Land-use effects on the chemical attributes of low-order streams in the eastern Amazon

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[1] Deforestation is altering small catchment hydrobiogeochemistry in the Amazon. To evaluate land use change effects on water chemistry and other measures of water quality, five low-order streams were studied in the eastern Amazon from April 2003 to October 2005. It was hypothesized that 1) cation loads would increase downstream as the area of cleared forest increased, particularly during the wet season, 2) increasing forest to pasture conversion would increase total solute loads, and 3) nitrate concentrations, which are high under mature forest, would decline with conversion to pasture, but would increase with increasing row crop agriculture. The first hypothesis was generally not supported, as there was no consistent observed increase in conductivity or cation concentrations from upstream to downstream. However, elevated wet-season measures of conductivity, alkalinity, and turbidity indicated increased wet season surface runoff of these constituents, with seasonal changes largest in the watersheds that had experienced the most deforestation. The second hypothesis was supported when all data were pooled in a mixed-model analysis such that conductivity declined with increasing percent forest or increased with increasing percent pasture; however, similar correlations with cations were not significant. The third hypothesis was supported, with decreasing nitrate concentrations observed as forest cover declined and pasture cover increased from upstream to downstream positions, except where crops were grown near the stream, which was associated with increased stream nitrate. In addition, stream temperature, dissolved oxygen, and pH were negatively correlated with percent forest cover while sodium, chloride, and turbidity also increased with percent crop cover. Turbidity, temperature, pH, and dissolved oxygen appear to be the simplest and most indicative parameters for detecting effects of land-use change on water quality in this region.

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1. Introduction

[2] Land use changes can lead to modifications in terrestrial energy and water balances and the availability of nutrients [*Richey et al.*, 1997]. As a consequence, the transport of sediments, organic matter, and nutrients to streams can also be altered. Understanding how these changes will affect the biological, chemical, and physical functions of Amazonian rivers of Brazil is important for minimizing or mitigating any potential adverse impacts [*Ballester et al.*, 2003; *Davidson et al.*, 2004]. Deforestation in the Amazon Basin may be altering stream hydrology and biogeochemistry over many thousands of kilometers of low-order stream channels [*Neill et al.*, 2006a]. Surprisingly, however, the first and second order streams that comprise 80% of the total amount of riverine habitat throughout this region have received little attention in this regard [*McClain and Elsenbeer*, 2001].

[3] Small scale, low-order streams are important hydrologic and biogeochemical elements in landscapes because they connect the terrestrial environment with larger rivers. The concentrations of particulate and dissolved materials in these small streams also generally reflect the delivery of material from the watershed and are traceable to activities in the watershed due to their limited size [*McClain and Elsenbeer*, 2001]. Most inputs of nutrients and organic matter from terrestrial to aquatic ecosystems enter via small streams [*Vannote et al.*, 1980] and often have a disproportionately large effect on nutrient transport from watersheds precisely

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because they have high surface area to volume ratios [*Alexander et al.*, 2000; *Peterson et al.*, 2001]. An improved understanding of small stream characteristics and the factors that control dissolved materials is important for identifying the influences of changing land use on biogeochemical processes, on stream functioning, and the degree to which these effects of land use change in small streams are transmitted downstream to larger rivers [*Thomas et al.*, 2004].

[4] Changes in water chemistry associated with land use conversion have been demonstrated previously in the Amazon region. For example, in the western Amazon in the Brazilian state of Rondônia, a watershed study that compared two small forested watersheds with two similarly sized pasture watersheds found a shift from forested streams with high NO_3 and high dissolved inorganic N to dissolved inorganic P ratios (DIN:DIP) to stream waters in pastures with low NO_3 and low DIN:DIP ratios [*Neill et al.*, 2001; *Thomas et al.*, 2004]. This shift in DIN:DIP was reported to shift the streams from P limited to N limited systems. A broader landscape scale survey of streams in this region also demonstrated nonlinearly increasing patterns of total dissolved N (TDN), total dissolved P (TDP), and Cl^- concentrations in the dry season with extent of deforestation in the watershed [*Biggs et al.*, 2004]. This work also found an important influence of soil type on stream water chemical responses. In a third study in the Rondônia region, *Ballester et al.* [2003] estimated that an increase of 10% in the pasture area of the lower Ji-Paraná River resulted in a threefold increase of phosphate concentration in stream water.

[5] In the eastern Amazon region around Paragominas, in the Brazilian state of Pará, land-use change in a mixed use watershed was reported to influence cationic stream concentrations [*Markewitz et al.*, 2001]. In this study, conversion of mature forest to pastures through slash and burn had enriched surface soils in exchangeable cations, which were slowly being lost to the stream. Biogeochemical perturbations and enhanced solute fluxes can continue for decades following deforestation for pasture [*Biggs et al.*, 2006; *Markewitz et al.*, 2004].

[6] The objectives of this study are to investigate chemical changes in stream water in response to land use change under the geologic and soil conditions of the eastern Amazon. We used an upstream-downstream sampling approach on low-order streams, with land use class quantification at each catchment sector. We address three hypotheses: (1) cation loads increase downstream, mostly in the wet season, as the percent area of cleared forest increases downstream; (2) increasing forest to pasture conversion increases total solute loads in the streams, although inorganic-N concentrations, which are high under mature forest, would decline; and (3) increasing row crop agriculture results in increased solute concentrations, including increasing inorganic-N concentrations. We conducted this research in a region of highly altered, complex landscapes in order to study the net effects of land-use changes as they have occurred in this region, rather than in experimentally controlled watersheds. While realistic, the disadvantage of this approach is that measured responses can also be complex, and attribution of causes is particularly difficult where land-use changes are distributed as a mosaic rather than uniformly over each watershed. Our objective is to evaluate the integrated response of stream water quality at the landscape scale.

2. Material and Methods

2.1. Research Sites

[7] Changes in stream chemistry were investigated along three streams from their headwaters in remnant mature forests, through pastures, secondary forests, and large fertilized fields of soybean, rice and corn in the Paragominas region of northeast Pará state, in the eastern Brazilian Amazonia (Figure 1). The three catchments are: *Igarapé Cinquenta e Quatro* (IG54) with 13,698 ha; *Igarapé do Sete* (IG7), with 16,143 ha; and *Igarapé Pajeú* (IGP), with 3,246 ha. These streams feed into the Uraim River, which is a tributary of the Gurupi River, which discharges into the Atlantic Ocean.

[8] Annual average rainfall for the period of 1973–2004 in Paragominas was 1743 mm [*Bastos et al.*, 2005]. For the years of this study, 2003–2005, annual rainfall was close to this 31-year average (Figure 2).

[9] The region around Paragominas was first settled in the early 1960s following the construction of the Belém-Brasilia highway and became a regional center for logging and ranching [*Nepstad et al.*, 1991]. The history of land use over the past four to five decades included an early period of selective logging as well as slash-and-burn conversion of many areas to pasture. As the most desirable timber species became scarce, many of the selectively logged forest were harvested again and often eventually converted to pasture [*Uhl et al.*, 1991]. Pastures were usually grazed for six to eight years, after which time they were abandoned to fallow or reformed under more intensive pasture management. Fallow areas typically return to secondary forest, although rates of recovery can be impacted by the intensity of previous grazing or the use of fire [*Uhl*, 1987; *Zarin et al.*, 2005]. Intensively managed pastures can be maintained in this region with about one head per hectare over long periods, provided that there are proper periodic inputs of phosphorus fertilizer (~50 kg-P ha^{-1}) and weed control [*Dias-Filho et al.*, 2001].

[10] Over the last decade, a new trend has emerged of land conversion to intensive agricultural production for upland soybean, rice and corn. These trends are similar to those for much of the Amazon region, particularly along the southern arc of deforestation [*Almeida and Uhl*, 1995; *Fearnside*, 2001]. The Institute of Applied Economic Research (IPEA) (www.ipeadata.gov.br) reported a twofold increase in row crops in the municipality of Paragominas from ~9,500 ha in 1995 to 22,000 ha by 2000. Furthermore, 500,000 ha of arable land were identified in Paragominas as available for crop production [*El-Husny et al.*, 2003].

