Impacts of land-use and land-cover change on stream hydrochemistry in the Cerrado and Amazon biomes

Rodolfo L. B. Nóbrega [a,*], Alphonce C. Guzha[b], Gabriele Lamparter[a], Ricardo S. S. Amorim[c], Eduardo G. Couto[c], Hermann F. Jungkunst[d], Gerhard Gerold[a]

[a] University of Goettingen, Faculty of Geosciences and Geography, Goettingen, Germany.

[b] U.S.D.A. Forest Service, International Programs, c/o CIFOR, World Agroforestry Center, Nairobi, Kenya.

[c] Federal University of Mato Grosso, Department of Soil and Agricultural Engineering, Cuiabá, Brazil.

[d] University of Koblenz-Landau, Institute for Environmental Sciences, Geoecology & Physical Geography, Landau, Germany.

* Corresponding author at: University of Reading, Whiteknights, Department of Geography and Environmental Science, Reading, United Kingdom, r.nobrega@reading.ac.uk.

Abstract – Studies on the impacts of land-use and land-cover change on stream hydrochemistry in active deforestation zones of the Amazon agricultural frontier are limited and have often used low-temporal-resolution datasets. We aimed to identify these impacts using an experimental setup to collect high-temporal-resolution hydrological and hydrochemical data in two pairs of low-order streams in catchments under contrasting land use and land cover (native vegetation vs. pasture) in the Amazon and Cerrado biomes. Our results indicate that the conversion of natural landscapes to pastures increases carbon and nutrient fluxes via streamflow in both biomes. These increases were the greatest in total inorganic carbon in the catchments in the Amazon biome and in K in those in the Cerrado biome, representing a 5.0- and 5.5-fold increase, respectively. Stormflow plays a substantial role in the carbon and nutrient fluxes, especially in the Amazon biome, as its contributions to hydrochemical fluxes are mostly greater than the volumetric contribution to the total streamflow. These findings demonstrate that assessments of the impacts of deforestation in the Amazon and Cerrado biomes should also take into account rapid hydrological pathways; however, this can only be achieved through collection of high-temporal-resolution data.

Keywords: carbon, nutrients, agricultural frontier, rainforest, savanna, deforestation.

1. Introduction

It has been widely acknowledged that surface conditions of terrestrial ecosystems have strong synergies with hydrological processes (Cuo et al., 2013; Neill et al., 2008; Recha et al., 2012; Rodriguez et al., 2010). This surface–water interface is often influenced by land-use practices, which, in turn, can change catchment responses, such as stream hydrochemistry (Crossman et al., 2014; El-Khoury et al., 2015; Oni et al., 2014; Öztürk et al., 2013; Salemi et al., 2013; Vogt et al., 2015). Because of large-scale environmental impacts resulting from the conversion of native habitats into agricultural frontiers (Schiesari et al., 2013), it is fundamental to comprehend how land-use and land-cover (LULC) change influences hydrochemical processes in pristine catchments undergoing anthropogenic changes (Jordan et al., 1997; Neill et al., 2013). Therefore, studies have often focused on regions under intensive forest degradation due to agricultural expansion, such as the Brazilian Amazon, to assess the impacts of LULC change on hydrochemistry processes (Dias et al., 2015; Figueiredo et al., 2010b; Germer et al., 2009; Neill et al., 2011; Recha et al., 2013; Williams and Melack, 1997).

The Amazonian agricultural frontier (AAF), also known as the arc of deforestation, extends from the eastern to the southwestern edge of the Brazilian Amazon, comprising a wide area along the Amazon–Cerrado ecotone (Do Vale et al., 2015; Durieux, 2003; Silva et al., 2013). Deforestation in this region has taken place due to agricultural expansion during recent decades, and represents most of the deforestation of the AAF (Brannstrom et al., 2008; Fearnside, 2001; Riskin et al., 2013; Tollefson, 2015). This ongoing change threatens the services provided by native ecosystems, such as water quantity and quality (Coe et al., 2013; Davidson et al., 2012). However, despite the important contribution of several research initiatives (e.g., Andreae et al., 2015; Lahsen and Nobre, 2007; Satinsky et al., 2014), an understanding of the influence of LULC change on water resources in the Brazilian Amazon region remains limited. Furthermore, the Cerrado biome, where most of the AAF deforestation has occurred (Klink and Machado, 2005), is often not integrated in studies regarding Amazon deforestation; consequently, it is one of the lesser-studied regions in terms of the environmental effects of LULC change resulting from agricultural expansion (Hunke et al., 2015a; Jepson et al., 2010; Oliveira et al., 2015).

