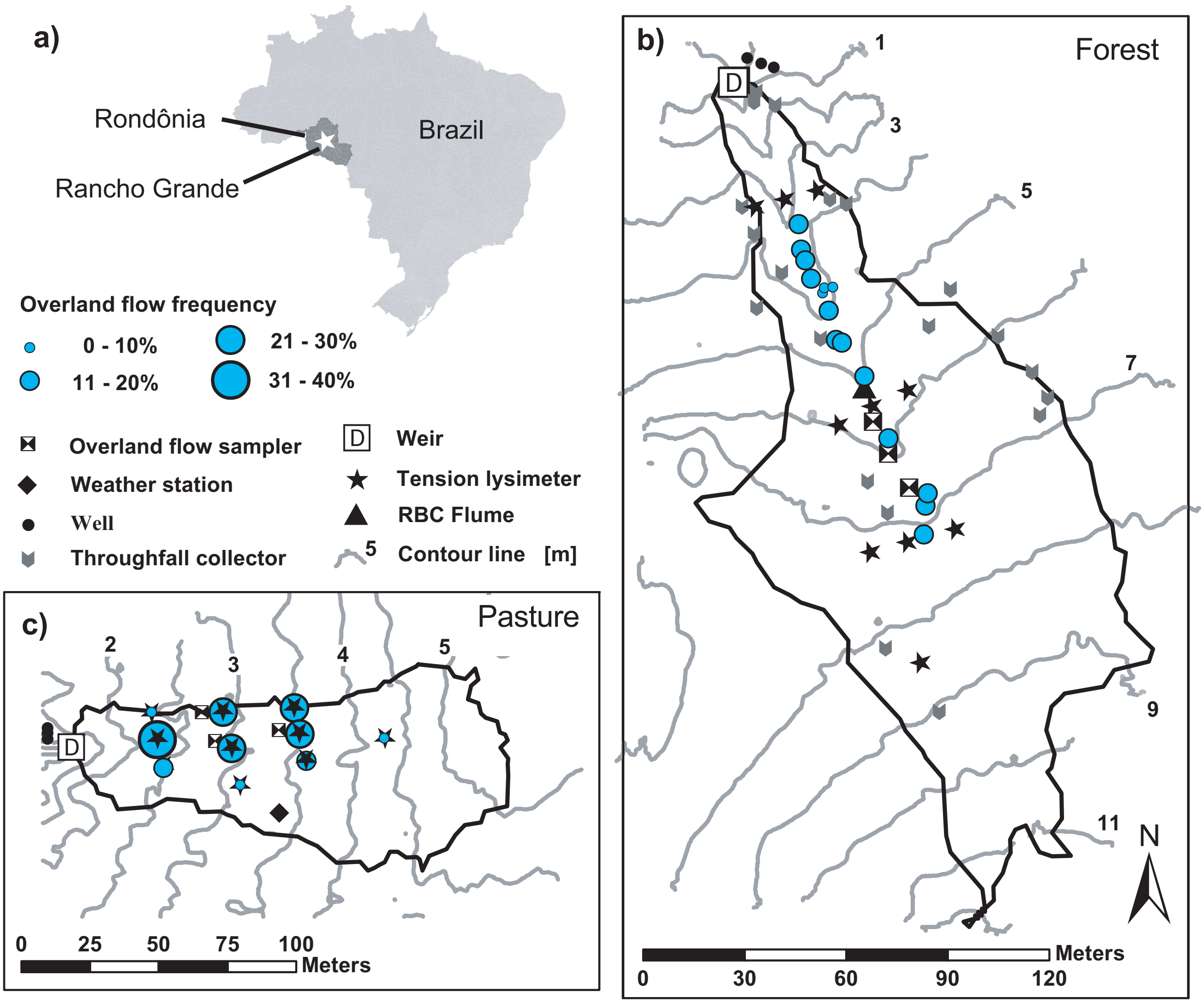


Figure 5.1 Map of the study site (a) and detailed maps for the forest (b) and pasture (c) catchments, showing instrumentation sites, observed overland flow frequency, and contour lines (meter). Wells for recording groundwater levels and piezometers up to a depth of 12.5, 20 and 50 cm for perched water table monitoring were situated in each instrument nest.

A tipping bucket rain gauge (Hydrological Services P/L, Liverpool Australia) with a resolution of 0.254 mm and a Campbell logger recorded five-minute rainfall intensity values adjacent to the pasture catchment. Both watersheds were equipped with 1.0 ft H-flume-type weirs for stream-flow monitoring (Blaisdell, 1976; Gwinn and Parsons, 1976) and water levels were recorded with TruTrack loggers every five minutes from September through November 2004 and from January to mid-April, and every fifteen minutes in December 2004 and from mid April to July 2005. Due to limited accuracy of low flow in the H-flumes, only events with a maximal discharge height greater than one centimeter were qualified as stream flow discharge events.

A total of 30 piezometers were installed in each catchment to monitor the existence and frequency of subsurface flow. In each instrument nest three piezometers were installed to a depth of 12.5, 20 and 50 cm. The piezometers were composed of a PVC tube with 24 mm inner-diameter, which was hammered into the soil to avoid gaps and artificial vertical flow between tube and soil. The piezometer hammer consisted of a metal rod of 23 mm diameter and slide hammer. Four piezometer triplets per catchment and event were equipped with TruTrack loggers recording water levels every five minutes. Logger positions were rotated over the study period to obtain water levels for a subset of events for each piezometer triplet.

One overland flow detector (Kirkby et al., 1976) was placed in each instrument nest in the pasture, while in the forest overland flow detectors were placed at 15 locations along the channel. Previous field observations (February 2004) during intense rainfall events indicated that overland flow did not occur in the forest at a certain distance from the channel. Groundwater levels were recorded with TruTrack WT-HR water height data loggers in the forest and Orphimedes (OTT Messtechnik) in the pasture at the 10 instrument nests in each catchment. Wells were drilled to a depth of 2-4 meters with a hand auger and equipped with a 5 cm diameter PVC casing.

Rainfall intensity and stream flow was monitored from August 2004 to July 2005. For the same hydrological year, we logged perched water levels from the end of September to the end of March and groundwater levels from January to July. Overland flow was monitored from mid-October to mid-March, excluding December and the first ten days of January.

