



Effects of land-use change on solute fluxes to floodplain lakes of the central Amazon

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Abstract. A time-series analysis of airborne photographs and Landsat thematic mapper (TM and ETM+) images and hydrochemical data were used to examine the effects of land-use change from 1930 to 2001 on solute inputs to Lake Calado, a floodplain lake in the central Amazon. Deforestation from slash-and-burn agricultural activities has dramatically decreased the amount of primary growth upland and flooded forests in the basin. The increasing area that is converted to agricultural plots and pasture in the Lake Calado basin has increased solute loading to the lake from upland tributaries (storm and base flow), bank seepage and overland flow, and decreased throughfall inputs. Whereas solute concentrations in stream water were generally higher in 1992 than 1930, Na^+ and Cl^- concentrations were also considerably higher in 2001 than 1992, likely because of an increase in the number of humans and cattle in the watershed. Estimates of solute inputs to Lake Calado via throughfall indicate that the mass transfer of some major solutes in the throughfall of undisturbed flooded forests can be larger than that from a combination of all other sources in areas that do not have a strong influence from the Solimões River. Chemical gains in rain as it passed through the forest canopy occurred for most major ions and relatively large gains were observed for PO_4^{3-} and Ca^{2+} . Although often neglected in studies of tropical forest ecosystems, throughfall can be an important source of solutes to relatively undisturbed lake environments in the central Amazon.

Introduction

The Amazon is the world's largest river system, draining 37% of South America and discharging about 20% of the freshwater reaching the world's oceans (Sioli 1984). The Amazon River system is fringed by a floodplain of about 110,000 km² that contains over 8000 lakes (Sippel et al. 1992). These floodplains are a mosaic of flooded forests, floating macrophytes, and open water which store and cycle large amounts of carbon and nutrients (Fisher et al. 1988; Engle and Melack 1993; Filoso et al. 1999) and are an important biogeochemical interface between terrestrial and aquatic ecosystems. Moreover, the Amazon River floodplain is one of the few areas in Amazonia with relatively high natural fertility and productivity due to the annual flooding with sediment-rich water and nutrients to the system (Junk 2002) and is, therefore, under increasing pressure from agricultural development.

The Amazon basin has been the focus of many studies concerning the effects of deforestation and land-use change on biogeochemical cycles for the past decade (Steudler et al. 1996; Neill et al. 1997; Neill and Davidson 2000). However,

although there are recent studies that address the effects of land-use change and colonization on the hydrochemistry of receiving waters (Williams and Melack 1997; Williams et al. 1977b; Biggs et al. 2002), the effects of these perturbations on the aquatic environment are still poorly understood.

Rainfall is an important source of solutes and nutrients to the central Amazon (Galloway et al. 1982; Lesack and Melack 1991; Williams et al. 1997a) and is a key factor controlling the water chemistry of dilute tributaries of the Amazon River, such as the Negro River (Gibbs 1970). The composition of rainfall in the central Amazon is dilute and only slightly affected by anthropogenic sources (Williams et al. 1997a; Filoso et al. 1999), and the majority of solutes originate locally from the biogenic aerosols of rainforests and soils (Harriss et al. 1988; 1990; Williams et al. 1997a). In contrast, solute concentrations in throughfall (the incident precipitation that passes through the canopy of trees) are affected by the leaching of material from plant tissues, the active uptake of material in rainfall by leaves or epiflora, and the washing-off and dissolution by rain of aerosols and particles that accumulate on forest canopies between rains (Parker 1983; Lovett and Lindberg 1984; Lindberg et al. 1986; Schaefer and Reiners 1989). Studies reviewed in Parker (1983) show that throughfall can result in large transfers of minerals to the rain falling onto an ecosystem. Reliable estimates of event-based solute fluxes via throughfall in the Amazon are available only for the Anavilhanas floodplain of the lower Negro River (Filoso 1996; Filoso et al. 1999) and indicate that throughfall is an important source of solutes to blackwater floodplain environments. Because the water budget of some floodplain lakes of the Amazon River is more regulated by upland runoff and rainfall than riverine sources (Lesack and Melack 1995), throughfall could be of major importance to the productivity and ecology of other floodplain lake ecosystems.

In this paper, we examine the effects of land-use change from 1930 to 2001 on streamwater chemistry and other solute sources to Lake Calado, a floodplain lake located on the Solimões River in the central Amazon. Moreover, we determine the deposition of major solutes from a large fraction of the precipitation and throughfall that occurred at Lake Calado during the period from December 1989 to May 1990. Using these data, we evaluate the effect of land conversion on flooded forests and the hydrochemical importance of throughfall in solute budgets of undisturbed and disturbed floodplain lake environments in the central Amazon.