[11] Given the history of land use around the Paragominas region nearly all watersheds have complex mixtures of land cover and legacies of land use activities, similar to the three watersheds of the current study. The streams are frequently dammed as they pass through each property in order to provide needed water storage and small-scale hydroelectric power generation. It is very difficult to find large watersheds under a single land cover or land use, and it is impossible to find large areas of pristine forest that encompass an entire

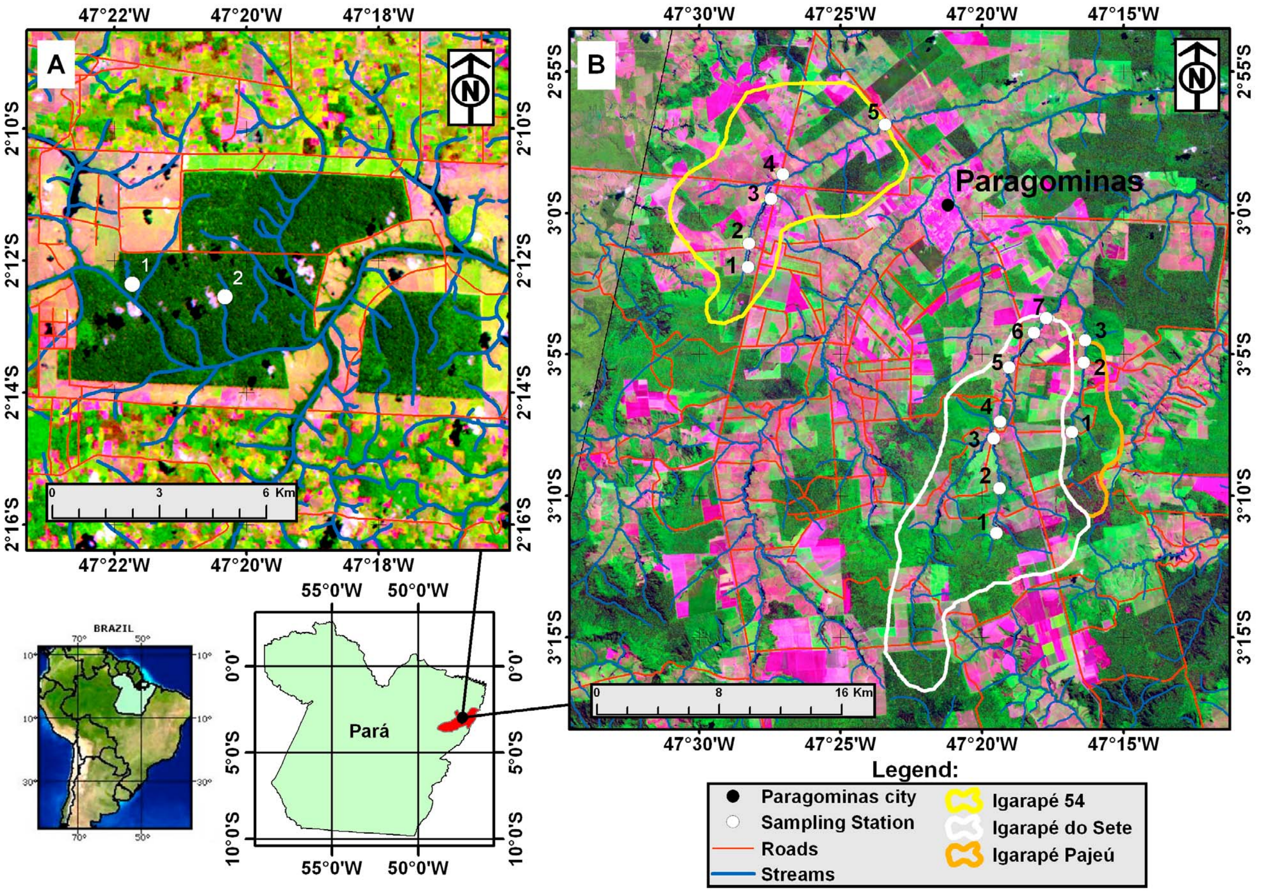

Figure 1. (a) The two pristine headwater streams and sample locations identified in Capitão Poço (indicated by the white dots and the numbers "1" and "2") that are part of the Arauaí River Basin (2002 LANDSAT imagery); and (b) the three study watersheds in Paragominas, with stream sampling locations identified by white dots (2004 LANDSAT imagery). Study sites are shown in relation to the Brazilian state of Pará and to South America. These TM Landsat images present composite coloring, where band 3 is blue, band 4 is green, and band 5 is red. Areas with green tones are associated with presence of significant biomass, whereas those with red tones indicate significant exposed soil.

watershed. Remnant forests are usually confined to small headwater stream areas. The headwater areas of the three streams in Paragominas selected for this research (Figure 1) were established to be utilized as mostly forested reference areas relative to the more disturbed downstream reaches, but even these headwater areas have been selectively logged, and have suffered some entry of pastoral and agricultural activities.

[12] To better quantify the hydrochemistry under fully forested conditions, two streams ~100 km distance from Paragominas (Figure 1) were also sampled. These catchments contribute to the Arauaí River in Capitão Poço municipality. The two streams are within a working ranch that has been managed according to Brazilian laws and thus has retained a 3,700 ha segment of unharvested mature forest. All sample handling and analysis were the same as for the three streams in Paragominas. The watershed area for these forested streams are much smaller (<20 ha) but are characterized by similar geologic and pedogenic history.

[13] Both Paragominas and Capitão Poço watersheds overlay the Ipixuna and Barreiras formations, where the predominant clay mineralogy is kaolinite [*Brasil*, 1973]. Paragominas soils have been classified as deeply weathered Oxisols (Haplustox, in the U.S. soil taxonomy, or Latossolos Amarelo in the Brazilian classification) in upper landscape positions, while in lower landscape positions, soils are classified as a clay-rich (40–60%) Plintossolos Haplicos (Plinthustults in the U.S. soil taxonomy), developed from both clay-rich colluvium from upslope and from the sandier Barreiras Formation [*Markewitz et al.*, 2004; *Moraes et al.*, 2006]. Soil studies in Capitão Poço municipality [*EMBRAPA-SNLCS*, 1990] also identified similar soil taxa in this region (i.e., Latossolos and Plintossolos) with similarly high clay contents [*Davidson et al.*, 2007].

2.2. Land Cover and Land Use Classification

[14] Land cover analysis of the three study catchments were done at the Remote Sensing Laboratory of Embrapa Amazônia Oriental, in Belém (Pará state, Brazil), using Spring 4.2 (Instituto Nacional de Pesquisas Espaciais Divisão de Processamento de Imagens (INPE/DPI). Spring: Sistema de processamento de informações georrefer-

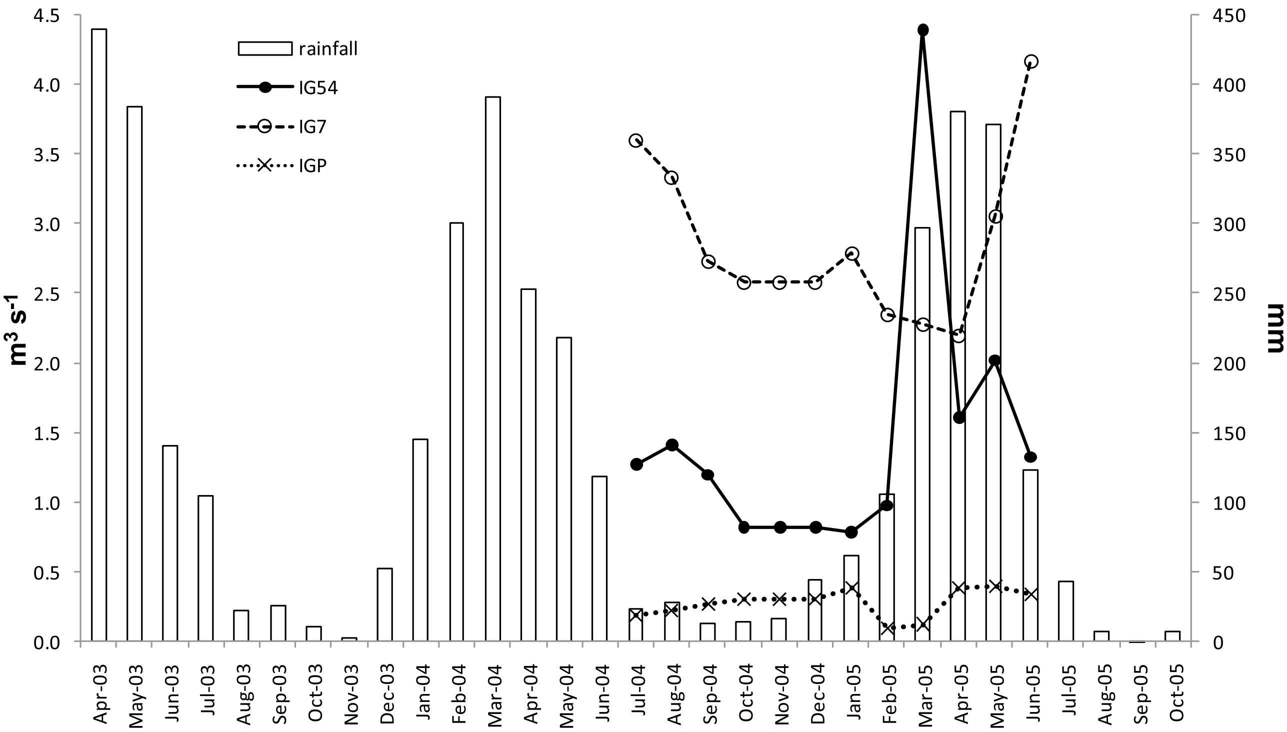

Figure 2. Rainfall in Paragominas from ANA (Brazilian Water Resources Agency) and measured discharge in IG54, IG7, and IGP streams from July 2004 to June 2005.

enciadas, http://www.dpi.inpe.br/spring, accessed January 2002) and Envi 4.0 (Environment for Visualizing Images (ENVI) Guia do ENVI, http://www.envi.com.br/guia_envi, accessed March 2005) software. Landsat TM bands 3, 4, and 5 were utilized (path 222, row 062) in images acquired on 28 June 2002, 9 June 2004, and 6 June 2005. A compacted Landsat image that was previously georeferenced by a high precision process (MrSID) was used as a cartographic base along with a digital database compiled from IBGE at a 1:100,000 scale. After georeferencing and registering the images, a radiometric normalization process was used to unify the land cover and land use aspects in the selected images. A supervised classification was used with a Bhattacharya algorithm and ground truthing [*Watrin et al.*, 2005]. In additional, to estimate the proportion of riparian vegetation remaining along the stream banks immediately upstream of each water sampling station, a 100 m wide buffer (50 m from each edge of the streams) that extended 200 m upstream from stream water sampling stations was classified as either forest cover (mature or secondary) or non-forest.