5.3. Results

5.3.1. Runoff response

The total incident rainfall at Rancho Grande from August 2004 to July 2005 was 2 286 mm, similar to the mean annual rainfall of 2 300 mm between 1984 and 2003. Total annual discharge was less frequent and much smaller in the forest (24 mm) than in the pasture (416 mm, Table 4.1). The cumulative curves of rainfall and stormflow illustrate that total discharge in the forest was dominated by two subsequent events, with 59% of total annual discharge, while in the pasture the same events generated just 17% of the total annual discharge (Figure 5.2). Smaller events were much more important for total annual discharge in the pasture than in the forest. Baseflow added little to total stormflow in both catchments (Germer et al., submitted). Continuous baseflow was detected from March 6 to March 9 in the forest and from January 20 to March 16 in the pasture. The onset of events that generated stormflow in both catchments were simultaneous in the pasture and the forest areas for 25 out of 37 events. However, stormflow response times to rainfall observed in the central well of transect 1 were shorter in the pasture during times of shallow groundwater levels compared to during the rest of the monitoring period (February 21 to March 20, $p<0.01$, Wilcoxon rank sum test). No temporal differences were recorded in the forest.

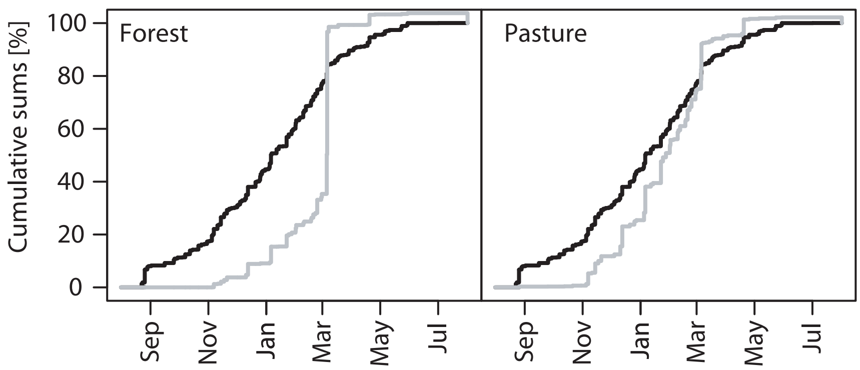


Figure 5.2 The cumulative sums of rainfall (black line) and stormflow (grey line) from August 2004 to July 2005.

5.3.2. Piezometric response

The sum of measured water level within the piezometers (pressure head) and the elevation head equals the total head. Water flows from high to low total head. Piezometric responses were observed in both catchments. While the 50 cm piezometers only responded to groundwater rises during periods of high groundwater levels (see section 5.3.4), the piezometers in 12.5 and 20 cm soil depth did respond to perched water table development, independently of groundwater levels. Although the pressure head varied in magnitude for different rainfall events, the response patterns for individual sites were consistent over time. The differences between forest and pasture piezometric responses were exemplified for a 64 mm rainfall event on November 14, 2004 (Figure 5.3, 5.4), during which piezometer water levels were logged in the central parts of the catchments (all nests of transect 2 and middle nest of transect 3).

During the November 14 event four out of eight piezometers responded in the forest, but only one had still a positive pressure head after stormflow ended (Figure 5.3). All sites exhibited downward water flow throughout the transition from dry to wet season (TDWS) event in the forest. The double-peak rainfall event was mirrored by the stormflow hydrograph and the orographic right piezometer pressure head in 12.5 cm depth, but not by the other three responding piezometers located within the channel. Pressure heads developed at 12.5 cm soil depth in the forest even though they were not expected according to median K_{sat} (131 mm h^{-1}). For the same event seven out of eight piezometers responded in the pasture and all pressure heads persisted after stormflow ceased (Figure 5.4). While the piezometers at most sites (Figure 5.4b, d, e) indicated downward water flow throughout the event, in the middle nest of transect 2 they showed a gradient change from downward to upward flow direction after 8:00 AM.