Study area

Lake Calado is located in the central Amazon basin (3°15'S, 60°34'W) on the north bank of the Solimões River (Amazon main stem) about 80 km SW of Manaus (Figure 1). The basin and lake areas at high water (June) are 59 and 5.6 km², respectively. The study area is a floodplain lake connected to the Solimões River year round and undergoes changes in depth from 1 to 12 m over the course of the annual hydrological cycle. Increasing river stage impounds runoff from upland catchments, flooding a combination of forested areas, heavily deforested shorelines,

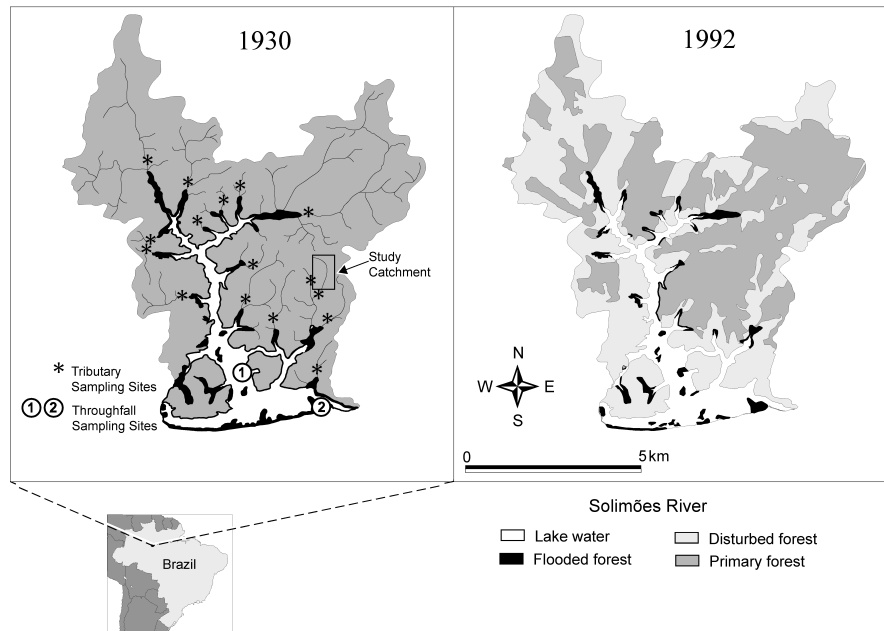


Figure 1. GIS analysis of Lake Calado in 1930 and 1992 indicating the flooded forest study-site plots where throughfall collectors were installed (Sites 1 and 2), the location of the 23-ha study-site catchment (Williams and Melack 1997; Williams et al. 1997b), and the stream network sampled during stream surveys in 1989 and 2000. In this analysis, we categorized the secondary growth forest, crops and recently cut areas into an area designated as 'disturbed', and thus the final categorization includes open water, and flooded, primary, and disturbed forests. Lake area not including flooded forests is 5.6 km².

and stretches of upland streams. Detailed descriptions of the study site are given in Williams and Melack (1997) and Williams et al. (1997a,b).

Methods

Land use/land cover. According to discussions with some of the original inhabitants of Lake Calado, small-scale land conversion of the watershed began in the 1930s. We conducted a GIS analysis of aerial photographs from 1976 (Companhia de Pesquisa de Recursos Minerais – CPRM) and Landsat images from 1992 (TM) and 2001 (ETM+ – Tropical Rain Forest Information Center – TRFIC) of the Calado basin to determine changes in the extent of several land uses and land covers (LULC). Cloud-free Landsat images from July 1992 and August 2001 were georeferenced and superimposed, and the boundaries of LULC patterns were digitized in ArcView. LULC in the 1976 aerial photo was reproduced in 2001 image by delineating disturbed areas on a plastic transparency and digitizing this image onto the 2001 outline of the Lake Calado basin. LULC was then categorized as

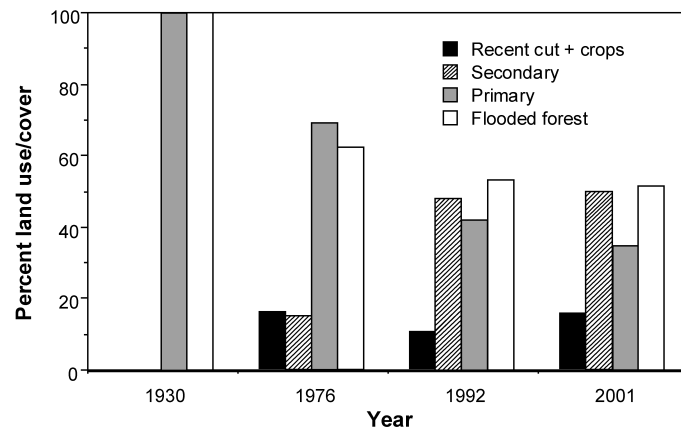


Figure 2. The percent area of different LULC types at Lake Calado in the years of 1930, 1976, 1992, and 2001. LULC was categorized as primary growth forest (> 50 years), secondary growth forest (2–50 years), crops and recent cuts (0–2 years). The areas of flooded forest in 1930 and 2001 were estimated as 1.5 and 0.7 km², respectively.

flooded forest, primary growth forest (> 50 years), secondary growth forest (2–50 years), and a combination of recently cleared areas and crops (0–2 years) (Figure 2); the latter two are categorized as disturbed areas, and thus the categorization in Figure 1 includes open water, and flooded, primary, and disturbed forests.