2.3. Stream Water Sampling

[15] Stream sampling was largely driven by issues of access. Land in this region is mostly privately held and roads are typically unimproved dirt roads on private ranches. As such, sample points were identified at five locations on IG54, seven locations on IG7, and three locations on IGP (Figure 1). Sample points in the mature forest watersheds of Capitão Poço were established at one location in each of the two streams (Figure 1). In all three Paragominas streams sampling was initiated in April 2003 and continued on a nearly monthly basis until October 2005. In the Capitão Poço streams sampling was begun in August 2003 and continued on a nearly monthly basis until June 2005.

[16] At the time of sample collection, turbidity, pH, temperature, and dissolved oxygen were measured in situ using a turbidity meter (Hanna, model HI93793, Woonsocket, RI), and a pH, temperature and oxygen meter (WTW, model Multiline P3, Gold River, CA). Stream water grab samples were collected in previously acid washed 250-ml polypropylene bottles. Bottles were filled to capacity to minimize headspace and were placed in cold storage (~4°C) within a few hours of collection.

[17] Samples were returned to a field laboratory in Paragominas, and after conductivity measurement (conductivity meter VWR, model L702674, West Chester, PA), they were analyzed for alkalinity by endpoint titrations with 1 m*M* HCl to pH 4.5 [*Clesceri et al.*, 1998]. If possible, samples were analyzed for alkalinity on the same day of collection, but many were retained cold for up to 4–5 days until analysis. Measures of pH in the laboratory (VWR probe) prior to alkalinity were well correlated with in situ pH measures ($r = 0.819$, linear Pearson correlation coefficient for $n = 370$). In fact, given some problems with the field pH meter during the study, laboratory data are presented in the results. After the above laboratory measurements, samples were filtered through 0.4 μm polycarbonate filters (Millipore, Billerica, MA) and stored at 4°C until analyses for the other chemical constituents in an EMBRAPA laboratory in the city of Belém.

[18] At EMBRAPA samples were analyzed for dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and total dissolved nitrogen (TDN) by combustion (Shimadzu TOC V CSN, Columbia, MD), and Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-},

Table 1. Land Use Classification From Landsat Imagery in 2002, 2004, and 2005[a]

	IG54			IG7			IGP		
Land use classes	2002	2004	2005	2002	2004	2005	2002	2004	2005
Mature forest	23.8	22.5	20.2	49.7	46.2	37.6	48.9	53.9	17.3
Secondary forest	22.4	14.8	14.2	9.9	4.5	11.9	19.3	11.5	17.7
Crops	4.1	11.6	22.1	0.5	3.9	3.2	0.0	4.5	5.5
Pastures	39.5	48.1	39.0	37.6	44.3	27.8	20.3	29.6	21.6
Reforestation	0.5	0.5	0.6	0	0	0.3	0	0	0.2
Suburban areas	2.4	1.8	2.4	0	0	0	0	0	0
Water bodies	0.9	0.7	1.6	1.0	1.1	1.0	0.4	0.5	0.8
Clouds	6.4	0	0	1.3	0	18.3	11.1	0.0	36.9

[a]The catchments IG54 (13,698 ha), IG7 (16,143 ha), and IGP (3,246 ha) are located in Paragominas. Land use classes are percent (%) of the total catchment area.

Ca^{2+}, Mg^{2+}, K^+, Na^+, and NH_4^+, by ion chromatography (Dionex DX-120, Sunnyvale, CA). Dissolved organic nitrogen (DON) was obtained by the difference between TDN and the sum of NO_3^--N and NH_4^+–N. Standard solutions (Shimadzu, Columbia, MD and Environmental Research Associates, Arvada, CO) were used with all analyses for quality assurance. Stream discharge was estimated monthly on a subset of points from July 2004 to June 2005 by measuring cross-sectional area and flow with a current meter (General Oceanic, model 2030W, Miami, FL). This measurement was done at the most downstream sampling stations in each stream for which a good cross section could be obtained (IG54-S5, IG7-S6 and IGP-S2) and followed the methods of *Rantz* [1982].

2.4. Data Analysis

[19] Monthly discharge was assessed against the antecedent 24–48 h rainfall as well as monthly rainfall using Pearson correlations. Water chemistry characterizations were evaluated by charge balance, and Spearman correlations among all chemical parameters were assessed. Transformations of hydrochemical data were performed to better approximate a normal distribution prior to tests of significance as required. Within each stream upstream-downstream trends were analyzed with a non-parametric Kendall Tau rank test while differences in the mean concentrations of dry and wet season months were tested with a two-way ANOVA (i.e., station and season). In addition, differences among the most upstream stations (i.e., the headwater areas) of the Paragominas streams (i.e., IG54-S1, IG7-S1, and IGP-S1) and the two Capitão Poço (CP) streams were tested similarly (i.e., stream and season).

[20] To evaluate land use impacts across all streams a number of repeated measure, mixed-effects models were tested with the following form:

$$Y_{ijk} = \beta_0 + \beta_1 \%cov + m_i + b_j + b_{k(j)} + e_{ijk}, \qquad (1)$$

where Y_{ijk} is the stream concentration for an element of interest for month i, stream j and station k within stream j. In this model, β_0 is the intercept, β_1 is the coefficient of the covariate percent land cover (*%cov*), m_i is the fixed effect of month i; b_j and $b_{k(j)}$ are random effects of stream j and station k within stream j with distributions $N\ (0,\sigma_m^2)$ and $N\ (0,\sigma_{st}^2)$, respectively, and e_{ijk} is the error term with distribution $N(0,\sigma^2)$.

[21] The percent land cover models were based on the 2004 coverage estimates and do not directly consider changes that occurred from 2002 to 2005. The models included percent forest, percent crop, percent pasture or their combination (i.e., forest and crop; pasture and crop). Forest and pasture were highly correlated (r = −0.88) so forest and pasture were not used together in predictive models. The repeated measure subject is station within a stream, and error terms associated with the same station at different time points are assumed to have a covariance structure. A number of repeated measures covariance structures were evaluated but a first-order autoregressive {AR(1)} and a first-order autoregressive with a moving average {ARMA (1,1)} usually produced the best models. Model fits were tested with −2 times the residual log likelihood, AIC (Akaike's information criteria), AICC (finite population corrected AIC), and BIC (Bayesian information criteria). We chose the model with a majority of the lowest criteria values, although in all cases criteria results were consistent. Residual plots of the best models were checked to make sure these models were properly specified.

[22] In addition to these statistical tests the mass fluxes of elements were also estimated to compare input-output budgets. As stream discharge data only exist for the Paragominas area streams for the period of July 2004-June 2005, this period was utilized for estimation, which limited mass output fluxes to eight elements: Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+N, NO_3^-N, Cl^- and SO_4^{2-}. Mass input fluxes (i.e., rainfall chemistry) are from *Markewitz et al.* [2004], which contains rainfall collections in the IG54 catchment from 1996 to 1998.

3. Results

3.1. Land Use Patterns

[23] A thematic map composed of six land cover units (excluding *Water Bodies* and *Clouds*) was developed for each watershed (Table 1 and Figure 3). *Mature* and *Secondary Forest* were separated based on the inner shadow promoted by structural differences, particularly the high canopy in *Mature Forest*, *Pasture* refers to cut-over fields in different degrees of degradation, and *Crops* is linked to bare soils in preparation for agricultural use or to visible row crops (e.g., soybean, maize and rice). The *Reforestation* class corresponds to Paricá plantations (*Schizolobium amazonicum Huber*), while the *Suburban* class refers to small villages including housing and industrial plants (mainly sawmill operations).