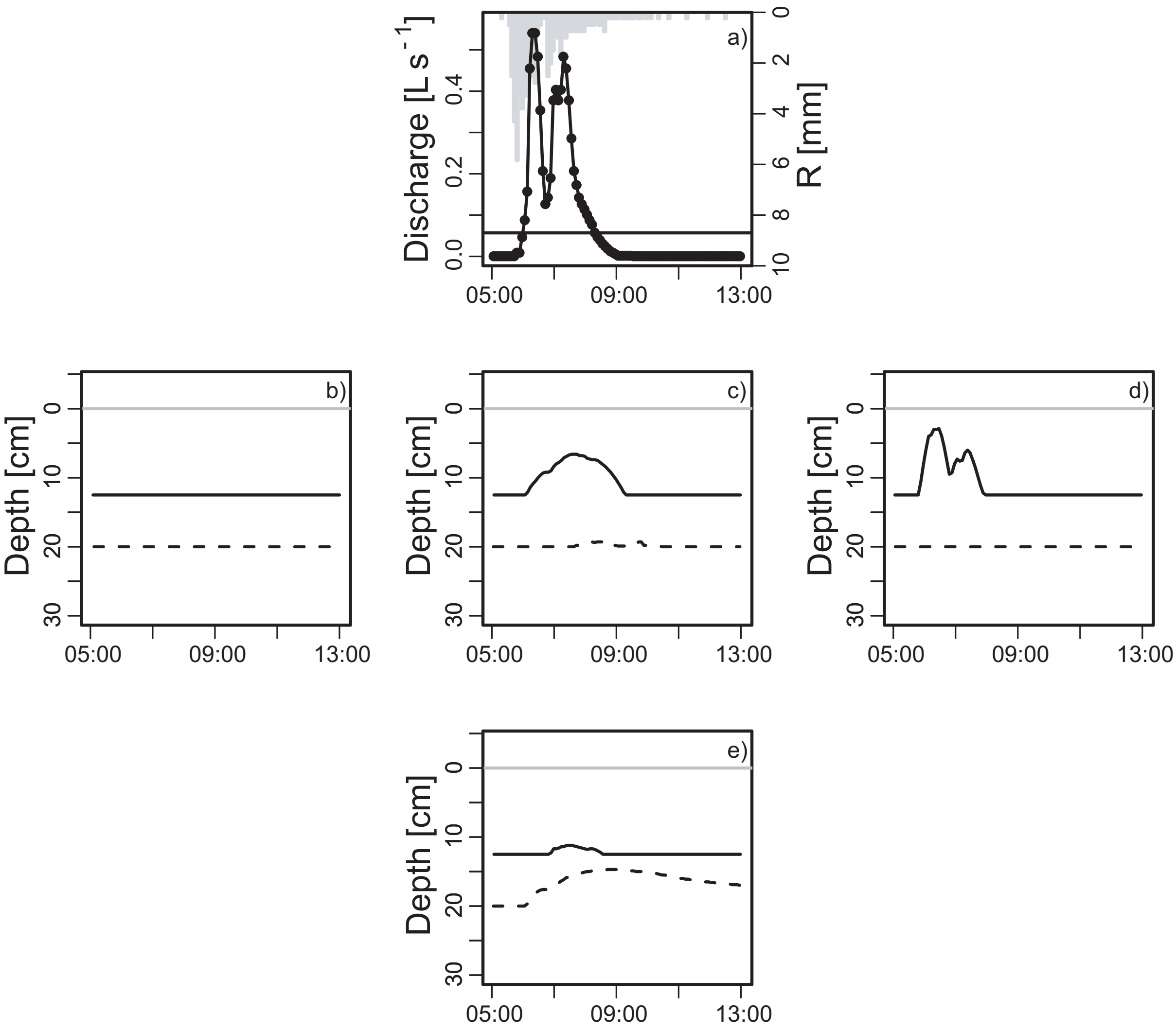


Figure 5.3 Forest stormflow hydrograph (plot a, line) response to rainfall (plot a, bars) for a 64 mm event on November 14, 2004 and the corresponding perched water table responses at the left (plot b), middle (plot c) and right (plot d) instrument nest on transect 2 and the middle nest on transect 3 (e). Pressure heads of perched water tables relative to the soil surface (grey line) are given for the soil depth of 12.5 cm (solid black line) and 20 cm (dashed black line).

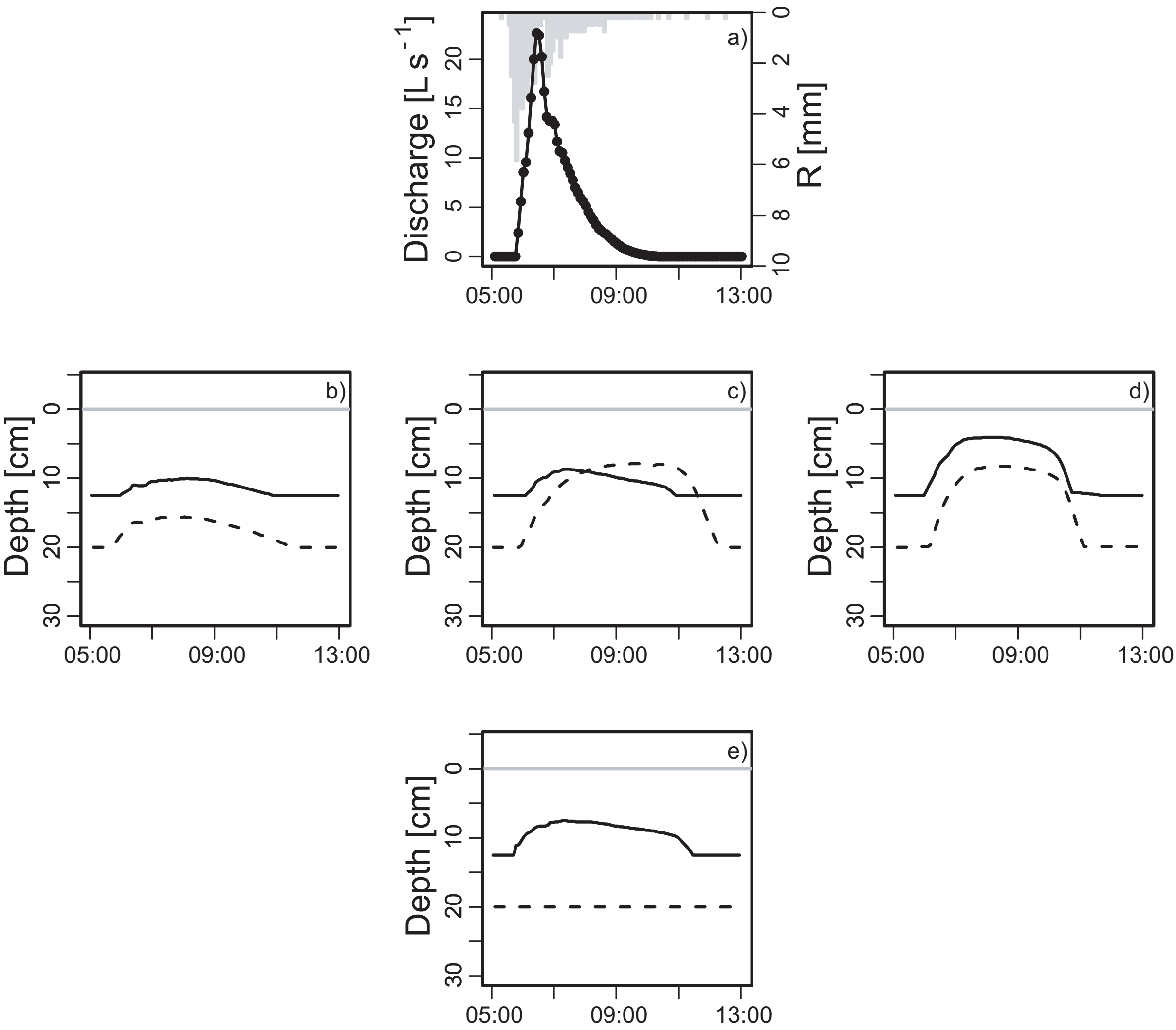


Figure 5.4 Pasture stormflow hydrograph (plot a, line) response to rainfall (plot a, bars) for a 64 mm event on November 14, 2004 and the corresponding perched water table responses at the left (plot b), middle (plot c) and right (plot d) instrument nest on transect 2 and the middle nest on transect 3 (e). Pressure heads of perched water tables relative to the soil surface (grey line) are given for the soil depth of 12.5 cm (solid black line) and 20 cm (dashed black line).

Table 5.1 Frequency of stormflow and perched water table (PWT) response during the period from September 25, 2004 to March 29, 2005 with a total of 139 rainfall events. The column 'per site' indicates the response frequency of ≥ 2 piezometers at least in on depth per site.

