



Influences of land use and stream size on particulate and dissolved materials in a small Amazonian stream network

SUZANNE M. THOMAS^{1,*}, CHRISTOPHER NEILL¹, LINDA A. DEEGAN¹,
ALEX V. KRUSCHE², VICTORIA M. BALLESTER² and REYNALDO L.
VICTORIA²

¹*The Ecosystems Center, Marine Biological Laboratory, 7 MBL Street, Woods Hole, MA 02543, USA;*

²*Centro de Energia Nuclear na Agricultura, Avenida Centenário, 303, CEP 13416000, Piracicaba, SP, Brazil; *Author for correspondence (e-mail: sthomas@mbi.edu; phone: 1-508-289-7479; fax: 1-508-457-1548)*

Received 4 December 2001; accepted in revised form 21 January 2003

Key words: Amazon, Deforestation, Land use change, Stream chemistry, Tropical forest, Tropical pasture

Abstract. We investigated the influences of forest or pasture land use and stream size on particulate and dissolved material concentrations in a network of second to third order streams in Rondônia, in the Brazilian Amazon. During the dry season, a second order stream originating in pasture had lower concentrations of dissolved oxygen and nitrate, higher concentrations of chlorophyll, total suspended solids, particulate organic carbon, particulate organic nitrogen, ammonium, and phosphate than a second order stream originating in forest. Where the second order forest stream exited forest and entered pasture, concentrations of dissolved oxygen dropped from 6 mg/L to almost 0 mg/L and nitrate concentrations dropped from 12 μ M to 2 μ M over a reach of 2 km. These changes indicated a strong influence of land use. During the rainy season, differences among reaches of all particulate and dissolved materials were diminished. Concentrations of oxygen, chlorophyll, total suspended solids, particulate organic carbon and nitrogen, nitrate, ammonium, and phosphate in the third order pasture stream more closely resembled the second order forest stream than the second order pasture stream, suggesting that conditions in the channels of larger pasture streams more strongly control concentrations of these materials. If this pattern is widespread in stream networks of regions that consist of a mosaic of forest and pasture lands, it may have important consequences for understanding the effects of deforestation on larger rivers of the Amazon Basin. This would indicate that the effects of forest clearing on the concentrations of many suspended and dissolved materials will be most easily detected in very small streams but potentially difficult to detect in larger streams and rivers.

Introduction

Small streams are important hydrologic and biogeochemical elements in landscapes because they connect the terrestrial environment with larger rivers. In small headwater streams the concentrations of particulate and dissolved materials reflect the combined effects of the delivery of material from the watershed and processing of material that occurs within the stream channel (Meyer and Likens 1979; Minshall

et al. 1985; McClain and Elsenbeer 2001). Most inputs of nutrients and organic matter from terrestrial to aquatic ecosystems enter via small streams (Vannote et al. 1980; Naiman et al. 1987). Forested headwater streams often have steep gradients, channels shaded by trees, and inputs dominated by allochthonous materials (Vannote et al. 1980; Triska et al. 1984). Some new work, however, suggests that small headwater streams have a disproportionately large effect on nutrient transport from watersheds precisely because they have high surface area to volume ratios and transform nutrients at high rates compared with larger river channels (Mulholland 1992; Alexander et al. 2000; Peterson et al. 2001; Wollheim et al. 2001).

Many studies of small streams show that changes in land use, such as from forest to agricultural land, or major disturbances, such as hurricanes or clearcutting, can dramatically alter the nature of particulate and dissolved material inputs to headwater streams (Dillon and Kirchner 1975; Likens and Bormann 1975; Attiwill 1991; Correll et al. 1991; Cooke and Prepas 1998). At the same time, the physical changes associated with land use alterations, such as increased light (Hill et al. 1995) or altered channel structure (Sweeney 1992; Wollheim et al. 2001) could also affect material uptake and processing. Knowledge of small stream characteristics and the factors that control particulate and dissolved materials is important for identifying the influences of changing land use and for understanding its effects on stream ecological functioning and on the delivery of materials to larger rivers.

Most of our understanding of changes in stream characteristics caused by land use or stream order has been developed in the temperate zone. However, both rapid rates of land use change in tropical regions during recent decades and the potential for changes to material and nutrient characteristics of large tropical rivers suggest that an extension of this understanding to tropical regions is needed. Forest clearing is now the dominant land use change occurring throughout much of the moist tropics (Matthews et al. 2000). This is especially true in the largest remaining rain-forest regions. In the Brazilian Amazon Basin, rates of forest clearing during the past decade ranged from 11,000 to 29,000 km²/year (INPE 2000), with the majority of cleared forest being converted to cattle pasture (Fearnside 1993).

The clearing of forest for cattle pasture alters soil nutrient cycles and influences the particulate and nutrient concentrations in small tropical streams. Several studies show that streamwater concentrations of nitrogen, phosphorus, and/or suspended sediments increase during or immediately following forest clearing (Malmer and Grip 1994; McDowell et al. 1996; Williams and Melack 1997). Richey et al. (1997) suggested that land use changes in tropical regions will be first reflected in the biogeochemistry of small streams. One influence that may differ from the pattern in the temperate zone is that streams draining pastures established on lands formerly covered by moist tropical forest can have lower concentrations of some nutrients (e.g., NO₃⁻) than forest streams, because nutrient availability is reduced in the soils of pastures (Neill et al. 2001). These changes to relative availability of nutrients and light in small pasture streams can alter the factors that limit periphyton growth (Neill et al. 2001). The degree to which the effects of land use change in small streams are transmitted downstream to larger rivers will depend on the distance over which these influences are maintained when streams pass from one land use to an-

other and the extent to which they are altered by in-channel processes as streams get progressively larger.

In this study, we investigated how the conversion from forest to pasture and an increase in stream size influenced dissolved and particulate materials in streams in the Brazilian Amazon. We examined changes in these materials in second order streams in forest and pasture, a stream that flowed from forest into pasture, and as a stream increased in size from second to third order.

Methods

Study area

Our study site was Fazenda Nova Vida, a 20,000 ha cattle ranch near the center of the Amazonian state of Rondônia, Brazil (10°13' S, 62°19' W). Small streams of first to fourth order flow through Nova Vida and into the Jamarí and Madeira rivers. This ranch contains a mixture of forest reserves and cattle pastures. The forest reserves were selectively logged between 1987 and 1990 by removing 1–2 trees/ha. Pastures were cleared in 1989 by cutting and burning to the stream edge, and then planted with *Brachiaria brizantha* in the uplands and *Paspalum* spp. in the floodplain. Pastures were not limed or fertilized. This region is humid tropical, with a dry season from May to October. The average yearly precipitation is 2,200 mm and the mean temperature is 26 °C (Bastos and Diniz TD 1982). The bedrock is generally Pre-Cambrian granite (Projeto RADAMBRASIL 1978) and the soils at the site are classified as Kandiodults and Paleudults (de Moraes et al. 1996).