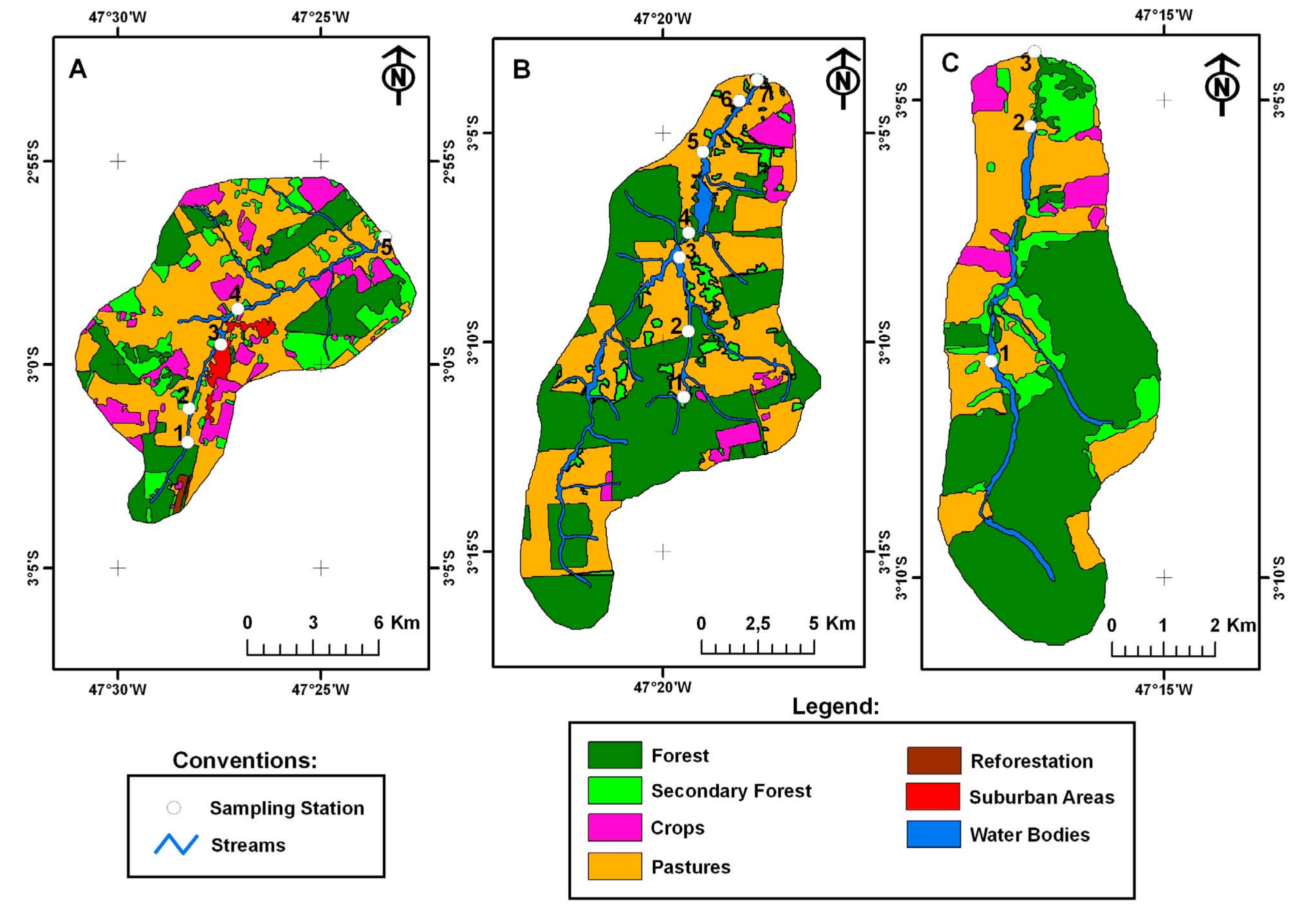

Figure 3. Land use maps of the three studied watersheds in Paragominas based on 2004 Landsat imagery. (a) Igarapé Cinquenta e Quatro (IG54); (b) Igarapé do Sete (IG7); (c) Igarapé Pajeú (IGP).

[24] By 2002 the majority classes were *Secondary Forest* and *Pasture*, with large segments (i.e., 45 to 80%) of the entire watersheds having already been cleared of mature forest and converted to pasture (20 to 39%). The *Suburban* class (2.4% of the total area) was only present in the IG54 catchment and the *Reforestation* class, despite being registered in all three catchments, occupied only 0.2 to 0.6% of the areas in IGP and IG7 and only in the last year analyzed.

[25] Between 2002 and 2005 the only clear trend over time was the continual increase in *Crops*. In fact, *Crops* grew fivefold in IG54 to 22% of the land base and from 0 to > 5% in IGP, although the total number of hectares of *Crops* in IGP and IG7 were relatively small (i.e., < 500 ha). In the drainage areas above the most upstream stations, *Mature Forest* class is smallest upstream of IG54-S1 compared to the other watersheds (Table 2). Field surveys also found that the forest upstream of IG54-S1 had been burned previously and its structure seriously damaged. Similarly, there were impoundments in the headwaters of IG7-S1 and IGP-S1, and pasture areas were close to the riparian margins of these impoundments. Therefore, some influence of cattle and pasture management is expected even in the headwater sample stations of the Paragominas streams.

[26] Based on the most cloud free 2004 image, upstream-downstream patterns from all three streams were consistent in having decreasing percent forest cover and increasing percent pasture cover (Figure 4), although IG54 has clearly had more forest-to-pasture conversion. The percent cropland is more erratic across the watersheds. In all cases the percent cover is estimated as a proportion of the watershed upstream of the sampling station, so for those portions of the watersheds where percent pasture is relatively constant (e.g., IG7), there is still an increasing absolute number of hectares in pasture.

Table 2. Land Use Classification From Landsat Imagery in 2004 for the Headwater Areas of IG54-S1 (933 ha), IG7-S1 (1284 ha), and IGP-S1 (1286 ha) in Paragominas, as Well as the Two Pristine Stream Catchments in Capitão Poço[a]

Land Use Classes	IG54-S1	IG7-S1	IGP-S1	CP
Mature forest	62.2	83.3	77.4	100
Secondary forest	13.7	2.1	3.1	0
Crops	0.6 (10.9, 3.4)[b]	10.4 (0, 17.3)	0 (0, 0)	0
Pastures	16.4	4.3	19.3	0
Reforestation	6.6	0	0	0
Suburban areas	0	0	0	0
Water bodies	0.4	0	0.2	0
Clouds	0	0	0	0

[a]Land use class units are percent (%) relative to the total headwater area. CP, Capitão Poço (<20 ha)
[b]Values in brackets are for 2002 and 2005, respectively.

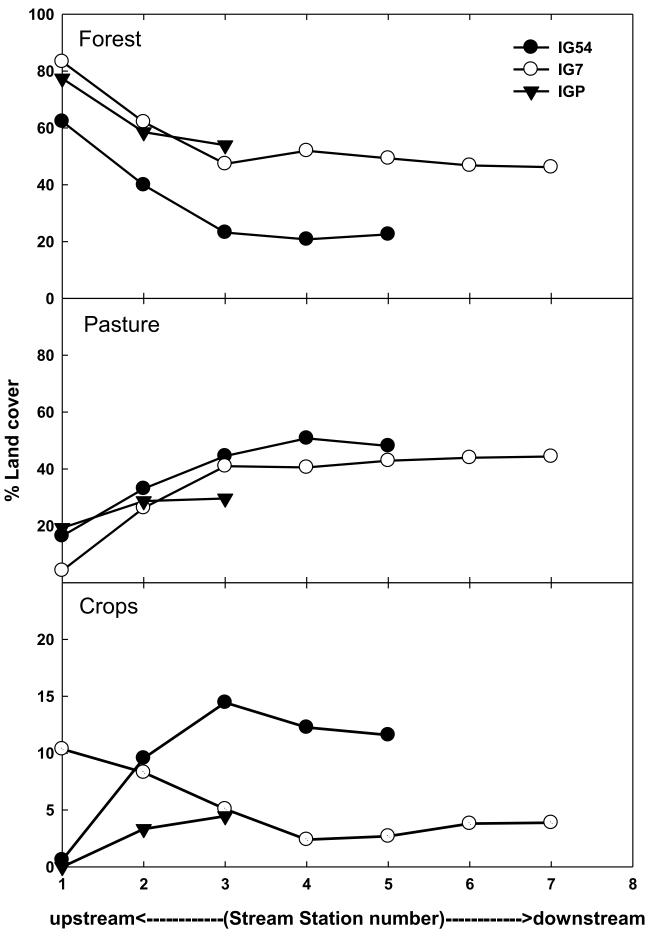

Figure 4. Upstream-downstream patterns of land use cover for streams in Paragominas based on 2004 Landsat image.

[27] Riparian areas (defined as 50 m of either side of the stream edge) were also heavily impacted by land use change. The percent forest cover along a linear segment 200 m immediately upstream of each stream water sampling station was 100, 0, 0, 0, and 0% for IG54-S1 to IG54-S5, respectively; 34, 100, 0, 100, 30, 0, and 44% for IG7-S1 to IG7-S7, respectively; and 100, 3, and 6% for IGP-S1 to IGP-S3, respectively.

3.2. Hydrology

[28] Based on the ANA rainfall data (Figure 2), the wet season is defined as all those months that rainfall is above 60 mm, which includes January to June; the dry season includes July to December. Discharge measured monthly from July 2004 to June 2005 at the most downstream sampling stations in each stream was poorly correlated to the antecedent 24–48 h rainfall, except for IG54-S5 (Pearson correlation coefficient of 0.91 and 0.93, to 24 and 48 h, respectively). However, discharge significantly correlated with monthly rainfall, when using a two month lag response in discharge relative to rainfall for IG54 and IG7 (r = 0.70 and 0.79, respectively) and a one month lag for IGP (r = 0.43) (Figure 2). Larger discharge was observed in IG54 in the wet season (1.85 ± 1.32 m^3 s^{-1}; mean ± 1 SD) versus the dry season (1.06 ± 0.27 m^3 s^{-1}) and IG7 had higher flow in May and June (Table 3). In the smaller IGP watershed, discharge was only slightly greater in the wet season (Table 3 and Figure 2).