	Stormflow	**Observed PWT frequency** Response of ≥ 2 piezometers			**Predicted PWT frequency**	
		12.5 cm	**20 cm**	**per site**	**12.5 cm**	**20 cm**
Forest	32 (23%, 378 mm)	14 (10%)	6 (4%)	15 (11%)	0%	27%
Pasture	60 (43%, 22 mm)	34 (24%)	34 (24%)	41 (29%)	27%	52%

This event illustrates typical piezometer responses in the forest and pasture. During the piezometer monitoring period 139 rainfall events were registered. In the forest, piezometer responses were observed more frequently in 12.5 cm than in 20 cm soil depth, while in the pasture the frequency was equal in both depths (Table 5.1). The piezometers responded more often in the pasture than in the forest; twice and five times as often in 12.5 and 20 cm depth, respectively (Table 5.1). Saturated soil conditions persisted longer in the pasture compared to the forest (Table 5.2). For example, from the beginning of December to mid January, the soil in the middle nest of the third transect was saturated for 21 hours in the pasture, while it was saturated for less than one hour in the forest. Upward water flow was observed only twice in the orographic right side of the forest catchment, but it was more common in the pasture. While the total head in 20 cm of soil exceeded that in 12.5 cm eight times in the middle of the pasture catchment (transect 2), it did so once on each side (transect 2). The water level in a piezometer (middle nest transect 2, 12.5 cm) was observed to exceed the soil surface once in the pasture.

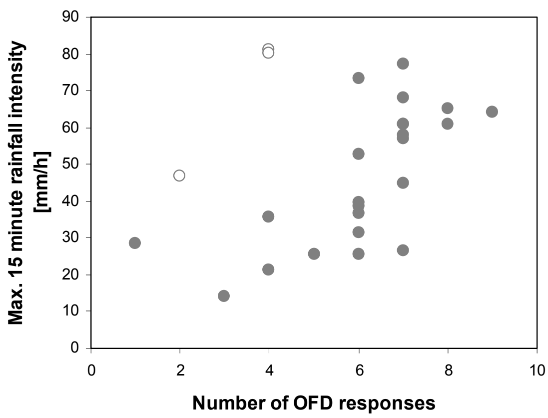
Table 5.2 Comparison of perched water table durations [minutes] in the forest and pasture as monitored at 12.5 and 20 cm soil depths in the catchments second and third transects according to Figure 5.1. Perched water table durations are listed for single events and as total duration for two different periods.

	Left nest				**Middle nest**				**Right nest**			
	Forest		**Pasture**		**Forest**		**Pasture**		**Forest**		**Pasture**	
Second transect	**12.5 cm**	**20 cm**	**12.5 cm**	**20 cm**	**12.5 cm**	**20 cm**	**12.5 cm**	**20 cm**	**12.5 cm**	**20 cm**	**12.5 cm**	**20 cm**
2004-11-04	0	0	355	363	15	0	80	210	15	50	305	190
2004-11-06	0	0	281	105	75	0	160	230	50	80	225	205
2004-11-10	0	0	205	55	35	0	105	200	50	0	145	155
2004-11-14	0	0	290	335	190	0	285	385	125	0	335	295
2004-11-17	0	0	295	75	20	0	135	230	60	25	180	140
2004-11-20	40	0	210	60	20	0	135	235	100	0	245	175
Sum	**40**	**0**	**1636**	**993**	**355**	**0**	**900**	**1490**	**400**	**155**	**1435**	**1160**
Third transect	**12.5 cm**	**20 cm**	**12.5 cm**	**20 cm**	**12.5 cm**	**20 cm**	**12.5 cm**	**20 cm**	**12.5 cm**	**20 cm**	**12.5 cm**	**20 cm**
2004-12-04	0	0	0	20	0	0	120	0	0	0	0	0
2004-12-10	0	0	0	5	0	0	180	0	0	0	120	10
2004-12-12	0	20	0	10	0	20	0	50	0	0	150	100
2004-12-20	0	0	0	0					0	0	0	0
2004-12-25	0	0	0	0	0	0	190	0	0	0	0	0
2004-12-26	0	0	0	0	0	0	470	0	0	0	0	0
2005-01-05	0	0	0	0	0	0	0	30	0	50	210	0
2005-01-11	0	0	0	0	0	0	315	0	0	0	0	0
Sum	**0**	**20**	**0**	**35**	**0**	**20**	**1275**	**80**	**0**	**50**	**480**	**110**

5.3.3. Overland flow response

Similar differences were observed for overland flow in the forest and pasture as for piezometer response. Overland flow detectors (OFD) responded about twice as often in the pasture as in the forest (Figure 5.1). Overland flow in the forest was only observed near the channel. In the pasture, overland flow could be observed over almost the whole catchment area for some events, but for others it was observed more frequently in the middle instrument nests of the three transects. For the first events after the end of the dry season overland flow was detected in fewer places in the pasture than for later events with similar intensities (Figure 5.5). This was not observed in the forest. Most of the events with more than 50% OFD responses in the pasture had maximum 15-minute rainfall intensities above 40 mm h^{-1} (Figure 5.5). The generation of stormflow in the forest did not always occur with overland flow generation within the monitored stream-bed section. In the pasture for each event that generated stormflow we also observed the generation of overland flow, but overland flow developed without a perched water table in 12.5 cm depth (two thirds of all monitored OFD events) or in both depths (one third of all monitored OFD events).

Figure 5.5 Number of overland flow detector (OFD) responses per event in the pasture plotted against the maximum fifteen minute rainfall intensity. The first three events of overland flow occurrence after the dry season are highlighted (open circles).



5.3.4. Groundwater response

Groundwater level rose faster during recharging conditions in the forest than in the pasture and at the beginning of groundwater monitoring (January 22, 2005) water levels were observed at 2 and 1 meter depths in the middle wells of the first instrument nest transects in the forest and pasture, respectively (Figure 5.6). Therefore we suppose that after the end of the dry season groundwater had fallen to lower levels in the forest compared to the pasture. Groundwater levels peaked in both catchments after the two big events on March 5 and 6 with 58 and 72 mm rainfall, respectively. Thereafter rainfall events exceeding 20 mm were rare and did not occur before mid April, when groundwater levels had fallen below 2 meters in most of the wells. Therefore groundwater level response to rainfall was minor after the beginning of March. Groundwater levels rose up to the soil surface only in the middle well of the first instrument nest transects in both catchments (Figure 5.6). Groundwater levels remained next to the soil surface for one week in the forest, but only for two days in the pasture. In both catchments, however, these wells recorded water levels above 0.5 m during one month (forest: February 22 – March 27, pasture: February 19 – March 20). For all wells water levels fell faster in the forest compared to the pasture.