We sampled four reaches within an approximately 10 km section that make up the Aldeia River network (Figure 1). Reach I was a second order forest stream, Reach II was a 2-km transitional reach downstream of the forest where it emerges into pasture, Reach III was a second order pasture stream, and Reach IV (Aldeia River) was the resulting third order stream formed by Reaches II and III, with surrounding land use dominated by pasture. These streams are typical of forest and pasture streams in the region. The pH among the reaches averaged 6.5 in the dry season and 5.8 in the rainy season.

Reach I (forest) had a sandy bottom and pool and riffle structure. Reach II (forest to pasture transition) began with a similar structure but ended with a fine-grained, organic-rich substrate and aquatic grasses in the channel. Reach III (pasture) had a similar structure to the downstream portion of Reach II, with vegetation that often covered the entire channel. Reach IV (third order pasture) was wider and had a pool and riffle structure, and a generally well-scoured sandy bottom similar to the upstream portion of Reach II. Land use in the drainage basin of the Aldeia River (Reach IV) determined from a 1999 Landsat image was 41% pasture and 57% forest and riparian areas.

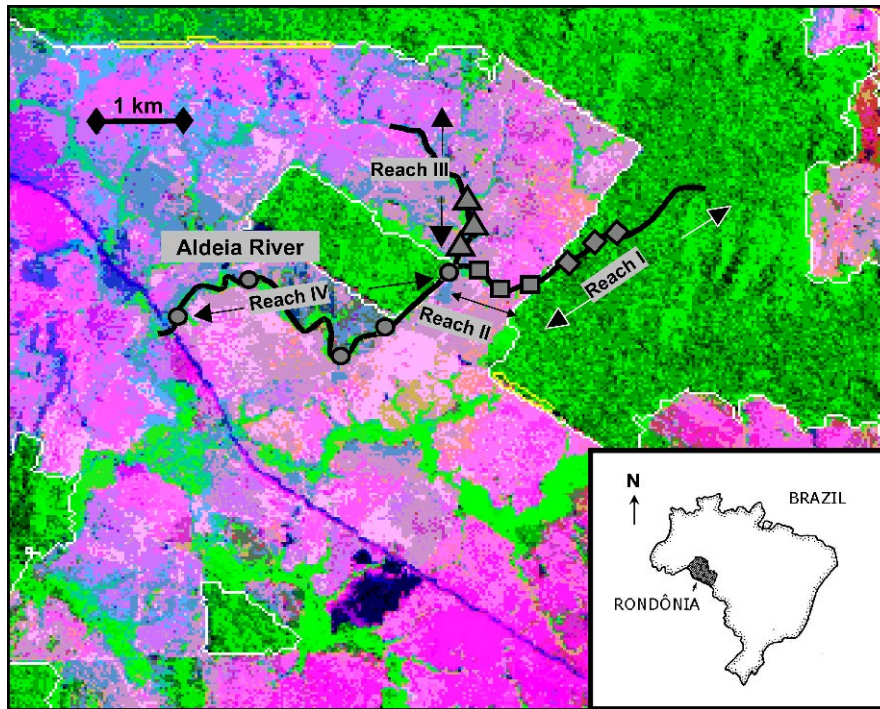


Figure 1. A 1998 Landsat TM image of Fazenda Nova Vida that shows the stream network sampled. Dark areas represent remaining forest and lighter areas represent pasture. Reach I is a second order forest stream. Reach II is a second order stream after it exits forest and enters pasture. Reach III is a second order pasture stream. Reach IV is a third order stream formed by the confluence of Reaches II and III. Sampling locations are marked.

Sampling and analysis

Samples were collected from a total of 14 stations during 5 dry and 4 rainy seasons from April 1994 to September 1999. Reaches I, II, and III had 3 stations each and Reach IV had 5 stations. Stations were at least 200 m apart. Typically, 9 to 11 transect stations distributed in the four reaches were sampled, although abbreviated transects of at least one station each in Reaches I, III, and IV were also sampled. Often, a full transect was accompanied by one or two other abbreviated transects for any given season. Samples were collected from Reaches I, III, and IV on 21 transects, and these data were used in the ANOVAs. At each station, we collected 1 L of streamwater that was placed on ice and filtered later the same day at the field laboratory for total suspended solids (TSS) and particulate organic carbon and nitrogen (POC and PON). One 60 mL sample for nitrate (NO_3^-), ammonium (NH_4^+), and phosphate (PO_4^{3-}), and total dissolved P (TDP) was filtered immediately through ashed glass fiber filters (Whatman GF/F), preserved with hydrochloric acid to $< \text{pH } 2$, and refrigerated. Another 60 mL sample for total dissolved N (TDN) was immediately filtered through ashed GF/F filters and frozen. Also in the field,

200 to 500 mL of streamwater was passed through a 47-mm diameter glass fiber filter (Whatman GF/C) for chlorophyll determination. This filter was immediately wrapped in foil, placed on ice, and then frozen upon return to the field laboratory. Dissolved oxygen was measured with a YSI Sonde (Yellow Springs Instruments Incorporated, Yellow Springs, OH). Water level heights were recorded from permanent staff gages in Reaches I and III at each water sampling. Continuous water level measurements in Reaches I and III were made over a one year period, from September 1999 through November 2000, using a water level datalogger (Global Water, Gold River, CA). Instantaneous discharge was calculated from stream cross-sectional area and velocity measurements (Hauer and Lamberti 1996). The water level measurements in 1999–2000 were converted to discharge by means of the stage-discharge relationships at Reaches I and III. Instantaneous discharge was also measured on selected dates in the downstream portion of Reach IV from cross-sectional area and velocity measurements.

Total suspended solids were measured by filtering a known volume of streamwater through pre-weighed, ashed 25-mm glass fiber filters (Whatman GF/F) and reweighed after drying overnight at 50 °C. Filters for POC and PON were prepared the same way and analyzed for C and N on a Perkin Elmer 2400 elemental analyzer. NO_3^- was measured by cadmium reduction (Alpkem method A303-S171-09) on an Alpkem RFA analyzer. NH_4^+ was analyzed by the phenol-hypochlorite method (Alpkem method A303-S020-02) and PO_4^{3-} was measured using the antimony/molybdate and ascorbic acid method (Alpkem method A303-S200-00). We calculated dissolved inorganic nitrogen to phosphorus ratios (DIN:DIP) as $(\text{NO}_3^- + \text{NH}_4^+)/\text{PO}_4^{3-}$. TDP was determined by acid persulfate digestion (Koroleff 1983). TDN was measured by alkaline persulfate digestion with HCl buffer solution (Modification of method 4500-N_{org} D, Eaton et al. (1995)). CertiPrep reference materials (SPEX Chemical, Metuchen, NJ) and laboratory-prepared solutions of ATP and nitrophenol were used to check the accuracy of the colorimetric methods and the efficiency of the TDN and TDP digestions. Dissolved organic nitrogen and phosphorus (DON and DOP) were calculated from the difference between TDN and TDP and inorganic N and P, respectively. Chlorophyll was extracted overnight from the frozen filters with a buffered 90% acetone solution. The extract was then analyzed using a fluorometer to determine chlorophyll a and phaeophytin concentrations (Strickland and Parsons 1972).