[29] These observed hydrological responses in discharge responded not only to precipitation patterns, but were also partly linked to the presence of earthen dams. For example, the discharge peak in IG54 on March 2005 coincided with a large storm and a dam failure during the storm. In another instance the streamflow decrease in IGP in February and March 2005 resulted from emptying and refilling of a farm impoundment in January 2005. Dams are a common

Table 3. Concentrations (Medians and Interquartile Range) for Dry (July to December) and Wet Seasons (January to June) Across All Sampling Stations in the Studied Paragominas Streams IG54 (5 Stations), IG7 (7 Stations), IGP (3 Stations) and a Pooled Value for the Two Pristine Headwater Streams in Capitão Poço[a]

		IG54		IG7		IGP		CP	
Component	UNIT	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Discharge	m^3 l^{-1}	1.01 (0.44)	1.46 (1.04)	2.65 (0.75)	2.56 (0.78)	0.28 (0.08)	0.36 (0.20)		
Turbidity	FTU	12 (32)	45 (81)**	1 (2)	9 (17)**	2 (6)	9 (18)**	3 (7)	13 (19)**
Temperature	°C	28.7 (2.9)	29.1 (2.7)*	28.4 (2.2)	29.1 (2.5)**	27.2 (1.8)	27.9 (2.2)*	25.0 (0.8)	25.5 (0.5)**
Dissolved oxygen	% sat	69.3 (42.2)	55.4 (44.9)	80.5 (25.0)	65.2 (38.2)**	55.3 (33.8)	57.9 (45.1)	49.4 (9.5)	46.0 (29.0)
Conductivity	μS cm^{-1}	38.4 (10.1)	38.0 (10.2)*	32.3 (3.1)	28.9 (4.6) **	36.6 (5.1)	33.2 (4.6) **	21.5 (3.4)	21.7 (4.8)
pH		5.41 (1.33)	5.72 (0.82)*	4.45 (0.51)	4.44 (0.66)	4.49 (0.39)	4.59 (0.63)	4.35 (0.37)	4.44 (0.54)
Alkalinity	μeq l^{-1}	73 (117)	196 (118)**	0.0 (14.5)	0.0 (27)*	0.0 (14.5)	2.5 (36.5)*	0 (12)	0 (13)
Na^+	μeq l^{-1}	167 (140)	107 (119)*	148 (106)	141 (107)	173 (133)	149 (163)	124 (71)	85.2 (43.7)
K^+	μeq l^{-1}	15.1 (86.9)	36.1 (78.0)**	7.2 (8.1)	10.2 (9.3)**	8.2 (7.4)	7.4 (12.0)	4.85 (4.34)	3.96 (4.85)
Ca^{2+}	μeq l^{-1}	68.8 (41.9)	76.3 (47.9)	20.9 (31.4)	42.4 (38.4)**	28.4 (39.4)	29.9 (47.4)	36.4 (30.9)	32.7 (18.7)
Mg^{2+}	μeq l^{-1}	40.3 (70.7)	70.7 (80.6)**	18.9 (28.4)	26.7 (23.4)**	21.4 (27.1)	20.6 (33.7)	14.8 (10.7)	9.5 (13.6)
NH_4^+ -N	μeq l^{-1}	3.16 (8.1)	9.0 (11.7)**	0.77 (4.9)	7.2 (5.7)**	4.77 (8.49)	5.44 (6.33)*	0.22 (6.44)	6.77 (8.05)**
Cl^-	μeq l^{-1}	218 (169)	118 (152)**	215 (145)	194 (153)	264 (207)	180 (208)	86.8 (62.3)	91.9 (68.3)
SO_4^{2-}	μeq l^{-1}	11.3 (25.3)	10.2 (12.9)	7.4 (8.3)	7.1 (8.4)	4.8 (7.9)	5.8 (9.2)	11.2 (5.6)	11.0 (10.6)
NO_3^- -N	μeq l^{-1}	0.58 (1.88)	0.7 (1.23)*	0.07 (0.98)	0.07 (1.29)	0.07 (0.81)	0.07 (1.10)	3.08 (6.77)	2.17 (6.16)
PO_4^{3-} -P	μeq l^{-1}	0.16 (0.0)	0.16 (0.00)*	0.16 (0.0)	0.16 (0.0)*	0.16 (0.0)	0.16 (0.0)*	0.16 (0)	0.16 (0)
DON	μmol l^{-1}	8.99 (15.9)	22.1 (16.3)	4.45 (6.20)	7.37 (6.09)**	4.06 (3.26)	8.00 (20.5)	2.7 (15.5)	–
DOC	μmol l^{-1}	104 (398)	316 (229)*	64.2 (44.7)	94.2 (38.3)*	70.0 (47.2)	94.5 (49.1)*	94.2 (40.4)	–

[a]Samples were collected monthly from April 2003 to October 2005: *, $p < 0.05$; **, $p < 0.01$ for dry versus wet season comparison. CP, Capitão Poço.

Table 4. Mean Values Estimated From Monthly Measurements at Sampling Stations From April 2003 to October 2005 in the Headwater of the Studied Streams *Igarapé Cinquenta e Quatro* (IG54-S1), *Igarapé do Sete* (IG7-S1), and *Igarapé Pajeú* (IGP-S1) in Paragominas, and in Two Pristine Headwater Streams in Capitão Poço[a]

Component	Unit	IG54-S1	IG7-S1	IGP-S1	CP
Turbidity	FTU	112a	4b	4b	4b
Temperature	°C	30.7a	26.6b	25.8c	25.0d
Dissolved oxygen	% sat	65.3a	49.1b	51.2b	47.8b
Conductivity	μS cm−1	44.2a	33.8b	38.0c	21.3d
pH		6.08a	4.18b	4.19b,c	4.38c
Alkalinity	μeq l−1	176.7a	1.3b	1.8b,c	2.2c
K^+	μeq l−1	88.7a	9.3b	8.0b	3.2c
Na^+	μeq l−1	90.7a	171.9b	148.4b	86.7a
Ca^{2+}	μeq l−1	88.0a	24.9b	23.6b	23.5b
Mg^{2+}	μeq l−1	116.8a	26.6b	23.6b	9.5c
NH_4^+-N	μeq l−1	5.9a	1.6b	2.6b	2.5b
Cl−	μeq l−1	122.0a	233.8b	193.2b	73.6c
SO_4^{2-}	μeq l−1	31.3a	6.5b	5.8b	6.7b
NO_3^--N	μeq l−1	0.5a,b	0.4b	0.5a,b	1.2a
PO_4^{3-}-P	μeq l−1	0.2a	0.2a	0.2a	0.2a
DON	μmol l−1	9.4a	3.5a	5.3a	3.1a
DOC	μmol l−1	347.5a	75.7b	56.3b	107.3b

[a]Letters (a, b, c or d) indicate differences between stream values; different letters mean difference at $p < 0.05$ for GLM means comparison analysis with Tukey's adjustment. CP, Capitão Poço.

landscape feature, with IG54-S2 and S3, IG7-S1, S3, and S6, and IGP-S1 and S2 all being in proximity to an impoundment. The reservoirs range from 1 to 10 ha in surface area but are all shallow (<2 m maximal depth), so mean residence time of water in the reservoirs is generally less than a day.

3.3. Stream Water Chemistry

[30] The average chemical composition of the three Paragominas streams as estimated during the dry season (i.e., July to December) demonstrated a preponderance of Na^+ and Cl^- contributing to the charge balance (Table 3). The same is true for the two pristine streams at Capitão Poço (CP), which demonstrated similar patterns (because of their similarity, only their mean concentrations are presented; see Table 3). The other major cationic and anionic elements (i.e., K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, and HCO_3^-) are about 2 to 3 times lower in concentration compared to Na^+ and Cl^- in all streams and represent a much smaller proportion of the charge balance. Average concentrations of Na^+ and Cl^- generally decrease from the dry to wet season, but many of the other elements have increasing concentrations. For all Paragominas streams, the maximum concentration observed for K^+, Ca^{2+}, Mg^{2+}, and HCO_3^- occurred in the wet season, although the wet season mean values were not always significantly greater than dry season mean values. In CP, only turbidity, temperature, and NH_4 increase significantly in the wet season. Concentrations of PO_4^{3-} are consistently low and at or below detection limits in all streams.

[31] The headwater intercomparison demonstrated similar concentrations for sampling stations of IG7-S1, IGP-S1, and the pristine CP-S1 for turbidity, dissolved oxygen, Ca^{2+}, NH_4^+, SO_4^{2-}, and DOC, whereas values at IG54-S1 were significantly greater (Table 4). In some cases values in IG54-S1 were orders of magnitude greater. For example, alkalinity ranged from 1.3 to 2.2 μeq l^{-1} in IG7-S1, IGP-S1, and CP but averaged 176.7 μeq l^{-1} at IG54-S1. For temperature, conductivity, pH, alkalinity, K^+, Mg^{2+}, and Cl^-, all Paragominas headwaters were significantly greater than the pristine CP streams, although even for these, IG54-S1 often greatly exceeded IG7-S1 and IGP-S1. For example, in the case of K^+ and Mg^{2+}, IG7-S1 and IGP-S1 exceeded the CP streams by threefold but IG54-S1 exceeded CP by 10-fold. These extreme chemical alterations in the headwaters of IG54 are inconsistent with the use of this headwater station as a reference condition and limit the comparison of upstream-downstream sampling stations for that particular stream. For example, upstream-downstream trends in pH are decreasing for IG54 while pH increases downstream in IG7 and IGP (Figure 5). In fact, rank tests for IG54 have negative slopes (i.e., decreasing concentrations from upstream to downstream) for most elements, with only Na^+, Cl^-, and NO_3^- having positive slopes (Table 5). Furthermore, these trends in IG54 were opposite to those of IG7 or IGP, except for conductivity, which declined downstream in all cases. Although we prefer to include all five streams where possible in subsequent analyses, the unusual headwater chemistry of IG54 prompted us to consider excluding it from some analyses (hereafter called "Four-Streams model").