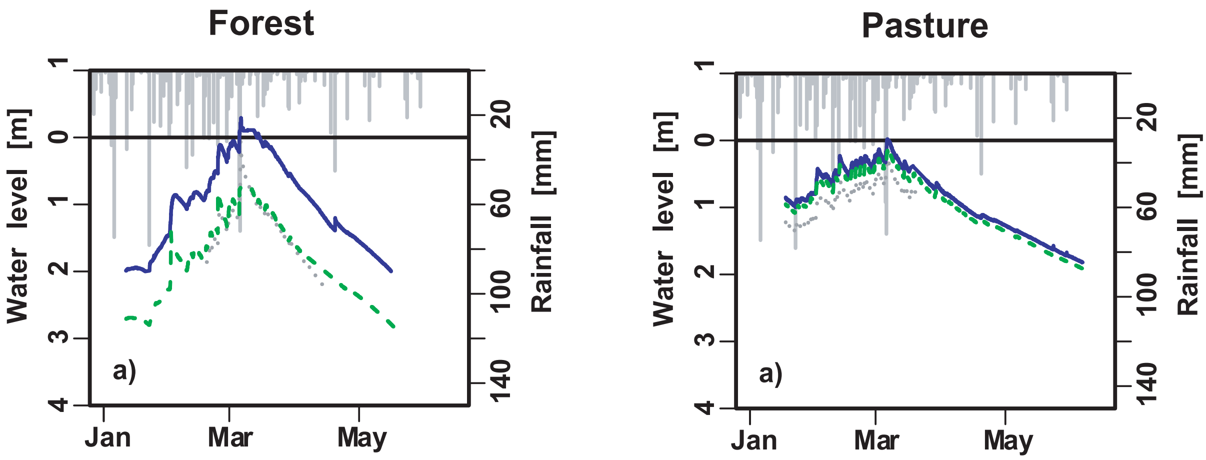


Figure 5.6 Groundwater levels in the forest (left) and pasture (right) of the orographic left (dashed line), middle (solid line) and orographic right (dotted line) well of transect 1. Water levels are given in depth relative to the soil surface. Bars from the top of each figure indicate the total rainfall per event.

5.4. Discussion

Land-use change from undisturbed forest to pasture is known to change physical soil characteristics, including bulk density, penetration resistance, porosity (Martínez and Zinck, 2004; Moraes et al., 1996) and near-soil-surface hydraulic conductivity (Lal, 1996; Moraes et al., 2006; Zimmermann et al., 2006). The decrease of hydrologic conductivity due to land-use change form undisturbed forest to pasture at our site provoked a more frequent development of perched water tables with longer persistence once they had developed. As a consequence We also observed an increase of overland flow frequency and volume,as a consequence. This effect is in line with elevated subsurface stormflow, overland flow and perched water table frequency found in a pasture compared to a forest under a Haplustox in Eastern Amazonia (Moraes et al., 2006) and it aligns with expectations of land-use change effects on physical soil properties. There is, however, much more that we can learn from the differences in the hydrology of both catchments as discussed in the following paragraphs.

5.4.1. Observation of saturation excess

Stormflow, overland flow and perched water tables at 12.5 cm depth were observed twice as often in the pasture compared to the forest (Table 5.1). The same relationship was expected from the hydrologic conductivity differences at 20 cm depth. The absolute frequency of perched water table occurrence was, however, lower than expected because saturation might have occurred above but not at the 12.5 cm piezometers during very intensive and short rainfall events. As the dynamic of the systems is very fast, it can be expected that for some events saturated conditions did not remain long enough to establish pressure heads and generate overland flow. These comparisons indicate that the relative frequency of saturated conditions might be estimated from hydrologic conductivity if we look at the 'correct' depth, which might be the depth of the greatest permeability change under the original land use. Following the land-use change the frequency increase was, however, much lower than the volume increase of stormflow (Table 5.1). This was probably due to a much smaller contributing area in the forest.

Table 5.3 Median and median absolute deviation (MAD) of the infiltrability and saturated hydrologic conductivity at 12.5 and 20 cm depth under forest and pasture (data source: Zimmermann et al., 2006).

	Infiltrability [mm h^{-1}]		**K_{sat} at 12.5 cm [mm h^{-1}]**		**K_{sat} at 20 cm [mm h^{-1}]**	
	Median	MAD	Median	MAD	Median	MAD
Forest	1690	501	131	137	22	17
Pasture	113	50	22	17	6	3

During November 2004 all of the events that generated perched water tables had maximum thirty minute rainfall intensities above the median K_{sat} (22 mm h^{-1}), measured at 20 cm and 12.5 cm soil depth in the forest and pasture, respectively. One could expect perched water to develop in all monitored piezometers in both catchments given the small differences of depth in which the same K_{sat} was measured in both catchments and hence differences in water depth to saturate the soil (e.g. 50% porosity: 10 mm maximum in forest and 6.25 in pasture) combined with high rainfall totals during November 2004. This was the case for the pasture, but not for the forest (Table 5.2). Variable perched water tables over short (10 m) distances have been reported previously for shallow soils in southwestern Australia (Cox and McFarlane, 1995). The authors concluded that the thickness and hydraulic conductivity of the soil above the impeding layer were the most important factors affecting the occurrence of perched water tables. The higher K_{sat} median absolute deviation (MAD) at 12.5 cm soil depth in the forest compared to the pasture (Table 5.3) supports the high importance of K_{sat} affecting small scale perched water table differences in the forest. A possible explanation for this variability might be local fast bypass water flow through the unsaturated soil as reported by Randulovich et al. (1992) for microaggregated tropical soils at La Selva Biological Station, Costa Rica. Macropores due to bioturbation were abundant up to a soil depth of 15 cm in our forest (Sobieraj et al., 2004) and return flow from soil pipes was observed during our study in the forest stream channel. This explains why perched water tables were observed more frequently in 12.5 than in 20 cm soil depth in the forest, as the impeding layer is situated between these two depths. In the pasture the same perched water frequency was observed in both depths, due to the small hydrologic conductivity difference and hence the absence of an abrupt change of permeability.