Dissolved constituents were measured in all transects and particulate constituents were measured on 19 transects. Instantaneous measurements of dissolved oxygen were taken on one dry (1999) and one rainy (2000) season transect. Dissolved oxygen was measured continuously for 72 hours at one station in Reaches I, III, and IV during the 1999 dry season.

Statistical analysis

We used a two-way ANOVA (SAS Institute 1998) to determine whether water quality characteristics differed among reaches (second order forest, second order pasture, or third order pasture) and between dry and rainy seasons. We included all

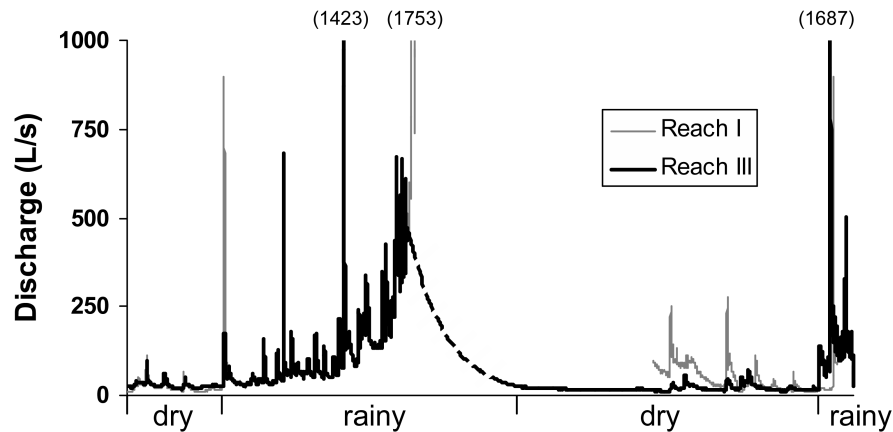


Figure 2. Streamwater discharge trace from September 1999 through November 2000. Stream height was converted to discharge using a stage-discharge relationship curve generated for each stream. Reach III (second order pasture stream) discharge is represented by the darker line, with interpolated values indicated by the dashed line. Reach I (second order forest stream) discharge is represented by the lighter line. Missing data were caused by logger failure.

sampling points in the second order forest stream (Reach I) and the second order pasture stream (Reach III) but only the three sampling points farthest downstream in the Aldeia River (Reach IV) to avoid the transition between reaches. To eliminate spatial-autocorrelation with a reach, we used the mean of the stations in each reach for each transect in all analyses. Data were $\log(x + 1)$ transformed to meet the assumptions of analysis of variance. Kolmogorov-Smirnov tests for normality and homogeneity of variance indicated variables were more nearly normal after transformation. If reach was significant, we conducted separate one-way ANOVAs and Fisher's PLSD pairwise comparisons for the dry and rainy seasons to determine significant differences among reaches. For all analyses, we used the sequential Bonferroni-Dunn method to adjust P-values for multiple tests performed on the same samples ($\alpha' = 1 - (1 - \alpha)^{1/k}$), where $\alpha = 0.05$ and k is the number of tests (Sokal and Rohlf 1995).

Results

Dry season discharges were typically 15–40 L/s in the forest (Reach I) and pasture (Reach III) streams (Figure 2). Rainy season discharges varied widely with peak discharges of > 500 L/s on several days. All reaches were gaining reaches in both seasons, with an approximate 16% increase in discharge from the beginning of Reach IV (the confluence of Reaches II and III) to the end of Reach IV (Table 1). Approximately eighty-six percent of the total water flux from the small pasture stream (for which we had the best continuous annual discharge record) occurred during the six months of highest flow (November through April).

Table 1. Discharges (L/s) in different reaches of the stream network measured August 28, 1999 (dry season) and March 13, 1998 (rainy season). Reach I is a second order forest stream; Reach III is the second order pasture stream; Reach IV is the larger pasture stream formed by Reaches I and III. Km indicates kilometers downstream in the transect and corresponds to the kilometers downstream in the figures. Discharges reflected typical seasonal values.

	Km	Dry season (L/s)	Rainy season (L/s)
Reach I	1.5	40	913
Reach III	3.0	30	354
Sum of Reaches I and III		70	1,267
Reach IV	8.5	82	1,506

Dissolved oxygen was lower in the second order pasture stream (Reach III) than in the second order forest stream (Reach I) during both the dry and rainy seasons (Figure 3). Dissolved oxygen concentrations in Reach III were < 1.0 mg/L during both dry and rainy seasons. Oxygen concentrations also changed within a short distance of the forest stream emerging into pasture. During the dry season, dissolved oxygen decreased from 6.4 mg/L in the forest stream to 2.5 mg/L after passing through 2 km of pasture in Reach II. This change was smaller during the rainy season (> 7 mg/L in forest compared with 6 mg/L in pasture). Dissolved oxygen in the third order stream (Reach IV) was similar to the forest stream. Dissolved oxygen did not vary diurnally in the forest stream (Reach I) or in the small pasture stream (Reach III) but varied by about 3 mg/L in the larger pasture stream (Reach IV) (Figure 4).

Chlorophyll, TSS, POC, and PON concentrations differed among reaches (Figure 3, Table 2). Chlorophyll concentrations were higher in the dry season but TSS, POC, and PON concentrations did not differ between seasons. Chlorophyll concentrations were higher in the pasture stream (Reach III) than in the forest stream (Reach I) during both the dry and rainy seasons. Chlorophyll was higher in the small pasture stream (Reach III) than the large pasture stream (Reach IV) during the rainy season but not during the dry season. Total suspended solids, POC, and PON followed similar patterns and were all significantly greater in the small pasture stream (Reach III) than in the forest stream (Reach I) during both the dry and rainy seasons.