Rain and throughfall. Rain was sampled and analyzed as described in Williams et al. (1997a). Bulk throughfall (referred to as throughfall) was sampled from January through April 1990 in events that were defined as discrete periods of measurable rainfall ≥ 2.5 mm and separated by at least a 2-h rain-free period. Throughfall was sampled with 10 collectors distributed randomly in 100 m by 100 m plots at sites 1 and 2 (Figure 1) in flooded forest only. Throughfall collectors were made of 4 L cubitainers screwed onto polyethylene gutters that were placed at least 10 m apart under trees in varying depths of water. Nylon nets (0.63 mm mesh) pre-leached with deionized water (DIW) were placed between the gutters and the containers to prevent coarse material from falling into the sample water. The gutters were tied by nylon lines to tree trunks to hold the collectors stationary under the forest canopy. Collectors were maintained at about 1 m above the water surface, or ground when the forest was not flooded. As the water level changed, the collectors were moved vertically, while avoiding lateral movement. Throughfall volume was measured with rain gauges placed adjacent to the collectors and did not interfere with the funnels.

Samples were collected about 2 h after a daytime rain event because trees remained wet and contributed to throughfall for more than 1 h after the end of a storm; events during the night were collected up to 10 h later. After collection, gutters were cleaned with DIW, and the cubitainers and nylon screens replaced. The

cubitainers containing the samples were capped and immediately taken to the field laboratory for analyses. After use, the cubitainers were washed with DIW and occasionally acid washed and rinsed with DIW until conductivity of the rinse water was below $1.0 \mu\text{S cm}^{-1}$. The nylon screens were replaced and collectors cleaned daily with DIW.

Chemical analyses. Analytical methods are summarized in Williams and Melack (1997). Volume-weighted means (VWMs) were calculated as described in Filoso et al. (1999) from the storm events collected during the 1989 and 1990 study period (Table 1). Quality controls used are detailed in Williams et al. (1997a) and statistical differences were determined by ANOVA.

Solute budgets. We used streamwater chemistry obtained from our streamwater surveys ($n = 16$ streams at high water) and intensively sampled catchments (Williams and Melack 1997; Williams et al. 1997b) to calculate basin-wide solute export in different years. Stream discharge was measured using a combination of salt dilution and cross-sectional area/velocity techniques (Williams 1993). We assumed that the streamwater chemistry of the intensively sampled, forested catchment in 1989 was representative of relatively pristine conditions. Accordingly, the solute chemistry for the intensively sampled, forested catchment stream in 1989 was applied to the 1930 coverage to represent pre-disturbance streamwater concentrations. Given the homogeneity of soil and vegetation types in a relatively small area such as the Calado drainage basin (59 km^2), there is ample justification for applying the intensively sampled, forested catchment data to the entire basin in 1930. In contrast, we used the survey data from the 1989 water year for the 1992 coverage to calculate solute inputs to Lake Calado during a period of extensive colonization and land-use change from forest to agriculture and pasture.

Other than the rain and throughfall data in Table 1, hydrochemical data for base and storm flow from Williams (1993), Williams and Melack (1997), and seepage and overland flow from Williams et al. (1997b) were used in our analysis. Additional streamwater surveys were conducted on four occasions in May, October and December 1999 and February 2000 to coincide with the 2001 ETM+ image. Rainfall was standardized (2800 mm) and runoff coefficients (runoff expressed as a fraction of rain depth) were empirically derived from the studies of Lesack (1993b) and Williams and Melack (1997) done in the same catchment when forested and partially deforested, respectively. Coefficients used were 0.57 (1930) and 0.66 (1992), respectively.

Solute concentrations of storm flow from Lesack (1993a) were used in the 1930 water year because of the negligible disturbed areas in the basin, and those from Williams and Melack (1997) were used in the 1992 water year when deforestation was more of a factor affecting solute inputs to receiving waters.

We assumed that the total volume of water via overland flow to the lake was about 65% of our stormflow volume in 1992. Moreover, we assumed that the amount of overland flow to Lake Calado in the 1930 water year was negligible. Bank seepage to the lake during falling water was estimated to be about 1.5 times

Table 1. VWM concentrations of sampled rain and throughfall events during the wet season. All concentrations are expressed in $\mu\text{eq L}^{-1}$, except TDN, TDP, DOC, formic and acetic acids, and SiO_2 (μM), and electrical conductance ($\text{EC} = \mu\text{S cm}^{-1}$). Negative ANC in rain is assumed to be zero in the \sum anions calculation. Deficit is the \sum anions minus the \sum cations and includes the contribution from organic acids. 'n' is the sample size. Throughfall collection sites 1 and 2 are indicated in Figure 1.

Constituent	Wet Season		Site 1		Site 2	
	Rain	n	Throughfall	n	Throughfall	n
Events		72		16		11
Volume (mm)	912		291		239	
Cl^-	4.6	72	26.1	111	35.2	67
NO_3^-	3.3	72	0.5	94	1.0	73
SO_4^{2-}	1.6	72	10.5	116	9.2	66
PO_4^{3-}	0.02	72	1.4	103	8.3	60
ANC	-5.0	33	44.4	96	50.1	61
Formate	2.9	36	2.3	9	1.5	12
Acetate	9.3	36	5.6	14	2.0	13
NH_4^+	1.2	72	0.6	97	1.0	63
Na^+	2.1	72	7.5	108	12.6	67
K^+	0.7	72	13.3	112	44.8	66
Ca^{2+}	2.4	72	52.2	115	39.5	67
Mg^{2+}	1.0	72	13.1	112	23.6	68
H^+	11.2	72	4.2	96	1.8	62
\sum anions	21.7		90.8		107.3	
\sum cations	18.6		90.9		122.3	
Difference	3.1		0.1		15.0	
DOC	159	48	400	16	880	23
SiO_2	0.0	10	3.3	12	45.3	3
EC	6.5	57	10.6	106	15.6	63
TDN	8.0	61	12.5	116	18.5	68
TDP	0.25	60	1.8	116	9.6	68