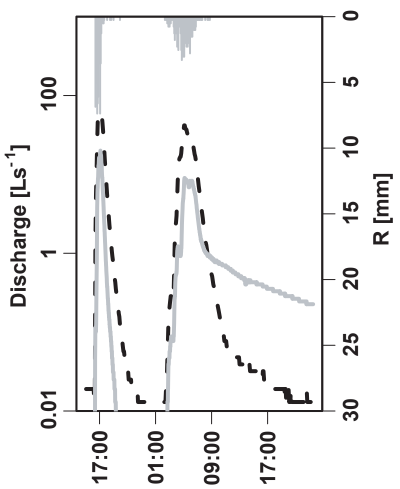
5.4.2. Land-use effect on stormflow generation

The more homogenous pattern of perched water table occurrence and the longer persistence of perched water tables in the pasture, explain the observation of overland flow over a larger area in our pasture catchment compared to the spatially limited occurrence along the concentration line in our forest catchment. Overland flow was generated by saturation excess as a result of rainfall falling on saturated soil above an impeding layer. Frequent and extensive overland flow in the pasture due to extensive perched water tables is one reason for the substantially increase of stormflow volumes compared to the forest.

Stormflow tended to start simultaneously in both catchments, but it rose more rapidly in the pasture during near-soil-surface groundwater levels. Near-surface groundwater levels during the peak of the wet season in the pasture and forest indicated, however, a second mechanism of increased overland flow generation in both catchments: saturation excess due to rainfall on an area of groundwater table emergency (return flow), which expands during rainfall events (Dunne and Black, 1970a; Dunne and Black, 1970b). The latter mechanism is known as the 'variable source area concept' (Hewlett and Hibbert, 1967).

Return flow was a third mechanism of overland flow generation that could be observed in the forest and pasture, but the underlying processes differed between catchments. The March 6, 2005 event was the only one during which forest baseflow (0.64 mm) exceeded pasture baseflow (0.25 mm). Comparison of the forest and pasture hydrographs of two successive rainfall events provides evidence of high return flow rates in the forest (Figure 5.7). Fast return flow is related to macropore flow and was observed in the forest at the end of the second stormflow event on March 6, 2005, but not for the first stormflow event on March 5, 2005. In contrast, frequent upward water flow in the middle of transect 2 in the pasture indicated slow lateral subsurface stormflow and return flow. For this event, the contribution of return flow to total stormflow was smaller for pasture than for forest due to low near-surface conductivities in the pasture.

Figure 5.7 Comparison of forest (grey solid line) and pasture (black dashed line) hydrographs from March 5-6, 2005. Discharge is plotted on a logarithmic scale to show small flow differences more clearly. Bars in the top of the figure indicate 5-minute rainfall (R) sums.



5.4.3. Comparison of different approaches for flowpath identification

Within the overall project of our study, three different approaches with differing key questions provided information about flowpaths that contributed to total runoff (Figure 5.8). This study is the physical approach based on a detailed hydrologic study of the two catchments. A combined physical and chemical approach that compared hydrographs and chemographs of stormflow was part of a second study (Germer et al., submitted). An end-member-mixing analysis (EMMA) (Chaves et al., 2007) provided the chemical based approach. All three approaches highlighted the overall importance of overland flow to total stormflow. As the EMMA did not use overland flow as an end-member in the forest it simply provided indirect evidence of the high contribution of overland flow by arguing that it is a mixture of throughfall and soil solution. Comparison of hydrographs and chemographs could show that overland flow is the main flowpath in the pasture due to distinct overland flow signals for K^+, Cl^- and Mg^{2+}. EMMA also demonstrated that overland flow had a distinct chemical signal. The interpretation of overland flow as a mixture of other end-members was not possible due to its location within the lower dimensional space. Although the EMMA indicated a greater percentage of soil solution contribution to total runoff in the forest than in the pasture, a conclusion of the involved flowpaths was not possible. Both, the combined and the hydrologic approach gave evidence of quick return flow through macropores in the forest, but not in the pasture. The comparison of hydro- and chemographs indicated the existence of return flow due to increased NO_3^- stormflow concentrations up to soil solution levels, but the same was not supported by K^+ concentrations. The authors interpreted these different patterns with a higher restocking rate of NO_3^- compared to K^+. The existence of macropore flow was supported by this study. The only contradiction that arose from comparing the three studies was the relative high proportion of groundwater contribution to total stormflow that resulted from the EMMA approach. This would not be expected from a hydrologic point of view due to the low proportion of slow baseflow compared to the amount of quick stormflow. The EMMA study was, however, a seasonal based study and it would be interesting to apply this technique on an event basis to investigate the reason for this contradiction.