Soil and hydrological changes on the AAF have been linked to forest clearing and conversion to pastures (Neill et al., 2008; Zimmermann et al., 2006). Indeed, LULC change on the AAF has been primarily driven by the expansion of pastures (Armenteras et al., 2013; Schierhorn et al., 2016). After some years, these pastures are often either replaced by cash crop systems (Barona et al., 2010; Cohn et al., 2016) or abandoned due to decreased grass productivity, ultimately reaching advanced stages of degradation (Davidson et al., 2012). Variations in nutrient input into rivers caused by LULC change on the AAF deserve particular attention because of their potential impact on both biogeochemistry and aquatic ecosystem functioning (Neill et al., 2011). Biggs et al. (2006) found evidence of long-term increases in solute fluxes following the conversion of forest to pasture in this region.

The initial effects of LULC change on the hydrochemistry of rivers have often been observed in low-order streams (Hope et al., 2004; Neill et al., 2001; Richey et al., 1997), which connect the terrestrial environment to large rivers and integrate environmental processes, especially landscapes undergoing change (Alexander et al., 2000; Moreira-Turcq et al., 2003). These characteristics qualify small streams as sensitive indicators of changes in ecosystems due to LULC change and allow their use as important references in carbon exportation studies and as early warning systems for ecological change (Christophersen et al., 1994). However, studies of carbon export dynamics in low-order tropical catchments are still scarce (de Paula et al., 2016), although there is increasing research interest in high-temporal-resolution data collection in low-order fluvial systems (Bass et al., 2014) that should also be taken into account in hydrochemistry studies (Hughes et al., 2005; Richey et al., 2011; Wohl et al., 2012). Studies of hydrology and carbon flux are better represented in detailed storm-event hydrological studies (Johnson et al., 2006), as most dissolved organic carbon (DOC) is exported in rivers during stormflow events (Clark et al., 2007). However, because of the rapid hydrological responses typical of small catchments, detailed streamflow changes can easily be missed (Bass et al., 2014).

Our hypothesis is that LULC change is impacting stream hydrochemistry in active deforestation zones of the Amazon and Cerrado biomes. Using high-temporal-resolution hydrological and hydrochemistry data from headwater catchments with similar physical characteristics but contrasting LULC, our study aims to identify the differences in stream carbon and nutrient (CAN) concentrations and output fluxes during prevalent baseflow and stormflow conditions, thereby contributing to the understanding of CAN drivers in low-order streams on the AAF.

2. Study area

Our study follows the space-for-time substitution approach to compare adjacent headwater catchments with different LULC but with similar characteristics, i.e. slope, geology, soils, aspect and climate (Troch et al., 2015). Studies have often used this approach to understand the effects of vegetation and land use on hydrological responses in small catchments (Brown et al., 2005; de Moraes et al., 2006; Germer et al., 2010; Muñoz-Villers and McDonnell, 2013; Ogden et al., 2013; Roa-García et al., 2011). It has also been applied to compare the impacts of LULC change on stream hydrochemistry of contrasting catchments (Sun et al., 2013; Zhao et al., 2010).