the volume of water that seeps into the groundwater reservoir during rising water (Lesack 1995). Using an annual rainfall of 2800 mm, bank seepage amounted to approximately $6 \times 10^6 \text{ m}^3$ in 1930. Given the higher rates of soilwater percolation in cut areas observed by Williams et al. (1997b), we increased the amount of bank seepage by $2 \times 10^6 \text{ m}^3$ to account for the larger proportion of deforested shoreline in 1992. Bank seepage in the wet season of both years was deemed negligible because of the tendency for water to seep into the lake bank during rising water.

Results

Rain and throughfall characteristics. The continuous record of rain at the watershed site included 155 events that ranged in size from 0.2 to 85 mm (wet season total = 1983 mm). The 72 events of rainfall chemically analyzed (46% of the total)

Table 2. The ratios in rain to throughfall for VWM concentrations of solutes in this study compared to those of the Anavilhanas archipelago in the wet season of 1991 (Filoso et al. 1999). Ratios with significant differences (ANOVA; $p < 0.05$) between Anavilhanas and either of the two sites at Lake Calado are indicated by italic type. 'NA' means data are not available.

Constituent	Wet season Anavilhanas	Site 1, Lake Calado	Site 2, Lake Calado
Cl ⁻	0.26	0.18	0.13
NO ₃ ⁻	<i>2.42</i>	<i>6.6</i>	<i>3.3</i>
SO ₄ ²⁺	<i>0.45</i>	<i>0.15</i>	<i>0.17</i>
PO ₄ ³⁻	<i>0.35</i>	<i>0.01</i>	<i>0.002</i>
ANC	< 0.00	< 0.00	< 0.00
NH ₄ ⁺	<i>0.45</i>	<i>2.0</i>	<i>1.2</i>
Na ⁺	<i>0.51</i>	<i>0.28</i>	<i>0.17</i>
K ⁺	0.02	0.05	0.02
Ca ²⁺	<i>0.36</i>	<i>0.05</i>	<i>0.06</i>
Mg ²⁺	0.11	0.08	0.04
H ⁺	3.02	2.7	6.2
Formate	NA	1.3	1.9
Acetate	NA	1.7	4.7
DOC	0.17	0.40	0.18
SiO ₂	NA	0.00	0.00
TDN	<i>0.14</i>	<i>0.64</i>	<i>0.43</i>
TDP	<i>0.23</i>	<i>0.14</i>	<i>0.03</i>

were evenly distributed over all storm sizes and the distribution resembles that of the entire population (Williams et al. 1997a). The wet season had a frequency of about 0.9 events day⁻¹, and the average daily rainfall total was 10.8 mm day⁻¹.

Most storms for throughfall (83%) were collected when the study plots were completely flooded. We calculated an average throughfall depth (i.e., mm of throughfall) of 85 ± 3% and 82 ± 4% of total rainfall at sites 1 and 2, respectively. The mean percentage of a rain event contributing to throughfall was 84 ± 4%, or 1666 mm of throughfall during the wet season. The average throughfall depth of 81 ± 2% calculated by Filoso et al. (1999) is similar to our values at Lake Calado and those in studies of *terra firme* (i.e., upland) forests in the central Amazon (Franken et al. 1982; Lloyd and Marques 1988; Lloyd et al. 1988).

Hydrogen ion typically had the highest concentration of any ion in rain and represented 60% of the sum of cations (Table 1). VWM concentrations of many solutes in rain were significantly lower than in throughfall, and VWM pH was higher in throughfall than rain. The concentration of H⁺ in throughfall was followed in descending order by Ca²⁺, Na⁺, NH₄⁺, Mg²⁺, and K⁺, while for the anions, the concentration of Cl⁻ was followed by NO₃⁻, SO₄²⁻ and PO₄³⁻. VWM DOC concentrations in throughfall were typically higher than in rain. Ratios of

VWM concentrations of rain to throughfall indicated that PO_4^{3-} and K^+ , followed by Ca^{2+} and Mg^{2+} were most enhanced in throughfall, whereas ratios > 1.0 were observed for H^+ , NO_3^- , NH_4^+ , organic acids and TDP (Table 2). Throughfall volumes varied between sites and this variation is commonly caused by differential interception and flow routing of rainfall by vegetation. The ratios of rainfall to throughfall deposition were similar for most solutes, albeit these ratios varied markedly between sites for NO_3^- , PO_4^{3-} and NH_4^+ .

There were no significant differences between the solute concentrations in the rain of Lake Calado (Williams et al. 1997a) and Anavilhanas, an archipelago located on the Negro River about 80 km NW of Manaus (Filoso et al. 1999). Hence, the solute ratios of rain to throughfall indicate that the deposition of many solutes is higher at Lake Calado than at Anavilhanas (Table 2). Phosphate, K^+ , Mg^{2+} , TDN, TDP and DOC concentrations in throughfall were significantly ($p < 0.05$) higher at Site 2 than at Site 1 at Lake Calado, and Cl^- , SO_4^{2-} , ANC, Ca^{2+} , Mg^{2+} and TDP were significantly higher at both sites at Lake Calado than at Anavilhanas; PO_4^{3-} and K^+ were significantly higher at Site 2 of Lake Calado than at Anavilhanas.