Nitrate concentrations were significantly lower in the pasture stream (Reach III) than in the forest stream (Reach I) during the dry season but not the rainy season (Figure 5, Table 2). Nitrate concentrations dropped rapidly in the transition from forest to pasture during the dry season, decreasing from 10 μ M to 1 μ M within 2 km. Ammonium, NO_3^- , and PO_4^{3-} concentrations also differed among reaches. Ammonium concentrations were higher in the small pasture stream (Reach III) than in the forest stream (Reach I) or the larger pasture stream (Reach IV) during the dry season. Ammonium concentrations among the reaches were similar during the rainy season. Phosphate concentrations were significantly higher in the small pasture stream (Reach III) than in the forest stream (Reach I) during both dry and rainy seasons. Concentrations of PO_4^{3-} did not change rapidly in the transition from for-

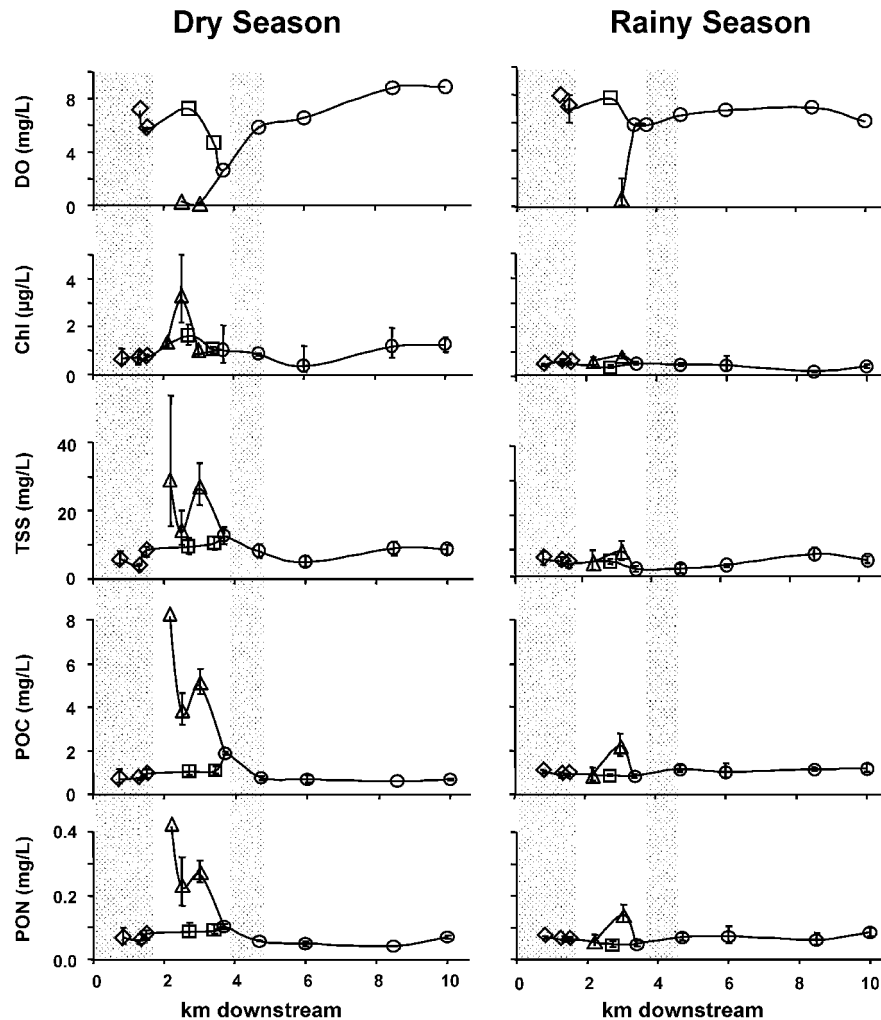


Figure 3. Streamwater concentrations of dissolved oxygen (DO), chlorophyll (Chl), total suspended solids (TSS), and particulate organic carbon and nitrogen (POC and PON) in four stream reaches at Nova Vida. Values from left to right go downstream in the transect. Reach I (\diamond) is a second order forest stream. Reach II (\square) is the same stream after it passes into pasture. Reach III (\triangle) is a second order pasture stream. Reach IV (\circ) is a third order stream formed by the confluence of Reaches II and III and flowing mostly through pasture. The shaded areas represent where the stream passes through or alongside forest. Values are geometric mean (\pm standard error) concentrations of all observations at a station over all years. In many cases, the error bars are smaller than the symbol.

est to pasture. Nitrate, NH_4^+ , and PO_4^{3-} concentrations were higher in the dry season but DON and DOP concentrations did not differ between seasons.

Dissolved inorganic nitrogen to phosphorus ratios reflected differences in NO_3^- and PO_4^{3-} concentrations along the transect. During the dry season, DIN:DIP was

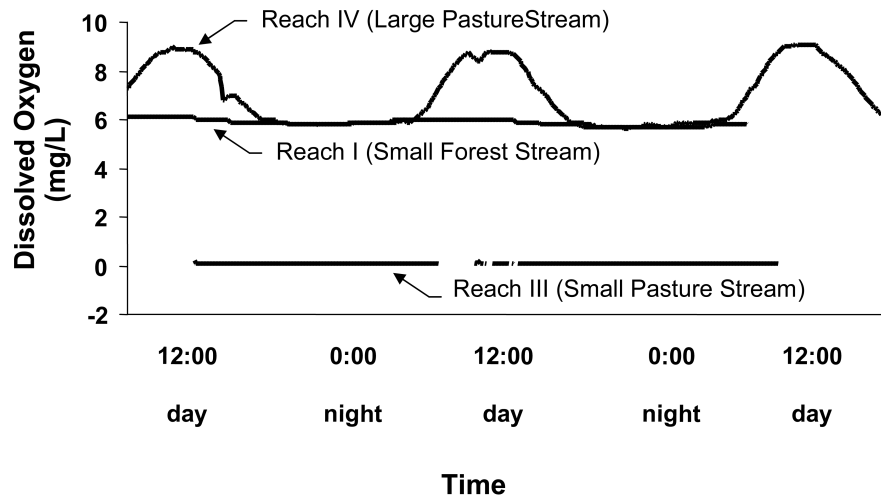


Figure 4. Continuous dissolved oxygen measurements at Reaches I, III, and IV over an approximate 72-hour period in each reach. These measurements were taken sequentially: Reach I was measured August 26–28, 1999; Reach III was measured August 28–30, 1999; and Reach IV was measured September 3–10, 1999.

consistently higher in the forest stream (Reach I) than in the pasture stream (Reach III) (Figure 5). The DIN:DIP in the forest stream (Reach I) decreased rapidly through Reach II where the land use changed from forest to pasture (from 80 to 30 in 2 km). During the dry season, DIN:DIP in the larger pasture stream (Reach IV) was intermediate between those in the forest and pasture streams. DIN:DIP was consistently higher during the dry season than during the rainy season throughout the transect, but the same pattern in the reaches was present during the rainy season. The forest stream (Reach I) had DIN:DIP > 16 during both dry and rainy seasons and the pasture stream (Reach III) had DIN:DIP < 16 during both seasons. The larger pasture stream (Reach IV), had DIN:DIP > 16 during the dry season but < 16 during the rainy season.