We used two pairs of microcatchments on the AAF (Fig. 1) with contrasting LULC. Each pair of catchments consists of a catchment with predominantly native vegetation land cover and a catchment with predominantly pasture land cover used for extensive cattle ranching. One pair of catchments is in the municipality of Novo Progresso (Brazilian state of Pará), which is a hotspot of deforestation in the Amazon biome (Pinheiro et al., 2016; Rufin et al., 2015), and the other pair is in the municipality of Campo Verde (Brazilian state of Mato Grosso), which is a region that has been massively deforested since the 1970s and is now a well-established agro-industrial area in the Cerrado biome. The catchments in Novo Progresso, hereafter referred to as the Amazonian catchments, are in the *Jamanxim* River watershed, which is one of the major southern subtributaries of the Amazon River. The catchments in Campo Verde, hereafter referred to as the Cerrado catchments, are in the *das Mortes* River watershed, the principal tributary of the *Araguaia* River.

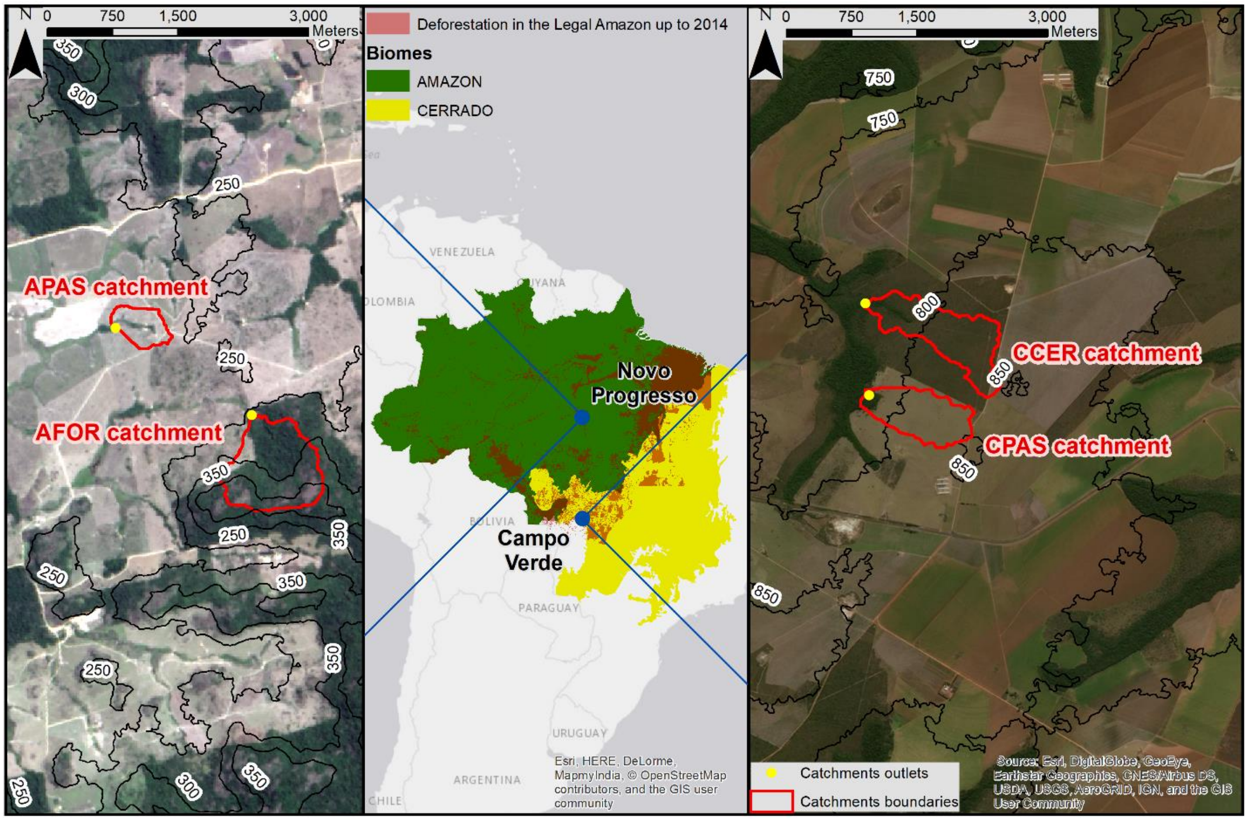

Figure 1. Study areas in the Amazon and Cerrado biomes.