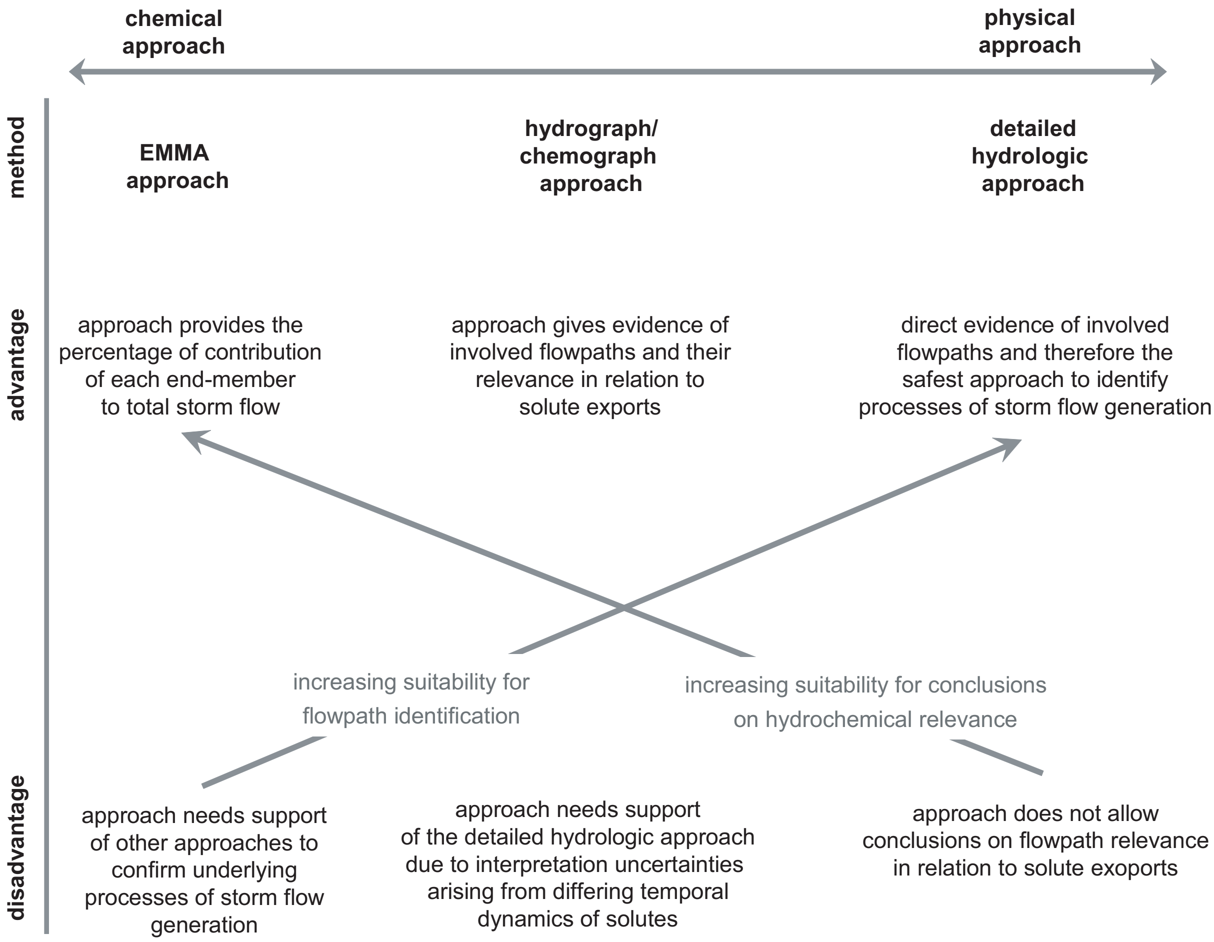


Figure 5.8 Comparison of different approaches for hydrological flowpath identification and their relevance for catchment hydrochemistry.

Comparison of the three approaches suggests that each one has its advantages and disadvantages (Figure 5.8). The physical approach provides direct evidence of involved flowpaths and is, therefore, the safest approach to understanding the process of stormflow generation. It does not, however, provide information on the biogeochemical relevance of the involved flowpaths. Conversely, the chemical based approach provides the percentage of contribution of each end-member to total stormflow, but it does not directly consider involved flowpaths and therefore requires the support of more physical approaches. The combined approach provides evidence of the involved flowpaths and their relevance in relation to solute exports but does require the support of the detailed hydrologic approach due to interpretation uncertainties arising from differing temporal dynamics as described above. We can conclude that the chemical approach is more suitable for making assumptions about geochemical relevance than the physical approach, while the physical approach is more suitable for flowpath identification and therefore increased understanding of the underlying processes. Additionally we can state that the detailed hydrological approach alone is reliable without the verification of other methods. The combined approach requires information from the detailed hydrological approach, and EMMA should be supported by both of the other methods.

5.5. Conclusions

The transformation of undisturbed forest into pasture increases the frequency of perched water table and overland flow occurrence. The relative frequency increase can be estimated by comparing rainfall intensities with hydraulic conductivities under both land uses, but no direct conclusion can be drawn for the change in total stormflow volumes. In our study the volume increase was several times higher than the increased frequency of stormflow. The disproportional increase of stormflow volume was possible due to overland flow generation over larger areas in the pasture than in the forest. Overland flow generation processes differed partly between the forest and pasture catchment. Saturation-excess overland flow due to both perched water table occurrence and saturation by groundwater existed in both land uses. Fast return flow through soil pipes was only observed in the forest, while slow return flow was generated from a continuous perched water table in the pasture. These results show that changing land-use from undisturbed forest to pasture not only increases the frequency and volume of stormflow, but also the manner in which the water travels through the soil towards the stream channel. A comparison of different approaches for flowpath identification for the same sites during the same hydrological year indicates that detailed hydrologic study is the basis for more chemically based approaches such as hydrograph and chemograph comparisons or end-member-mixing analysis. However, the most useful method is to combine all of these methods if such an approach is practical.

6.
Summary of results and implications for future research

On the beginning of this dissertation I proposed that modifications to the near-surface hydrologic processes due to land-use change directly affect solute exports and therefore solute budgets. Soil compaction due to land-use change from undisturbed forest to pasture is expected to increase the significance of fast lateral flowpaths in favor of slow vertical ones. As each flowpath has its one fingerprint, the assumption that a shift of the significance of individual flowpaths affects solute exports is obvious. The relationships between underlying hydrologic processes and their effect on solute exports are, however, not yet established. With this synthesis I aim to provide a small contribution to knowledge of these relationships.

The next three subsections will summarize the results from chapters 2 to 5. Rainfall and throughfall hydrology and chemistry are examined first (section 6.1.) by summarizing the results of chapter 2 and 3. The following two sections on ‘water and solute fluxes’ (section 6.2.) and ‘near-surface hydrology’ (section 6.3.) will summarize the results of chapter 4 and 5, respectively. At the end of this synthesis major limitations of this study are reported (section 6.5.) and the implications of this study for future research are discussed (section 6.6.).

6.1. Rainfall and throughfall hydrology and chemistry

For a pasture catchment with a total area of <1 ha rainfall can be regarded as evenly distributed within the catchment. The same is not true if the canopy of a tropical rainforest is present. As we could demonstrate, rainfall is redistributed within the forest canopy. Palms were especially effective in funneling rainfall, resulting in very high local throughfall intensities. The observed locally increased water fluxes were, however, not stable over time. We attributed the spatial dynamic of rainfall distribution to control by the babassu palms and their leaf growth. We further found that the funneling effect was pronounced for events with maximum 10-minute rainfall intensities exceeding a threshold of 30 mm h^{-1}.

Rainfall and throughfall chemistry were affected by land-use change in two ways. Firstly, rainfall and throughfall concentrations were highly dynamic over time, partly due to biomass burning activities. Concentrations in both rainfall and throughfall declined during the transition from dry to wet season as well as during individual rain events. These patterns appeared to be exaggerated by biomass burning, which was abundant in Rondônia at the end of the dry season and during the transition to the wet season. As biomass burning is not only linked to the practice of deforestation (undisturbed and secondary forests), but also to common local pasture management, these findings might still be relevant if deforestation rates were to decline in the near future. The second effect of land-use change on rainfall and throughfall chemistry was a regional increase of fluxes for some solutes. We compared our data to that from less disturbed regions where biomass burning and agricultural activities were less extensive as in central Amazonia for example. We found that annual solute input fluxes at our site were particularly elevated for those solutes originating from pyrogenic emissions.