Discussion

The patterns we observed in the Aldeia stream network strongly indicated that concentrations of some particulate and dissolved materials were coupled to land use. First, higher concentrations of chlorophyll, TSS, POC and PON, and lower concentrations of dissolved oxygen, NO_3^- , and DIN:DIP in the small pasture stream compared with the small forest stream were similar to the more general patterns found in the Neill et al. (2001) paired watershed study, which included an additional pair of similar-sized forest and pasture streams and more intensive sampling of single stations from the forest (Reach I) and pasture (Reach III). Second, after the forest stream exited forest into pasture and flowed downstream for 2 km, con-

Table 2. Results of two-way analysis of variance and Fisher's PLSD pairwise comparisons of the effects of season and reach on streamwater characteristics. Characteristics included were chlorophyll (Chl), total dissolved solids (TSS), particulate organic carbon and nitrogen (POC and PON), nitrate (NO_3^-), ammonium (NH_4^+), dissolved organic nitrogen (DON), phosphate (PO_4^{3-}), and dissolved organic phosphate (DOP). Seasons were dry and rainy seasons. Reaches were Reach I (second order forest stream), Reach III (second order pasture stream), and Reach IV (third order pasture stream). P values that exceed the sequential Bonferroni-Dunn correction value are indicated with an asterisk. Within dry and rainy season, reaches with different capital letters were significantly different ($p < 0.05$). Residual degrees of freedom were: Chl (47), TSS (53), POC (27), PON (27), NO_3^- (56), NH_4^+ (37), DON (28), PO_4^{3-} (56), and DOP (32).

ANOVA			Fisher's PLSD pairwise comparison										
Reach	Season		Reach * Season		Dry season				Rainy season				
	P <	F	P <	F	P <	I	III	IV	I	III	IV		
Particulate													
Chl	9.81	0.0003*	16.51		0.0002*	1.33	0.2745	A	B	AB	A	B	A
TSS	6.99	0.0020*	1.92		0.1715	2.07	0.1368	A	B	A	A	A	A
POC	40.89	<0.0001*	1.48		0.2343	7.50	0.0026*	A	B	A	A	B	A
PON	31.94	<0.0001*	6.93		0.0138	7.84	0.0021*	A	B	A	A	B	A
Dissolved													
NO ₃ ⁻	7.74	0.0011*	66.40		<0.0001*	6.48	0.0029*	A	B	A	A	A	A
NH ₄ ⁺	9.19	0.0006*	44.60		<0.0001*	9.93	0.0004*	A	B	A	A	A	A
DON	0.07	0.9332	0.27		0.6078	0.75	0.4802						
PO ₄ ³⁻	39.40	<0.0001*	19.67		0.0001*	17.00	<0.0001*	A	B	A	A	B	A
DOP	0.28	0.7558	1.46		0.2360	0.77	0.4698						

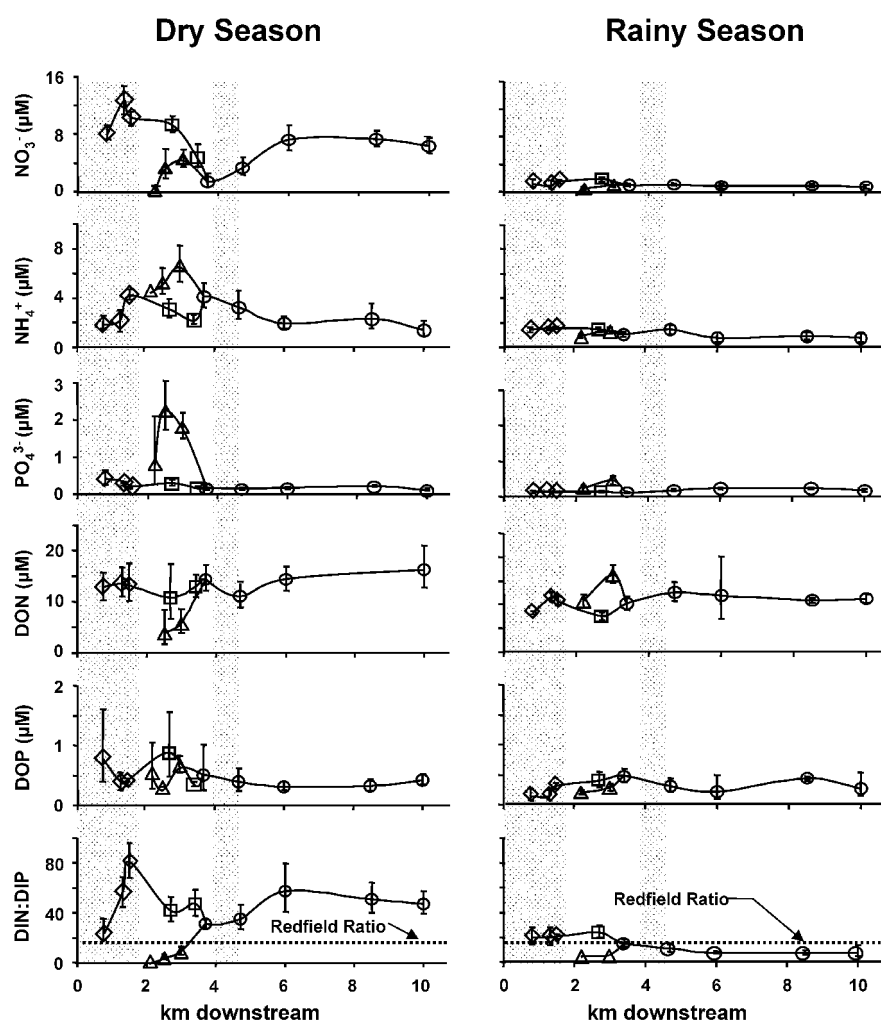


Figure 5. Streamwater dissolved nutrient concentrations in four stream reaches at Nova Vida. Values from left to right go downstream in the transect. Reach I (\diamond) is a second order forest stream. Reach II (\square) is the same stream after it passes into pasture. Reach III (\triangle) is second order pasture stream. Reach IV (\circ) is a third order stream formed by the confluence of Reaches II and III and flowing mostly through pasture. The shaded areas represent where the stream passes through or alongside forest. The dashed line on the DIN:DIP graph represents the Redfield DIN:DIP ratio of 16:1. Values are geometric mean (\pm standard error) concentrations of all observations at a station over all years. In many cases, the error bars are smaller than the symbol.

centrations of dissolved oxygen, NO_3^- , and DIN:DIP approached the concentrations in the pasture stream. This pattern indicated that adjacent land use influenced dissolved oxygen, NO_3^- , and the DIN:DIP over that distance. Although concentrations of TSS, POC, PON, NH_4^+ , and PO_4^{3-} were higher in the small pasture stream compared with the small forest stream, these characteristics did not change as rapidly

in the same reach, suggesting they were less influenced by adjacent land use over the same distance.