Streamwater surveys. Discharge at the sampling stations ranged from $< 10 \text{ L s}^{-1}$ in smaller catchments to 530 L s^{-1} in the dry season at low lake stage. The largest discharges were obtained from catchments whose tributaries joined as lake stage decreased. In contrast, discharge during the wet season ranged from 10 to 580 L s^{-1} . The ranking of cations in stream water were similar in both surveys, albeit we were unable to measure a complete set of chemical constituents in the 2000 survey. The highest concentration of any cation in 1989 was Na^+ , followed by Ca^{2+} , H^+ , Mg^{2+} , K^+ , and NH_4^+ , and that of the anions was Cl^- , followed by NO_3^- , SO_4^{2-} , and PO_4^{3-} . Sodium accounted for 44% of the cation total, followed by Ca^{2+} (24%), H^+ (17%), Mg^{2+} (9%), K^+ (5%), and NH_4^+ (1%), whereas Cl^- accounted for 56% of the anion total, followed by NO_3^- (31%), SO_4^{2-} (13%), and PO_4^{3-} ($< 0.1\%$). Chemical results of the other hydrochemical pathways included in this manuscript are described in detail elsewhere (Williams and Melack 1997; Williams et al. 1997 a,b).

Discussion

Comparison of throughfall in black- and whitewater environments. Differences in the solute concentrations of throughfall among sites were probably due to the type and duration of floodwater influence (Filoso et al. 1999) since these partially regulate the species composition of flooded forests (Revilla 1981, 1991). Accordingly, the stronger influence of the Solimões River at Site 2 at Lake Calado than at Site 1 may account for differences observed in throughfall composition. Moreover, the flooding regime of the lower Negro River includes a large component of nutrient-rich white water of the Branco River that has a strong influence on the northern lakes of the Anavilhanas archipelago (Filoso 1996; Filoso and Williams 2000). Hence, similar to the chemical differences observed between sites at Lake Calado, these differences may exist among northern and southern lakes in the Anavilhanas

archipelago (Filoso et al. 1997). The solute balance of these lakes indicated, as expected, that the influence of throughfall in the northern lakes (white water) was less than in the southern lakes (black water).

It is difficult to extrapolate solute differences in throughfall between black- and whitewater environments to floodplain lakes of the entire Amazon floodplain. However, given that our data from Anavilhanas and Lake Calado were derived from experimental designs that account for a large amount of spatial variability, and that our throughfall sampling was from a large number of events spanning the range of storm sizes measured, it is clear that there is a larger deposition of most solutes in throughfall than that which occurs in rainfall. The implications of larger solute deposition in throughfall for nutrients, such as PO_4^{3-} and K^+ , are that they may be important in the overall solute budgets of some floodplain lakes.

Effects of changing land use on solute budgets. In our analysis of land-use change, it is important to recognize that forest cutting has variable effects on the responses of runoff during various stages of forest re-growth (Hamilton and King 1983; Swank et al. 1988). Moreover, it is well documented that solute losses are enhanced immediately following cutting and that retention is enhanced and the exhaustion of mobilized solutes occurs (e.g., base cations) during vegetation re-growth (Likens et al., 1970; Vitousek et al., 1979; Uhl and Jordan 1984). Although we are unable to quantify the magnitude, duration, and recovery of solute fluxes to varying degrees and types of disturbance in the Lake Calado basin, the relative proportion and temporal changes of fluxes in our budget analysis are likely representative of the actual changes occurring in the lake basin because solute concentrations were measured for a number of important solute sources in forested and partially deforested catchments in 1990 and the stream water of the entire network of tributaries in 1990 and 2000. Moreover, our streamwater data are from a period of land-use change where there is a relatively constant level of recent disturbance and secondary vegetation (i.e., 1992 and 2001), and increasing populations of humans and cattle in the watershed (personal observation). The presence of humans and cattle is commonly associated with solute mobilization (Biggs et al. 2002; Williams et al. 2003) and increased fluxes to receiving waters and these fluxes are largely unaffected by vegetative growth dynamics.

VWM concentrations of solutes in stream water in the surveys conducted in 1990 and 2000 differed slightly among the tributaries of Lake Calado compared to concentrations measured in 18-ha forested and 23-ha partially-deforested catchments in 1990 (Table 3), albeit Na^+ and Cl^- in the 2000 survey were 3–4 times higher in concentration. The generally higher concentrations of base cations, fractions of total P, and lower H^+ in the streamwater survey data compared to that of the study site catchment (Williams and Melack 1997) are likely indicative of the increasing development in the Calado basin. Our results indicate that land conversion of the Calado basin has increased the export of solutes to Lake Calado via base flow by factors of about 2 and 8 for N and P, respectively, from 1930 to 1992 (Table 4). The general trends in baseflow export show an increase over this period for most solutes, with the exception of H^+ , that decreases.