[32] The mixed model analysis relies on the percent land cover (i.e., forest, pasture, crops, forest + crops, pasture + crops) at each station as a predictor of stream chemical concentrations and allows for a pooling of all the stream data. This accounts for the differences in forest clearing among the watersheds (i.e., greater clearing in IG54) and the non-monotonic patterns in land cover (i.e., percent crops). These models also include a seasonal component (i.e., 12 monthly coefficients) as well as accounting for the covariance between stations within a stream and the repeated measures within a station.

[33] Based on all five streams, the best predictors of stream chemical concentrations were percent crop area for turbidity, dissolved oxygen, Na^+ and Cl^-, percent pasture area for conductivity, K^+, Mg^{2+}, SO_4^{-2} and NO_3^-, and percent forest area for temperature (Table 6). Although percent pasture (i.e., increasing pasture cover) was the best predictor based on the model selection criteria, since pasture and forest are strongly correlated, percent forest (i.e., decreasing forest cover) was also a significant predictor of the hydrochemical components. Given the anomalous patterns for IG54, the model was also analyzed without this stream. The results of the Four-Streams model indicate percent forest is the best predictor for temperature, dissolved O_2, conductivity, pH, and NO_3^-, while percent crop is significant only for Na^+. The trends with land cover in the Four-Streams model indicate increases in temperature, dissolved oxygen, conductivity, and pH with decreasing forest cover and a decline in NO_3^- (Figure 6).

3.4. Element Fluxes Through Stream Water

[34] The elemental flux outputs through the lowest sampling station of the three studied streams were compared to elemental flux inputs through rainfall estimated previously for this region (Table 7). The annual transport of elements past the most downstream station reveals a high mass loss of Na^+ and Cl^-. On the other hand, K^+ had a net negative balance in all streams, revealing a trend for retention in the studied catchments. Other major cations and anions dem-

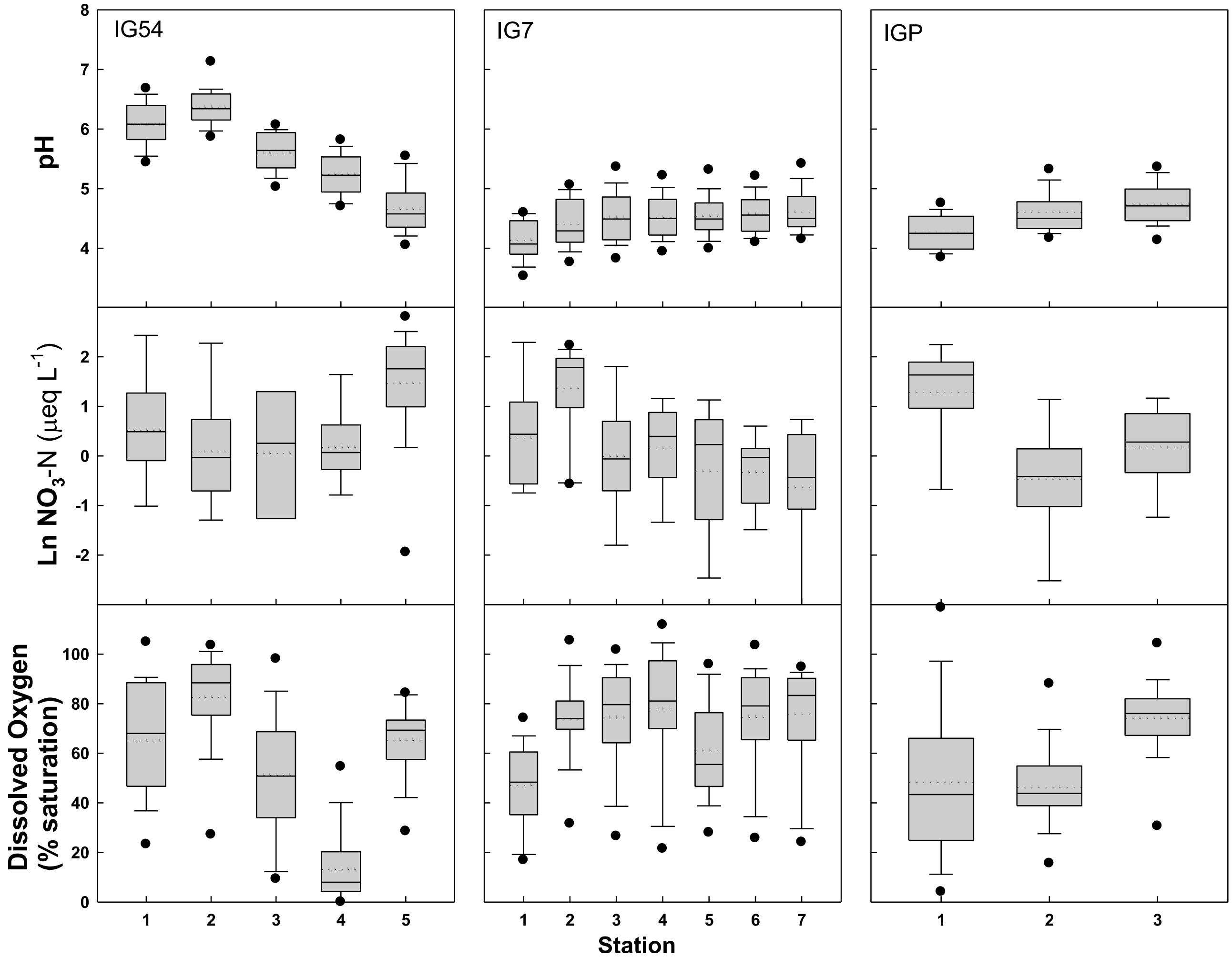

Figure 5. Upstream-downstream trends for pH, Ln NO_3^--N, and DO in three streams of Paragominas. Samples were collected monthly from April 2003 to October 2005. Lower and upper boundaries of the box are 25th and 75th percentile, whiskers are 10th and 90th, dots are 5th and 95th, solid line is median, and dotted line is mean.

onstrated relatively small net differences close to zero. In the case of dissolved inorganic nitrogen (i.e., NH_4^+-N and NO_3^--N) net differences were small and overall output fluxes were low.

4. Discussion

[35] Forest cover has clearly been replaced by pastures in the area of Paragominas, and presently pasturelands are being converted to row crop agriculture. Many of the stream reaches are void of riparian forest cover. The pattern of land use change in this studied area is similar to other regions in Amazonia where agriculture frontiers have been expanding. For example, in an area of 75,000 km^2 within the Ji-Paraná river basin, located in the State of Rondônia, Western Amazonia, *Ballester et al.* [2003] characterized large areas as under extensive clearing with a predominance of pastures and agricultural land. The trend of deforestation for timber products, followed by pastures for cattle grazing, and most recently establishment of large row crop agriculture is common. Further expansion of pastures and agricultural land is likely [*Soares-Filho et al.*, 2006].

[36] It was hypothesized that forest to pasture conversion would increase stream water cation loads and total solute

Table 5. Kendall Tau Rank Correlation Coefficients for Stream Sampling Stations From Headwaters (Station 1) to Most Downstream Station[a]

Stream	Stations	Turb	Temp	O_2	Cond	pH	Alk	K	Na	Ca	Mg	NH_4	Cl	SO_4	NO_3	PO_4
IG54	5	−0.42	−0.60	−0.23	−0.19	−0.64	−0.50	−0.49	0.28	−0.33	−0.45	-	0.24	−0.36	0.17	-
IG7	7	-	0.36	0.18	−0.23	0.21	0.13	-	−0.11	-	-	-	−0.10	−0.20	−0.25	-
IGP	3	-	0.18	0.41	−0.30	0.39	0.21	-	-	-	-	-	-	-	-	-

[a]Samples were collected from April 2003 to October 2005 for the studied catchments in Paragominas. Presented values are significant at $p < 0.05$.

Table 6. Land Use Cover Attribute Selected as the Best Model Predictor of Stream Water Chemical Component[a]

	Four-Streams Model			All-Streams Model		
Component	Predictor	P Value	Sign of Correlation	Predictor	P Value	Sign of Correlation
Temperature	% Forest	0.001	-	% Forest	0.0060	-
O_2	% Forest	0.0001	-	% Crop	0.0109	-
pH	% Forest	0.03	-	-	-NS-	
Conductivity	% Forest	0.001	-	% Pasture	0.0004	+
NO_3^-	% Forest	0.0001	+	% Pasture	0.0479	-
Na^+	% Crop	0.018	+	% Crop	0.0010	+
Cl^-	-	-NS-		% Crop	0.0008	+
Turbidity	-	-NS-		% Crop	0.0330	+
Mg^{2+}	-	-NS-		% Pasture	0.0003	-
K^+	-	-NS-		% Pasture	0.0020	-
SO_4^{2-}	-	-NS-		% Pasture	0.0509	-
Alkalinity	-	-NS-		-	-NS-	
Ca^{2+}	-	-NS-		-	-NS-	
NH_4^+	-	-NS-		-	-NS-	
PO_4^{3-}	-	-NS-		-	-NS-	

[a]The repeated-measures mixed model included month and season as fixed effects and stream and station within stream as random effects. Four-Streams model included CP1, CP2, IG7, and IGP, and All-Streams model added IG54. Streams were sampled between April 2003 and October 2005 in Paragominas and Capitão Poço. Sign of correlation are relative to increasing percent of forest, pasture, or crop. NS, non-significant.

loads. The study was designed with the intent that headwater stations would serve as a reference to downstream stations relative to land use in these complex landscapes of land-use mosaics. The hydrogeochemical comparison among headwaters, however, demonstrated differences among the reference remnant headwater forests in the Paragominas region and also with the pristine forests of the Capitão Poço region (Table 4). For example, IG54-S1, which has a smaller upstream percent area of forest, had particularly elevated concentrations for many elements even relative to IG7-S1 and IGP-S1. Upstream of IG54-S1 there are pastures and other areas of secondary vegetation, as well as some evidence of previous cropping and burning. Furthermore, IG54 is the only watershed with suburban development and a paved highway bisects a portion of this watershed, although downstream of sampling station 1.