6.2. Water and solute fluxes

Land-use change from undisturbed forest to pasture dramatically increased the volume and frequency of quickflow due to decreased soil permeability. A comparison with other studies suggested that low runoff coefficients in small undisturbed forest catchments significantly increased after conversion to pasture, but that these differences were much less apparent in catchments of less than 1 km². We concluded that the dampened increase of the runoff coefficient is related to the dominance of baseflow in the total streamflow of larger catchments compared to the domination of quickflow in total streamflow of smaller catchments.

Total K^+, Mg^{2+} and Cl^- pasture output fluxes increased in the pasture compared to forest output fluxes. Greater solute exports from the pasture resulted from increased overland flow water fluxes. Additionally, pasture overland flow concentrations were very high for K^+, Mg^{2+} and Cl^- possibly due to cattle excrement. Hence the solute flux increase in pasture can be related to land-use change effects on the hydrology and to land management practices on overland flow chemistry. Tight nutrient cycles that minimized nutrient losses existed in our forest catchment, but conversion to pasture suggested increased losses of some solutes. While the forest was a sink for Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, and Ca^{2+}, about balanced for K^+ and Mg^{2+}, and a source of Na^+, the pasture was a sink for NO_3^-, SO_4^{2-}, NH_4^+, and Ca^{2+}, balanced for Cl^-, and a source of Na^+, K^+, and Mg^{2+}.

6.3. Near-surface hydrology

Slow vertical water flow through the soil towards groundwater predominated over faster lateral flowpaths directly towards the stream channel in the forest. The contribution of small rainfall events to annual stormflow totals was minimal. Lateral flowpaths led to considerable event stormflow only for events with very wet preconditions and high rainfall volumes. In the forest, saturation overland flow was only observed near the stream channel. Perched water tables were, however, also observed at some distance from the steam channel. Considerable return flow from soil pipes was observed in the forest for just one major rainfall event under wet preconditions. Return flow contribution to stormflow by this event was reflected in the forest hydrograph by high late event flow rates.

The land-use conversion from undisturbed forest to pasture changed the processes of stormflow generation. Fast lateral flowpaths became more significant after pasture installation. In contrast to the forest, smaller rainfall events contributed noticeably to total annual stormflow. Perched water tables and saturation overland flow were observed over large areas. Saturated soil in the pasture, indicated by perched water, was observed more frequently and persisted for longer periods than in the forest. Slow return flow existed, but did not contribute substantially to total stormflow. Fast return flow from soil pipes was not observed in the pasture.

Comparison of maximum 30-minute rainfall intensities and the hydrologic conductivities in the forest and the pasture suggested that land-use conversion from undisturbed forest to pasture might double the frequency of saturation overland flow. This is in line with our observations, but this approach does not allow conclusions on the effective increase of overland flow volume, which was increased 17-fold from forest to pasture in our example.

A comparison between different approaches for flowpath identification in our catchments indicated that a detailed hydrological study is essential for the interpretation of results from more chemical approaches. The latter are of course needed to assess the biogeochemical significance of hydrologic alterations after land-use change.

6.4. Limitations of this study

Before drawing the final conclusions it is reasonable to examine the limitations of this study. The limitations are related

1) To the conceptual approach; and

2) To applied field methods.

The general conceptual approach in this study was a space-for-time substitution in order to study land-use changes. By studying different sites instead of studying the same site before and after land-use change we run the risk of studying two sites that already differed one from another before deforestation. We sought to minimize this risk by choosing two nearby sites with the same soil type and similar topography.

Due to limited resources we had to deal with some technical constraints. Rainfall could be measured in the pasture catchment but not above the forest. Differences in rainfall amount and in particular in the timing of rainfall onset for the two catchments might have escaped our observations. Concerning stormflow and perched water table logging we had to deal with the limitation that logging intervals of every five minutes were too long to reveal possible response time differences for both catchments. With an impeding layer in the top 20 centimetrers of the soil, the ecosytems responded rapidly to rainfall. Shorter logging intervals perhaps could have provided more information about the underlying processes. Furthermore, we could not log all piezometers at the same time. The loggers were relocated several times during the study period. Therefore possible seasonal differences in perched water table generation could not be studied.

6.5. Implications for future research

There is one principal implication from this study for future research. When studying solute fluxes in catchments it is worthwhile examine the underlying hydrological processes. The variations in solute fluxes due to land-use change can only be explained if the flowpath that rainfall travels along to the stream is known.

Additionally, several of our hydrologic results or conclusions suggest testing for their effects on solute fluxes. Very high throughfall or stemflow intensities due to the presence of babassu palms might result in local soil saturation and overland flow generation. At least for stemflow we know that concentrations are very high for some solutes (unpublished data). It would be interesting to study the effects of high intensity water fluxes with high concentrations of some solutes on the export of these solutes and on possible spatial differences in soil solution chemistry.

Solute concentrations in throughfall and rainfall were highest during the transition from dry to wet season and for individual events during the first few rainfall or throughfall millimeters. This implies that solute concentrations were highest when runoff by overland flow was minimal. These seasonal and event effects should be considered in future research into runoff chemistry in this environment. For an end-member-mixing analysis, for example, throughfall solute concentrations for all events during a one year period, including events of all sizes and both seasons, would not represent solute concentrations of those events that generate stormflow.

In contrast to small catchments, runoff coefficients appeared not to change significantly after land-use change in bigger catchments, apparently due to the high baseflow contribution to total runoff. If the contribution of baseflow is high, then the increased solute export after land-use conversion that we found might be dampened for bigger catchments. We came to this conclusion because the increased solute export in our small pasture catchment was linked to increased overland flow. The effect of land-use change from undisturbed forest to pasture on runoff characteristics and their implications for solute exports should be addressed in future research conducted in larger catchments.

Furthermore, future studies should consider that a land-use change induced decrease in hydrologic conductivity might ‘only’ double the percentage of rainfall events that exceed the respective values, but the increase of overland flow volume could be many times higher.

7.
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