Table 3. Temporal comparison of VWM solute concentrations in stream water at base flow for the tributaries ($n = 16$ at high water) of the Lake Calado basin in 1990 and 2000. Data for the forested and partially deforested catchment streams are from Williams and Melack (1997) and Williams et al. (1997b). Stream survey data are from Williams (1993) and additional surveys done in 1999 and 2000. Nitrogen and phosphorus fractions are in μM ; all other ions are in μeqL^{-1} . Concentrations with significant differences (ANOVA; $p < 0.05$) between the partially deforested and forested catchments and between the stream surveys are indicated by italic type.

Constituent	Partially deforested catchment 1990 ($n = 52$)	Forested catchment 1990 ($n = 28$)	Stream survey 1990 ($n = 53$)	Stream survey 2000 ($n = 42$)
H^+	<i>11.1</i>	<i>24.5</i>	7.5	NA
NH_4^+	1.0	0.7	0.7	NA
NO_3^-	11.7	11.5	7.8	13.6
TDN	19.7	15.3	22.4	NA
TN	24.3	17.2	26.7	NA
PO_4^{3-}	0.06	0.03	0.01	NA
TDP	<i>0.48</i>	<i>0.08</i>	0.30	NA
TP	<i>0.61</i>	<i>0.13</i>	0.89	NA
Na^+	<i>15.6</i>	<i>6.3</i>	<i>19.9</i>	<i>66.1</i>
K^+	3.9	0.6	2.4	4.0
Ca^{2+}	<i>4.0</i>	<i>0.8</i>	10.9	8.7
Mg^{2+}	2.2	0.7	4.0	5.7
Cl^-	14.7	13.0	<i>14.1</i>	<i>71.2</i>
SO_4^{2-}	1.8	2.0	3.3	4.3

Storm flow is also responsible for increased solute loading to Lake Calado, but is less of a factor than base flow because of the relatively small quantity of storm flow that occurs annually. Stormflow is a minor factor in this system because of well-developed root mats in forested areas and riparian vegetation and second growth forest that quickly recolonize in disturbed areas. For instance, Williams and Melack (1997) observed that storm flow was responsible for about 6% of the annual runoff from a forested catchment at Lake Calado, and is probably higher in very disturbed catchments because of overland flow. However, solute concentrations are generally higher in storm flow than in base flow, and can amount to over 50% of the annual solute export from partially deforested catchments (Williams and Melack 1997). As expected, the concentrations of solutes in storm flow generally increased (Table 4) due to the larger amount of disturbed area in the Calado basin in 1992 compared to 1930 (Figure 2).

The perimeter of the lake is a heavily colonized and deforested area, resulting in direct inputs of solutes and particulates to Lake Calado. Using the 1992 coverage, we estimated that the total perimeter of the lake shore (74 km) that was disturbed (> 80%) equaled about 65% of the total length of tributaries in the Calado basin

Table 4. Wet season and annual (parentheses) solute fluxes to Lake Calado in 1930 (below) and 1992 (next page) using a standardized rainfall of 1983 and 2754 mm (wet season and annual, respectively) respectively. Wet season and annual (ann) volumes are 10^{-3} the actual volumes; similarly, fluxes in equivalents are 10^{-3} the actual values. Percent flooded forest throughfall is designated as 'TF'. In 1930, total basin area is 5977 ha, lake area is 556 ha, and flooded forest area is 150 ha. In 1989, basin area is the same, lake area is 623 ha, and flooded forest area is 80 ha. The fractions of total nitrogen and phosphorus are in units of moles and all other solutes are in units of equivalents. 'NA' means the data are not available.

1930	Base flow	Storm flow	Seepage	Overland	Flooded forest	Rain	TF
<i>Volumes</i>							
Wet season (annual)	61414 m ³ (82992 m ³)	3685 m ³ (4980 m ³)	1 m ³ (6000 m ³)	1 m ³ (500 m ³)	2998 m ³ (4163 m ³)	11303 m ³ (15698 m ³)	Wet season (annual)
<i>Constituent</i>	(Eq)	(Eq)	(Eq)	(Eq)	(Eq)	(Eq)	Percent
H ⁺	1504 (2033)	45 (61)	0 (84)	0 (1)	13 (17)	127 (176)	1 (1)
NH ₄ ⁺	43 (58)	4 (5)	0 (2)	0 (4)	2 (2)	14 (19)	3 (3)
NO ₃ ⁻	706 (954)	28 (38)	0 (210)	0 (4)	2 (2)	37 (52)	0 (0)
TDN	940 (1270)	58 (78)	0 (222)	0 (21)	38 (52)	90 (170)	3 (3)
TN	1057 (1427)	142 (192)	NA	NA	NA	122 (151)	NA
PO ₄ ³⁻	2 (2)	0.2 (0)	0 (1)	0 (1)	4 (6)	0.2 (0)	63 (57)
TDP	5 (7)	1 (1)	0 (1)	0 (1)	5 (1)	3 (6)	8 (8)
TP	8 (11)	2 (3)	NA	NA	NA	5 (6)	NA
Na ⁺	387 (523)	51 (69)	0 (190)	0 (20)	23 (31)	24 (33)	5 (4)
K ⁺	37 (50)	16 (16)	0 (20)	0 (13)	40 (55)	8 (11)	40 (33)
Ca ²⁺	49 (66)	4 (5)	0 (73)	0 (13)	157 (217)	27 (38)	66 (53)
Mg ²⁺	43 (58)	10 (13)	0 (39)	0 (7)	39 (55)	11 (16)	38 (29)
Cl ⁻	798 (1079)	30 (41)	0 (92)	0 (12)	78 (109)	52 (72)	8 (8)
SO ₄ ²⁻	123 (166)	9 (12)	0 (128)	0 (15)	32 (44)	18 (25)	18 (11)

Table 4. (continued).