[37] Given these impacts in the headwaters of IG54, upstream-downstream patterns differ substantially from those of IG7 and IGP (Table 5 and Figure 5). In IG54, most correlation coefficients are negative indicating a decline in the attribute downstream, which may reflect dilution of the headwaters as groundwater with more typical chemistry of the region enters the stream. On the other hand, Na^+, Cl^-, and NO_3^- increase downstream in IG54, which may reflect increasing agricultural intensification as discussed further below. IG7 and IGP have fewer significant upstream-downstream trends than IG54. Increasing pH and alkalinity downstream is consistent with the hypothesized increase in total cation loads, although K^+, Ca^{2+}, and Mg^{2+} do not, independently, have significant downstream patterns in either IG7 or IGP (Table 5). Conductivity is the one component with consistent downstream patterns among the three streams, although the negative slope is counter to the hypothesized downstream increase in total dissolved loads. Decreasing conductivity may reflect a dilution effect from increasing stream discharge as stream size increases in the lower portion of each watershed or may result from greater in-stream processing. In-stream processes could include transformations occurring in impoundments, which might substantially alter the chemical and deposition environment [*Verhoeven et al.* 2006].

[38] It was also hypothesized that solute loads would be greater during the wet season as surface runoff inputs to streams increased. Contrary to this expectation, changes is stream water conductivity from the dry to wet season decline slightly for the three Paragominas streams, although no such decline is apparent in the headwater stations of the CP streams (Table 3). CP does share a seasonal increase in temperature, turbidity, and NH_4^+–N with the three other streams. Water temperature increases are consistent with warmer surface water inputs mixing with cooler groundwater, and increasing turbidity can result from soil erosion and from suspension of in-stream sediments with increasing wet-season discharge [*Dunne and Leopold*, 1978]. The source of NH_4^+-N is uncertain, but flushing of N from riparian zones with increasing surface runoff has been previously demonstrated [*Creed et al.*, 1996]. Beyond these three components, CP has no increases in cations or other element concentrations in the wet season.

[39] In contrast to the pristine CP streams and in contrast to seasonal conductivity results for the Paragominas streams, the wet-season increases in alkalinity for all three Paragominas streams and for K^+, Ca^{2+}, and Mg^{2+} in IG54 and IG7 are consistent with the hypothesized increase of surface runoff contributions from cleared forest lands (Table 3). Previous research in IG54 demonstrated a reduction of macropores and a decrease in saturated hydraulic conductivity in pasture relative to forest that promoted larger volumes of overland flow (i.e., 19% of annual rainfall) [*Moraes et al.*, 2006], which could contribute surface soil nutrients. A pattern of increasing alkalinity and cation concentrations with increasing flow was also previously demonstrated at IG54-S5 [*Markewitz et al.*, 2001], and a similar pattern was observed in a Peruvian Amazonian

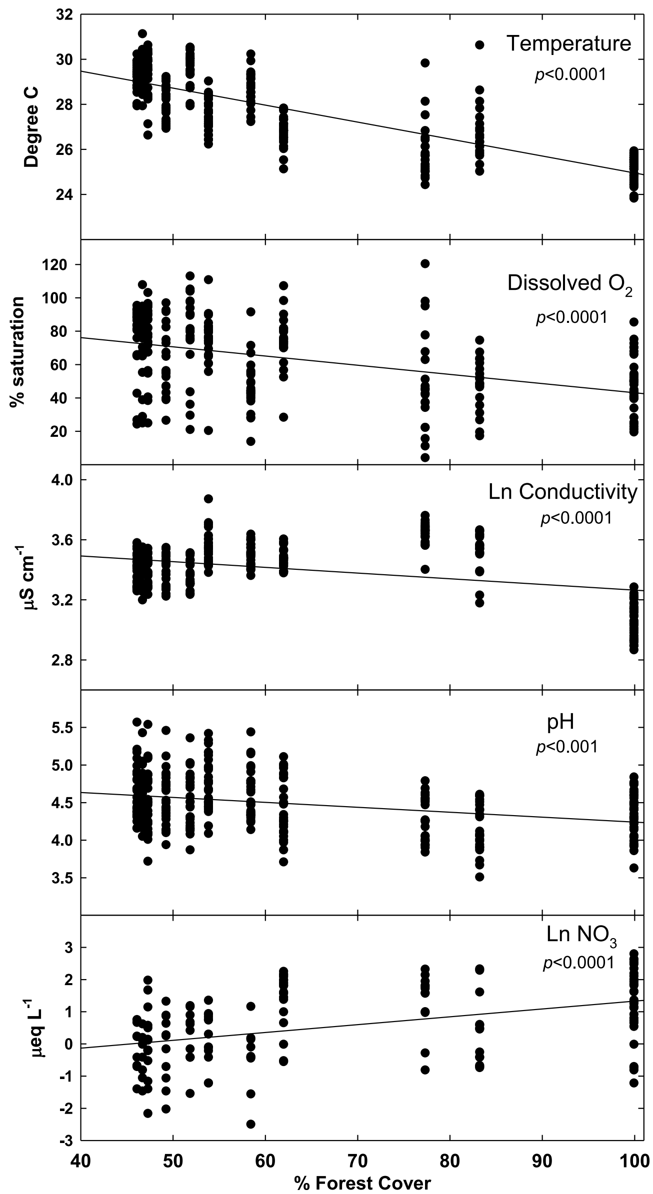

Figure 6. Stream water concentrations for attributes significantly related to percentage of forest area at sampling stations along four studied streams in the eastern Amazon. Samples were collected from April 2003 to October 2005; *p* values are for test of slopes significantly different from zero.

stream [*Saunders et al.*, 2006], with stormflow paths exporting a pulse of nutrients to the stream. Increasing wet season concentrations of K^+, Ca^{2+} and Mg^{2+}, as well as alkalinity, in IG54 and IG7 (Table 3) also support a response of stream water to more rapid flow paths within the deforested areas. Finally, there was also a pattern of a larger seasonal increase from dry to wet seasons where a larger fraction of the watershed was in pasture; i.e., the ranking of seasonal change was CP < IGP < IG7 < IG54.

[40] It was also hypothesized that in addition to the upstream-downstream increases in solute loads that solute loads would be better predicted knowing the extent of forest to pasture conversion (i.e., percent forest, pasture, or crop; equation (1)). This hypothesis was partly due to an expectation of decreased evapotranspiration and increased overland flow, as observed for forest-to-pasture conversion in the IG54-S5 catchment by *Moraes et al.* [2006]. In the Four-Streams model, declining percent forest is a significant ($p < 0.001$) predictor of increasing conductivity while in the All-Streams model increasing percent pasture is the best predictor for increasing conductivity. There is ample evidence of increasing conductivity in stream and soil solutions shortly after forest clearing in a range of ecosystems [*Bruijnzeel*, 1991; *Likens and Bormann*, 1995; *Williams and Melack*, 1997]. This initial increase in stream and soil solution concentrations is often followed by slowly declining concentrations [*Likens et al.*, 1998; *Uhl and Jordan*, 1984]. In the current case, if increasing percent forest clearing is related with the age since clearing, then an initially increasing trend followed by a decreasing or stable pattern for conductivity downstream may be consistent with long-term re-equilibration and lower rates of ionic leaching from these old pasture soils (Figure 6).

[41] For stream water components other than conductivity, in the Four-Streams model, percent forest was the only significant predictor, except for Na^+, which was correlated to percent crop. In the All-Streams model, however, which includes the IG54 watershed that is most heavily impacted by conversion to cropland, percent crop was a significant predictor for numerous elements (Table 6). In fact, in the analysis with all streams, percent forest was the best model predictor only for temperature while all other significant models were best fit with percent crop or percent pasture (Table 6 and Figure 7). This change suggests an increasing role of row crop agriculture on stream composition in this region.