The low dissolved oxygen, low NO_3^- , and higher PO_4^{3-} found in the second order pasture stream occurred nowhere else in the stream network. The low dissolved oxygen concentrations we measured in the small pasture stream were in the range typically associated with heterotrophy resulting from high organic matter inputs, such as those that occur in Amazonian floodplain lakes (Melack and Fisher 1983; Welcomme 1985). Low dissolved oxygen was not found in the larger pasture stream, despite its adjacent pasture land use. We hypothesize that the physical structure of stream channels played a key role in creating this pattern. A switch from sandy bottoms, unvegetated point bars, and a pool and riffle structure in forest headwater streams to fine-grained, organic-rich bottoms with channel infilling by aquatic vegetation (*Paspalum* in our study area) in headwater pasture streams reduces dissolved oxygen in the water column. As pasture streams increase in size, channel infilling by vegetation decreases and the amount of autochthonous primary production and turbulent mixing increase, leading to well-oxygenated conditions. Substantial diurnal fluctuations in dissolved oxygen concentrations during the dry season (Figure 4) supported the interpretation that this reach had greater autochthonous production.

Dissolved oxygen concentrations can influence stream NO_3^- and PO_4^{3-} concentrations in ways that would create the pattern we observed in our stream network. Release of PO_4^{3-} from sediments by dissolution of iron oxides occurs under anoxic conditions in soils and waters with low PO_4^{3-} concentrations, and higher dissolved oxygen can facilitate PO_4^{3-} adsorption to iron and aluminum oxides (Syers et al. 1973; Patrick and Khalid 1974; Khalid et al. 1977; Allen 1995). Low dissolved oxygen inhibits nitrification and promotes denitrification, leading to elevated concentrations of NH_4^+ and lowered concentrations of NO_3^- (Seitzinger 1988; Christensen et al. 1990).

We could not distinguish between the sources and sinks of streamwater NO_3^- in this study, but both inputs from soil solution rich in NO_3^- (McDowell et al. 1992; Neill et al. 2001) and nitrification in the stream channel (McClain et al. 1994; Brandes et al. 1996) could be sources of NO_3^- to the small forest stream. We suggest that higher dissolved oxygen concentrations in the small forest stream and the larger pasture streams promote nitrification, decreases NO_3^- demand by denitrifiers, and facilitate the adsorption of PO_4^{3-} by iron and aluminum oxides. In the small pasture stream, lower rates of NO_3^- production, lower solution NO_3^- concentrations in pasture soils (Neill et al. 1995; Verchot et al. 1999), and NO_3^- consumption associated with low dissolved oxygen all were consistent with lower measured streamwater NO_3^- concentrations. In the larger pasture stream, low groundwater inputs (Table 1) and low soil solution NO_3^- typical of pasture made it unlikely that groundwater inputs alone accounted for the observed increase in NO_3^- concentration with increasing stream order. On those dates for which we had data on discharge of all three reaches to calculate mass fluxes, the increase in streamwater NO_3^- in Reach IV could be accounted for solely by the decrease in NH_4^+ . Nitrification in the stream channel is an important source of streamwater NO_3^- in many

temperate streams (Newbold et al. 1983; Richey et al. 1985; Mulholland et al. 2000). We do not know enough about the hydrology and sources of groundwater in the area to exclude the possibility of inputs of old groundwater formed before forests were cut; however, the generally rapid subsurface flowpaths that dominate on tropical Ultisols (Elsenbeer 2001) and the time since clearing of adjacent forest (11–22 years at the start of sampling) make this source unlikely.

Higher concentrations of particulate material (including TSS, POC, and PON) in the second order pasture stream during the dry season were consistent with a number of studies that indicate high fluxes of TSS from small agricultural watersheds (Burwell et al. 1977; Omernik et al. 1981; Reid and Frostick 1994). However, we did not observe elevated TSS during the rainy season, nor were TSS, POC, or PON concentrations in the larger pasture streams higher than those in the forest stream. Other studies of grazed small watersheds suggest that TSS losses are not substantially higher than from forested watersheds (Owens et al. 1983; Correll et al. 1999). In the second order pasture stream, organic C made up more than 30% of TSS. This is much higher than in many agricultural watersheds and supports the conclusion that the density of aquatic plants, rather than increased erosion, contributes to the high particulate load observed in the small pasture stream during the dry season.

Lower concentrations of chlorophyll, NO_3^- , NH_4^+ , and PO_4^{3-} and smaller differences among reaches during the rainy season suggested that the effect of land use was suppressed by dilution during the rainy season when the majority of total water flux (86%) occurred. This dilution contrasted with the pattern found by Markewitz et al. (2001) of a positive correlation of flow with cations, NO_3^- , and SO_4^{2-} concentrations in a 10,000 ha watershed of mixed land use on Oxisols in the Brazilian Amazon state of Pará. They attributed higher concentrations at higher flows with surface flushing of ions from pastures deforested 30 years ago. The same mechanism did not appear to operate in the Nova Vida pasture streams.

The DIN:DIP ratios of > 16 in the second order forest stream and < 16 in the second order pasture stream in both dry and rainy seasons suggested that conditions favoring P limitation in the forest and N limitation in the pasture predominated year-round in these reaches. DIN:DIP above 16 indicated N rather than P limitation of algal production (Redfield 1958). Nutrient limitation of stream periphyton has been shown to change from light and P in the forest stream to N in the pasture stream (Neill et al. 2001). In the third order pasture stream DIN:DIP shifted seasonally from > 16 during the dry season to < 16 during the rainy season. This raises the possibility that algal production in the larger, open-canopy stream can be P limited during the dry season but N limited during the rainy season. Seasonal shifts in N versus P limitation have been observed in Amazonian floodplain lakes (Setaro and Melack 1984). Ratios of N:P delivered by rivers can have important consequences for the productivity of receiving waters (Fisher et al. 1992; Justic et al. 1995).

The particulate and dissolved materials that we measured were potentially sensitive indicators of land use change in stream watersheds and biogeochemical transformations in stream channels. We recognize that this is only one stream network,

but if the trends are similar in other small streams of this region, then these results may have important consequences for understanding and detecting the effects of deforestation on larger rivers of the Amazon Basin. The lower concentrations of dissolved oxygen and NO_3^- and higher concentrations of TSS, POC, PON, NH_4^+ , and PO_4^{3-} in the small pasture stream were diminished or absent downstream in a slightly larger third order pasture stream. We hypothesize that these changes were driven by lower NO_3^- inputs from pasture land cover and by channel structure and organic matter inputs that lead to low dissolved oxygen, NO_3^- consumption, and PO_4^{3-} release in small pasture streams but higher dissolved oxygen, nitrification, and PO_4^{3-} precipitation in larger pasture streams. If confirmed by process studies and surveys of other stream networks in tropical forest regions undergoing land use change, this suggests that the effects of forest clearing on the concentrations of these materials will be most easily detected in small streams but potentially difficult to detect in larger streams and rivers.