1992	Base flow	Storm flow	Seepage	Overland	Flooded forest	Rain	TF
<i>Volumes</i>							
Wet season (annual)	95940 m ³ (129649 m ³)	8635 m ³ (11657 m ³)	1 m ³ (8000 m ³)	5612 m ³ (7576 m ³)	1666 m ³ (2313 m ³)	12890 m ³ (17901 m ³)	Wet season (annual)
<i>Constituent</i>	(Eq)	(Eq)	(Eq)	(Eq)	(Eq)	(Eq)	Percent
H ⁺	533 (720)	13 (18)	0 (112)	7 (10)	7 (10)	144 (200)	1 (1)
NH ₄ ⁺	50 (67)	13 (17)	0 (3)	43 (58)	7 (1)	16 (21)	5 (1)
NO ₃ ⁻	554 (748)	167 (225)	0 (280)	42 (57)	7 (1)	43 (59)	1 (0)
TDN	1590 (2149)	397 (536)	0 (296)	246 (333)	21 (29)	103 (193)	1 (1)
TN	1896 (2562)	944 (1275)	NA	NA	NA	139 (260)	NA
PO ₄ ³⁻	1 (1)	1 (1)	0 (1)	8 (10)	2 (3)	0.2 (0)	17 (19)
TDP	21 (29)	6 (8)	0 (2)	17 (23)	1 1(1)	3 (7)	2 (1)
TP	63 (85)	17891 (24)	NA	NA	NA	5 (12)	NA
Na ⁺	1412 (1909)	660 (892)	0 (254)	227 (306)	12 (17)	27 (38)	1 (1)
K ⁺	170 (230)	251 (338)	0 (27)	146 (197)	22 (31)	9 (13)	4 (4)
Ca ²⁺	774 (1046)	137 (185)	0 (97)	147 (198)	87 (121)	31 (43)	7 (7)
Mg ²⁺	284 (384)	87 (117)	0 (52)	80 (108)	22 (30)	13 (18)	5 (4)
Cl ⁻	1001 (1353)	44 (59)	0 (122)	134 (180)	44 (60)	59 (82)	3 (3)
SO ₄ ²⁻	235 (317)	109 (147)	0 (170)	174 (235)	17 (24)	21 (29)	3 (3)

lacking riparian buffers. The distance of disturbed stream banks were used to make estimates of storm flow. Similarly, the distance of disturbed lake shoreline was used to adjust our bank seepage, overland flow, rain, and flooded-forest throughfall estimates since they vary with the proportion of cut area. The considerable length of deforested shoreline in 1992 is responsible for solute fluxes from overland flow to the lake that are generally larger than those of storm flow from upland catchments for certain solutes (Table 4). In contrast, solute fluxes from flooded forests were lower in 1992 than in 1930 because of a reduction in the amount of flooded forests. Our estimates of the total export of solutes to Lake Calado show a general increase from 1930 to 1992 followed by a continued increase to 2001 in Na^+ and Cl^- concentrations only (Table 3).

Throughfall fluxes to floodplain lake environments. The importance of throughfall to Lake Calado was evaluated using a combination of the chemical measurements described above and estimates of flooded forest areas. Areas designated as flooded forests were verified during field surveys of the lake in 1989 and 2000, and the area of the lake including flooded forest is about 7.1 km^2 at high water. From our field surveys and images, we determined that the area of flooded forest is an average of 10 m around the perimeter of the lake, and that larger swaths of flooded forest located in the mouths of larger streams (*igarapés*) or in areas within the lake boundary are approximately the same in 1930 and 2001. Hence, in a relatively undisturbed basin, we estimated that the area of flooded forest during high water was about 1.5 km^2 . Therefore, the flooded forest to lake area (FF:LA) ratio was 0.27 in 1930, indicating that roughly 27% of the rain that falls onto the surface of Lake Calado is intercepted by flooded forest canopy during the period of forest flooding. The solute balance for the wet season in 1930 using estimates of throughfall, rain, bank seepage, overland flow, stream (base and storm flow) and residual solutes (i.e., solutes left in the lake at low water, which are assumed to be negligible) indicated that solute fluxes from throughfall ranged from zero to 66% of the combined inputs of solutes from all hydrological sources (not including the Solimões River). Phosphate and Ca^{2+} were the most influential, whereas N fractions and H^+ were the least (Table 4). The sensitivity of these solutes to a doubling of most fluxes was insignificant, except for base flow. Nevertheless, a doubling of base flow only decreased the importance of PO_4^{3-} and Ca^{2+} to 48 and 55%, respectively, in the wet season of 1930.