[42] The observed downstream decline in NO_3^- concentrations was hypothesized as a response to forest clearing. Tropical forests in the Amazon are often rich in soil NO_3^- and declines in soil solution NO_3^- concentrations [*Markewitz et al.*, 2004] or associated N trace gases fluxes [*Verchot et al.*, 1999] have been demonstrated with forest clearing. Decreases in stream water NO_3^- within small (<1 ha)

Table 7. Annual Element Mass Fluxes (kg ha^{-1}) Estimated From Monthly Measurements at Downstream Sampling Stations From July 2004 to June 2005 for the Studied Catchments *Igarapé Cinqüenta e Quatro* (IG54), *Igarapé do Sete* (IG7), and *Igarapé Pajeú* (IGP) in Paragominas and Their Respective Input-Output Annual Balances[a]

Component	Rainfall[b] Input	IG54		IG7		IGP	
		Output	Balance	Output	Balance	Output	Balance
K^+	5.0	2.1	−2.9	1.8	−3.2	0.9	−4.1
Na^+	4.7	12.5	7.8	15.3	10.6	8.5	3.8
Ca^{2+}	3.2	3.8	0.6	4.6	1.4	2.3	−0.9
Mg^{2+}	1.2	1.8	0.6	1.4	0.2	0.7	−0.5
Cl^-	10.7	22.5	11.8	36.0	25.3	13.6	2.9
SO_4^{2-}	2.4	1.5	−0.9	1.5	−0.9	0.8	−1.6
NH_4^+-N	1.5	0.1	−1.4	0.5	−1.0	0.3	−1.2
NO_3^- -N	0.20	0.22	0.02	0.01	−0.19	0.01	−0.19

[a]Negative values in the balance column indicate net retention of the nutrient, whereas positive values indicate net loss, although agricultural inputs are not included.

[b]Rainfall data from[*Markewitz et al.* 2004].

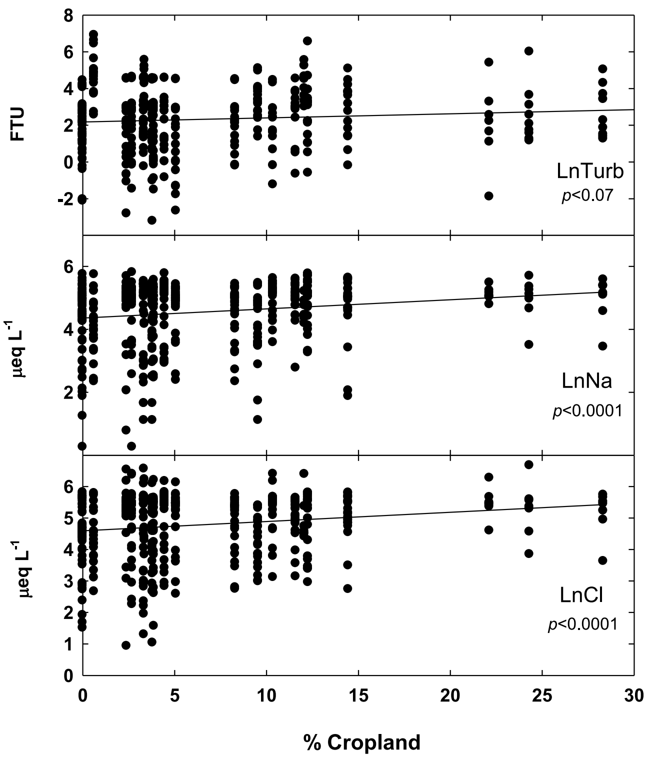

Figure 7. Stream water concentrations for attributes significantly related to percentage of crop area at sampling stations along five studied streams in the eastern Amazon. Samples were collected from April 2003 to October 2005; *p* values are for test of slopes significantly different from zero.

forest watersheds converted to pastures have also been observed [*Neill et al.*, 2006b] with NH_4^+ and NO_3^- uptake by in stream microbes or riparian grasses within the pasture stream. As such, it is not surprising that NO_3^- declines were associated with decreasing percent forest.

[43] Within IG54, there was a significant increase of NO_3^- with increasing percent crop, which reached as much as 20% crop cover in the lower sampling stations along the stream. IG54 had a significant increase in wet season NO_3^- concentrations (Table 3) and had a positive slope downstream for the rank correlation coefficient of NO_3^- (Table 5 and Figure 5). There were also site-specific effects of sharply increasing NO_3^- apparent at IG54-S5 (Figure 5), which, like much of this stream, had zero riparian forest. During field campaigns tilling for rice cultivation was observed just a few meters from this sampling station and a visible increase in suspended sediments was noted. As soils of these pasture catchments have low extractable or mineralizable NO_3^- to leach, the inputs of N are likely related to fertilizers. Amendments for crop fields in this region vary from 70 to 500 kg ha^{-1} N, typically as urea, depending on the crop cultivated [*Gonçalves*, 2007].

[44] Despite the above presumptions regarding fertilizer N inputs, the annual mass fluxes for dissolved inorganic nitrogen indicated net retention of N relative to rainfall inputs in IG7 and IGP and a near zero balance for NO_3^- in IG54. This current mass balance likely does not reflect decades-old land cover changes but likely does reflect current land use activities. For other tropical watersheds the reported range of annual fluxes for NO_3^- (0.60 to 6.10 kg ha^{-1}) and NH_4^+ (0.13 to 0.89 kg ha^{-1}) [*Lewis et al.*, 1999] are generally greater than those observed in Paragominas streams. In Fazenda Nova Vida streams in Rondônia, mean concentrations of NH_4^+ (4.0 to 6.9 μeq l^{-1}) and NO_3^- (3.5 to 10.7 μeq l^{-1}) are also both greater than Paragominas concentrations. Because conversion of forest to pasture began in the 1960s in the Paragominas region, many of the pastures have experience repeated fire, which may have invoked significant N limitation in the soils [*Davidson et al.*, 2007]. In contrast, the pristine CP streams have relatively high NO_3^- concentrations (2.2 to 3.1 μeq l^{-1}).

[45] In addition to changes in NO_3^-, the IG54 stream also demonstrated a site-specific decrease in DO at IG54-S4, which was low in all sampling dates (Figure 6). This station is located just downstream of a cropland and has no riparian forest upstream of the sampling station. Agricultural inputs are suspected of promoting the observed NO_3^- spike and dissolved oxygen collapse. As seen in Figure 5, the average DO from IG54-S1 to IG54-S4 decreases 80% (from 65 to 13%) as crop areas increase from less than 5% of the drainage area to more than 20% (Figure 4).

[46] In the All-Streams model Na^+, Cl^-, and turbidity also appear to reflect increasing agricultural intensification and are best predicted by percent crops (Table 6). In an earlier study in the western Amazon in Rondônia, higher concentrations and fluxes of Na^+ and Cl^- were found in streams draining pastures relative to streams draining forests in both the wet and dry seasons, although crop cover was not analyzed [*Biggs et al.*, 2002]. These authors attributed the increase in Na^+ and Cl^- export from pastures to mineral supplementation for cattle. There is a clear preponderance of Na^+ and Cl^- in all streams of this study, including those in CP, and the two elements are nearly in charge balance (Table 3). In relation to other stream chemical data for Amazonian watersheds, some thousands of kilometers from the ocean [*Markewitz et al.*, 2006], it appears that these catchments in Paragominas have a larger atmospheric Na^+ and Cl^- input. For example, four streams in Fazenda Nova Vida in Rondônia state, a site thousands of kilometers from the ocean, had Na^+ concentrations ranging from 63 to 104 μeq l^{-1} [*Neill et al.* 2006b], which on average were more than two times smaller than the Paragominas streams. These two ions were also the only ones that showed a clear mass flux output in the three studied catchments in Paragominas (Table 7). Oceanic sources of Na^+ and Cl^- inputs would be expected to be conservative with inputs nearly equaling outputs. The sedimentary geology of the region and highly weathered soils are dominated by kaolinitic mineralogy, so likely do not contribute Na^+ or Cl^- significantly to soil or water chemistry. Mineral salt supplementation for cattle in this region ranges from 20 to 90 tons per farm and is ~15% Na^+ and 20% Cl^- [*Gonçalves*, 2007]. Given the many farms and ranches within these meso-scale catchments, mineral supplements may reasonably contribute a few tons of Na^+ and Cl^- to the streams annually.

[47] Finally, stream temperature and pH were correlated with forest cover (Table 6). Taken together with evidence of effects of increasing crop land on turbidity and DO, these four stream quality parameters may be the most readily

detected indicators of effects of land use change on stream habitat quality.

5. Conclusions

[48] Within these watersheds of the eastern Amazon Basin, results demonstrated significant responses in stream water that are related to land use conversion from forest to pasture and to a growing influence of row crop agriculture. Patterns of increasing temperature and turbidity, and decreasing DO are consistent with generally declining stream water quality associated with forest clearing. Increasing solute loads, however, were only weakly expressed with increasing forest conversion. Nutrient cations (i.e., Ca^{2+}, Mg^{2+}, and K^{+}) increased in the wet season in a number of the streams, indicating greater surface water inputs during the wet season. In addition, Na^{+} and Cl^{-}, which comprise a substantial proportion of the charge balance in these near-ocean watersheds, responded with increased concentrations with forest conversion and were the only elements estimated to have large positive net output fluxes. The presumed source of the net export of these elements is cattle supplements. Finally, the hypothesized decline in nitrate concentrations with increasing pastures was observed, and some site-specific increases in nitrate concentrations were observed where crop lands bordering stream margins were evident.

[49] As the pattern of land use change in the studied area is similar to other expanding agricultural frontiers in Amazonia, similar responses could be expected elsewhere. The present study suggests that turbidity, temperature, pH, and dissolved oxygen might be the simplest and most indicative water quality parameters to be monitored for the purposes of governmental environmental planning and regulations in this region of agribusiness expansion in Pará state. These indicators might be useful to identify land use effects and to evaluate the efficacy of riparian buffer zones and other mitigation measures to protect water quality.

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