Acknowledgements

We thank our colleagues at the Centro de Energia Nuclear na Agricultura in Piracicaba, especially Jean Pierre Ometto and Marcelo Bernardes, who helped with sample collection. Carlos Cerri, Jerry Melillo, Paul Steudler, and Diana Garcia-Montiel provided important advice and support. João Arantes, Jr. kindly provided us access and facilities at Nova Vida. Special thanks to José Cardoso and Wanderley Zucoloto for field logistical support at Nova Vida. Two anonymous reviews provided very insightful comments. Yosio Shimabukuro of the Instituto Nacional de Pesquisas Espaciais kindly provided the satellite image of Nova Vida. Support for this study was provided by NSF-EAR-9630278, NASA NAG5-3859, NASA-NCC5-279, and the Mellon Foundation.

References

- Alexander R.B., Smith R.A. and Schwarz G.E. 2000. Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. *Nature* 403: 758–761.
- Allen J.D. 1995. *Stream Ecology: Structure and Function of Running Waters*. Kluwer Academic Publishers, Dordrecht, The Netherlands.
- Alpkem Corporation 1986. *Alpkem RFA Methods Manual*. Alpkem Corporation, Clackamas, OR, USA.
- Attiwill P.M. 1991. The disturbance of forested watersheds. In: Mooney EM H.A., Schindler D.W., Schulze E.D. and Walker B.H. (eds), *SCOPE 45: Ecosystem Experiments*. Wiley, New York, pp. 193–213.
- Bastos T.X. and Diniz TD A.S. 1982. *Avaliação de Clima do Estado de Rondônia Para Desenvolvimento Agrícola*. Vol. 44. EMBRAPA-CPATU, Belém.
- Brandes J.A., McClain M.E. and Pimentel T.P. 1996. ^{15}N evidence for the origin and cycling of inorganic nitrogen in a small Amazonian catchment. *Biogeochemistry* 34: 45–56.

- Burwell R.E., Schuman G.E., Heinemann H.G. and Spomer R.G. 1977. Nitrogen and phosphorus movement from agricultural watersheds. *Journal of Soil and Water Conservation* 32: 226–230.
- Christensen P., Neilson L.P., Lorensen J. and Revsbech N.P. 1990. Denitrification in nitrate-rich streams: diurnal and seasonal variation related to benthic oxygen metabolism. *Limnology and Oceanography* 35: 640–651.
- Cooke S.E. and Prepas E.E. 1998. Stream phosphorus and nitrogen export from agricultural and forested watersheds on the Boreal Plain. *Canadian Journal of Fisheries and Aquatic Sciences* 55: 2292–2299.
- Correll D.L., Jordan T.E. and Weller D.E. 1991. Nutrient flux in a landscape: Effects of coastal land use and terrestrial community mosaic on nutrient transport to coastal waters. *Estuaries* 15: 431–442.
- Correll D.L., Jordan T.E. and Weller D.E. 1999. Precipitation effects on sediment and associated nutrient discharges from Rhode River watersheds. *Journal of Environmental Quality* 28: 1897–1907.
- de Moraes J.F.L., Volkoff B., Cerri C.C. and Bernoux M. 1996. Soil properties under Amazon forest and changes due to pasture installation in Rondônia, Brazil. *Geoderma* 70: 63–81.
- Dillon P.J. and Kirchner W.B. 1975. The effects of geology and land use on the export of phosphorus from watersheds. *Water Research* 9: 135–148.
- Eaton A.D., Clesceri L.S. and Greenberg A.E. 1995. *Standard Methods for the Examination of Water and Wastewater*. 19th edn. American Public Health Association, Washington, DC, USA.
- Elsenbeer H. 2001. Hydrologic flowpaths in tropical rainforest soils— a review. *Hydrological Processes* 15: 1751–1759.
- Fearnside P.M. 1993. Deforestation in Brazilian Amazonia: The effect of population and land tenure. *Ambio* 22: 537–545.
- Fisher T.R., Peele E.R., Ammerman J.W. and Harding L.W. Jr 1992. Nutrient limitation of phytoplankton in Chesapeake Bay. *Marine Ecology Progress Series* 82: 51–63.
- Hauer F.R. and Lamberti G.A. 1996. *Methods in Stream Ecology*. Academic Press, New York.
- Hill W.R., Ryon M.G. and Schilling E.M. 1995. Light limitation in a stream ecosystem: Responses by primary producers and consumers. *Ecology* 76: 1297–1309.
- INPE 2000. Monitoramento da floresta Amazônica Brasileira por satélite, 1998–1999. Instituto Nacional de Pesquisas Espaciais, São José dos Campos, Brazil.
- Justic D., Rabalais N.N. and Turner R.E. 1995. Stoichiometric nutrient balance and origin of coastal eutrophication. *Marine Pollution Bulletin* 30: 41–46.
- Khalid R.A., Patrick W.H. Jr, DeLaune R.D. and Stewart B.A. 1977. Phosphorus sorption characteristics of flooded soils. *Soil Science Society of America* 41: 305–310.
- Koroleff F. 1983. Determination of total phosphorus by acid persulphate oxidation. In: Grasshoff K., Ehrhardt M. and Kremling K. (eds), *Methods of Seawater Analysis*. Verlag Chemie, Weinheim, Germany, pp. 134–136.
- Likens G.E. and Bormann F.H. 1975. Nutrient-hydrologic interactions. In: Hasler A.D. (ed.), *Coupling of Land and Water Systems*. Springer-Verlag, NY, pp. 1–63.
- Malmer A. and Grip H. 1994. Converting tropical rainforest to forest plantation in Sabah, Malaysia. Part II. Effects on nutrient dynamics and net losses in streamwater. *Hydrological Processes* 8: 195–209.
- Markewitz D., Davidson E.A., Figueiredo R.O., Victoria R.L. and Krusche A.V. 2001. Control of cation concentrations in stream water by surface soil processes in an Amazonian watershed. *Nature* 410: 802–805.
- Matthews, Payne E.R., Rohweder M. and Murray S. 2000. *Pilot analysis of global ecosystems: forest ecosystems*. World Resources Institute, Washington, DC, USA.
- McClain M.E. and Elsenbeer H. 2001. Terrestrial inputs to Amazon streams and internal biogeochemical processing. In: McClain M.E., Victoria R.L. and Richey J.E. (eds), *Biogeochemistry of the Amazon Basin*. Oxford University Press, New York, pp. 185–208.
- McClain M.E., Richey J.E. and Pimentel T.P. 1994. Groundwater nitrogen dynamics at the terrestrial-lotic interface of a small catchment in the Central Amazon Basin. *Biogeochemistry* 27: 113–127.