The importance of throughfall to the aquatic environment was also investigated at Lake Prato in the Anavilhanas archipelago of the Negro River (Filoso et al. 1999). The lake area of Lake Prato was estimated as 4.2 km^2 , and the FF:LA at high water was 0.55 (i.e., 55:100). Therefore, roughly half of the rain that fell onto the surface of Lake Prato was intercepted by forest canopy during peak flooding. A mass balance indicated that throughfall accounted for 30–64% of the total in the lake at high water. Similar to the large PO_4^{3-} fluxes observed in the throughfall at Lake Calado, the deposition of dissolved P, often limiting in tropical lakes such as those of the Negro River floodplains, increased about seven times from rain to throughfall.

The northern reaches of Lake Calado are influenced more by throughfall than the southern lake basin because of essentially two factors. First, the FF:LA in the southern basin is much lower than that of the northern section of the lake (0.05 vs. 0.45, respectively). Second, the southern lake basin is predominately composed of water from the Solimões and Manacapuru rivers that typically impounds runoff from upland catchments in the northern half of the lake (i.e., north of Site 1, Figure 1) during rising water. This observation is supported because upland streamwater runoff was responsible for about 57% of the annual water budget to Lake Calado in 1984 (Lesack and Melack 1995), whereas the Solimões River was responsible for about 21% (rain, seepage and adjacent lakes were 11, 4, and 6%, respectively). Hence, concentrated throughfall is commonly less influential in the southern lake basin during rising river stage because there is a consistently strong influences of solute-rich whitewater from the Solimões River.

Representativeness of the throughfall results. An important consideration of this study is its applicability to other lakes. As shown above, an indicator of whether throughfall is an important source of solutes to the aquatic environment of a lake is its FF:LA ratio. Lakes with relatively large ratios can include all sizes, but more likely a larger number are smaller sized lakes that have a proportionally larger perimeter (relative to lake area), and therefore flooded forest area, than larger lakes. In the Amazon basin, ria lakes (both composite and dendritic morphotypes) represent a relatively large class of lakes that have large local catchment areas and can have a portion of their upland runoff impounded by river water, similar to Lake Calado. These constitute about 13% of the 8000 lakes on the Amazon floodplain (Sippel et al. 1992). Other lakes, such as oxbow lakes, can become temporarily isolated from the river after some period of flooding. These lakes would likely have a large influence from throughfall since there is no riverine influence after isolation occurs, and increased light penetration because of siltation could accentuate primary productivity associated with increased nutrient fluxes to surface waters. The high number of floodplain lakes that undergo periods of isolation from the Negro River in the Anavilhanas archipelago suggests that the enrichment of surface waters via throughfall to temporarily isolated lakes is common on the Amazon floodplain.

Extending our analysis to a larger floodplain area of the central Amazon was done using data from the SIR-C synthetic aperture radar (Hess et al. 1995). Classifying a radar swath of about 20×40 km (scene center latitude, longitude: $3^{\circ}30'S$, $60^{\circ}45'W$) in April 1994 (approaching high water) the area of flooded forest was about 42% of the total inundation area (i.e., the area of flooded forest divided by the sum of open water, floating macrophyte, and flooded forest) whereas about 28% was observed during October (approaching low water). Considering that a large amount of open water is from the Solimões and Negro rivers, these numbers underestimate the extent of flooded forest on lateral floodplains. However, assuming that these numbers approximately represent the area of flooded forest on the Amazon River floodplain, over 40% of surface water on the floodplain receives throughfall during high water. This analysis indicates that throughfall may be important well into the dry season, since about 30% of the flooded area is covered

by flooded forest in October (although rainfall in the dry season is about 30% of the annual total). In conjunction with our analyses above, this indicates that throughfall is an important source of major solutes, especially PO_4^{3-} and Ca^{2+} , to the Amazon floodplain during periods of forest flooding.

Conclusions

Our GIS analysis indicates that the LULC composition of the Lake Calado basin has changed dramatically from 1930 to 2001 and the basin had less than 50% of its original coverage of primary and flooded forests in 2001. Moreover, in our analysis of aerial and satellite images of the Calado basin, the proportion of recently cut areas was relatively invariant from 1976 to 2001. Based on a combination of our streamwater survey and small catchments data (Williams and Melack 1997) and the increasing populations of humans and cattle in the watershed, our budget analysis indicates that solute fluxes in stream water to Lake Calado are higher now than they were prior to colonization of the watershed and have remained relatively invariant from 1992 to 2001, with the noteworthy exception that Na^+ and Cl^- concentrations were significantly higher in 2001 than in 1992. The higher Na^+ and Cl^- concentrations in 2001 than 1992 are likely due to relatively larger populations of humans and cattle (Biggs et al. 2002) in the watershed after 1992 as opposed to the effects of deforestation.

Additionally, we determined that throughfall deposition is an important mechanism of nutrient and solute fluxes to floodplain lake environments of the central Amazon in relatively undisturbed floodplain lake environments. In contrast, deforestation of flooded forests significantly reduces throughfall fluxes to receiving waters. Floodplain lakes with a large FF:LA ratio that do not receive solute-rich flood waters are most influenced by throughfall, although the extent of the influence depends on the hydrologic dynamics of a particular floodplain lake and the extent and type of land use. Since PO_4^{3-} has one of the largest gains in concentration from rain to throughfall, it is likely that PO_4^{3-} from throughfall to receiving waters influence the primary productivity of undisturbed floodplain lakes during periods of flooding and is an important source of nutrient enrichment in many undisturbed floodplain lakes of the Amazon River system.

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