- McDowell W.H., Bowden W.B. and Asbury C.E. 1992. Riparian nitrogen dynamics in two geomorphologically distinct tropical rain forest watersheds: subsurface solute patterns. *Biogeochemistry* 18: 53–75.
- McDowell W.H., McSwiney C.P. and Bowden W.B. 1996. Effects of hurricane disturbance on groundwater chemistry and riparian function in a tropical rain forest. *Biotropica* 28: 577–584.
- Melack J.M. and Fisher T.R. 1983. Diel oxygen variations and their ecological implications in Amazon floodplain lakes. *Archiv fur Hydrobiologie* 98: 422–442.
- Meyer J.L. and Likens G.E. 1979. Transport and transformation of phosphorus in a forest stream ecosystem. *Ecology* 60: 1255–1269.
- Minshall G.W., Cummins K.W., Petersen R.C., Cushing C.E., Bruns D.A., Sedell J.R. et al. 1985. Developments in stream ecosystem theory. *Canadian Journal of Fisheries and Aquatic Sciences* 42: 1045–1055.
- Mulholland P.J. 1992. Regulation of nutrient concentrations in a temperate forest stream: Roles of upland, riparian, and instream processes. *Limnology and Oceanography* 37: 1512–1526.
- Mulholland P.J., Tank J.L., Sanzone D.M., Wollheim W.M., Peterson B.J., Webster J.R. et al. 2000. Nitrogen cycling in a forest stream determined by a ^{15}N tracer addition. *Ecological Monographs* 70: 471–493.
- Naiman R.J., Melillo J.M., Lock M.A., Ford T.E. and Reice S.R. 1987. Longitudinal patterns of ecosystem processes and community structure in a subarctic river continuum. *Ecology* 68: 1139–1156.
- Neill C., Piccolo M.C., Steudler P.A., Melillo J.M., Feigl B.J. and Cerri C.C. 1995. Nitrogen dynamics in soils of forests and active pastures in the western Brazilian Amazon Basin. *Soil Biology and Biochemistry* 27: 1167–1175.
- Neill C., Deegan L.A., Thomas S.M. and Cerri C.C. 2001. Deforestation for pasture alters nitrogen and phosphorus in small Amazonian streams. *Ecological Applications* 11: 1817–1828.
- Newbold J.D., Elwood J.W., Schulze M.S., Stark R.W. and Barmeir J.C. 1983. Continuous ammonium enrichment of a woodland stream: Uptake kinetics, leaf decomposition, and nitrification. *Freshwater Biology* 13: 193–204.
- Omernik J.M., Abernathy A.R. and Male L.M. 1981. Stream nutrient levels and proximity of agricultural and forest land to streams: Some relationships. *Journal of Soil and Water Conservation*: 227–231.
- Owens L.B., Edwards W.M. and Van Keuren R.W. 1983. Surface runoff water quality comparisons between unimproved pasture and woodland. *Journal of Environmental Quality* 12: 518–522.
- Patrick W.H. Jr and Khalid R.A. 1974. Phosphate release and sorption by soils and sediments: Effect of aerobic and anaerobic conditions. *Science* 186: 53–55.
- Peterson B.J., Wollheim W.M., Mulholland P.J., Webster J.R., Meyer J.L., Tank J.L. et al. 2001. Control of nitrogen export from watersheds by headwater streams. *Science* 292: 86–90.
- Projeto RADAMBRASIL 1978. Geología, geomorfología, pedología, vegetação e uso potencial da terra. Folha SC20-Porto Velho. Departamento Nacional de Produção Mineral (DNPM), Rio de Janeiro, Brazil.
- Redfield A.C. 1958. The biological control of chemical factors in the environment. *American Scientist* 46: 205–221.
- Reid I. and Frostick L.E. 1994. Fluvial sediment transport and deposition. In: Pye K. (ed.), *Sediment Transport and Depositional Processes*. Blackwell, London, pp. 89–155.
- Richey J.E., Wilhelm S.R., McClain M.E., Victoria R.L., Melack J.M. and Araujo Lima C. 1997. Organic matter and nutrient dynamics in river corridors of the Amazon Basin and their response to anthropogenic change. *Ciência e Cultura* 49: 98–110.
- Richey J.S., McDowell W.H. and Likens G.E. 1985. Nitrogen transformations in a small mountain stream. *Hydrobiologia* 124: 129–139.
- SAS Institute 1998. *Statview II*. SAS Institute, Cary, North Carolina, USA.
- Seitzinger S. 1988. Denitrification in freshwater and coastal ecosystems: ecological and geochemical significance. *Limnology and Oceanography* 33: 702–724.
- Setaro F.V. and Melack J.M. 1984. Responses of phytoplankton to experimental nutrient enrichment in an Amazon floodplain lake. *Limnology and Oceanography* 29: 972–984.

- Sokal R.R. and Rohlf F.J. 1995. Biometry. W. H. Freeman, NY, USA.
- Strickland J.D.H. and Parsons T.R. 1972. A Practical Handbook of Seawater Analysis. Fisheries Research Board of Canada, Ottawa.
- Sweeney B.W. 1992. Streamside forests and the physical, chemical, and trophic characteristics of Piedmont streams in eastern North America. *Water Science and Technology* 26: 2653–2673.
- Syers J.K., Harris R.F. and Armstrong D.E. 1973. Phosphate Chemistry in Lake Sediments. *Journal of Environmental Quality* 2: 1–14.
- Triska F.J., Sedell J.R., Cromack K. Jr, Gregory S.V. and McCorison F.M. 1984. Nitrogen budget for a small coniferous forest stream. *Ecological Monographs* 54: 119–140.
- Vannote R.L., Minshall G.W., Cummins K.W., Sedell J.R. and Cushing C.E. 1980. The river continuum concept. *Canadian Journal of Fisheries and Aquatic Sciences* 37: 130–137.
- Verchot L.V., Davidson E.A., Cattaneo J.H., Ackerman I.L., Erickson H.E. and Keller M. 1999. Land-use change and biogeochemical controls of nitrogen oxide emissions from soils in eastern Amazonia. *Global Biogeochemical Cycles* 13: 31–46.
- Welcomme R.L. 1985. River Fisheries. Food and Agriculture Organization Fisheries Technical Paper 262., Rome.
- Williams M.R. and Melack J.M. 1997. Solute export from forested and partially deforested catchments in the central Amazon. *Biogeochemistry* 38: 67–102.
- Wollheim W.M., Peterson B.J., Deegan L.A., Hobbie J.E., Hooker B., Bowden W.B. et al. 2001. Influence of stream size on ammonium and suspended particulate nitrogen processing. *Limnology and Oceanography* 46: 1–13.