Table 1 shows the main characteristics of the catchments. The Amazonian catchments consist of one catchment covered by evergreen rainforest, with indications of logging and tree regrowth (AFOR), and one catchment that is covered by degraded pasture grassland (APAS). The AFOR catchment is the only catchment that is drained by a non-perennial stream; it typically flows from November to July. The Cerrado catchments are approximately 200 m apart, consisting of a catchment covered by cerrado sensu stricto vegetation (CCER) and a catchment covered by pasture grassland with signs of degradation (CPAS). The cerrado sensu stricto is characterized as dense orchard-like vegetation consisting of many species of grasses and sedges, and mixed with a great diversity of forbs and trees with an average height of 6 m (Canadell et al., 1996; Furley, 1999; Goodland, 1971; Goodland and Pollard, 1973; Ratter et al., 1997). The APAS catchment was established in 1984, and the CPAS catchment was established in 1994. Both pasture catchments are mostly covered by grasses (*Brachiaria* grass species) that exhibit low productivity rates. Lime (calcium carbonate) was applied in the pasture catchments several years before the study period. The climate in the Amazonian catchments is humid tropical, with a mean precipitation of ca. 1,900 mm yr^{-1}, and a tropical wet and dry climate in the Cerrado catchments, with a mean precipitation of ca. 1,700 mm yr^{-1}. More details regarding the climate, soils, morphology and hydrology of this region can be found in Lamparter et al. (2016), and Guzha et al. (2015) and in Nóbrega et al. (2017) for the Amazonian and Cerrado catchments, respectively. For clarity and to simultaneously compare the contrasting catchments within their respective biomes, we use the term native vegetation catchments to refer to the AFOR and CCER catchments, and the term pasture catchments to refer to the APAS and CPAS catchments. We instrumented these catchments during the dry season of 2012 and monitored them from the wet season of 2012/2013 until the dry season of 2014.

Table 1. Main characteristics of the catchments.

	Amazonian catchments		**Cerrado catchments**	
	AFOR	APAS	CCER	CPAS
Biome	Amazon		Cerrado	
Area (ha)	93.4	23.1	77.8	58.4
Mean precipitation (mm yr^{-1})	1,900		1,700	
Wet season	Nov–May		Oct–Apr	
Farm property	*Paraíso* farm		*Rancho do Sol* farm	*Gianetta* farm
Coordinates	7.032° S, 55.363° W	7.023° S, 55.375° W	15.797° S, 55.332° W	15.805° S, 55.336° W
Soil classification (IUSS Working Group WRB, 2015, and Soil Survey Staff, 2014)	Lixisols, Oxisols		Arenosols, Entisols Quartzipsamments	
Predominant land cover	Rainforest	Pasture	Cerrado sensu stricto	Pasture
Aspect	E-W			
Average slope (%)	23.6	7.5	8.4	7.7
Average elevation (m)	292.4	223.0	811.1	817.8

3. Methods

3.1 Soil physical and chemical properties

To support our findings related to CAN stream dynamics, we used evidence from soil chemical and textural analyses. We collected disturbed soil samples from the topsoil (0–10 cm soil depth), from 6 to 8 approximately equally spaced points along a topographic sequence of landscape positions from a gently sloping upper plateau, to a middle slope and a low-gradient valley bottom on the basis of digital elevation models (DEMs) derived from a topographic survey in each catchment. The topographic survey conducted in the Cerrado catchments is described in detail in Nóbrega et al. (2017); the described procedure was also used for the Amazonian catchments. We analyzed these soil samples to determine pH, total carbon (TC), total nitrogen (TN), Al, Ca, Fe, K, Mg, Na, P, S and particle size distribution. The particle size distribution was measured using the Köhn pipette method (DIN ISO 11277:2002-08, 2002). pH was measured using the potentiometric method (inoLAB® pH Level 2, Wissenschaftlich-Technische Werkstätten GmbH). TC and TN were quantified using an elemental analysis method (TruSpec® CHN, LECO Instrumente GmbH). For chemical analysis, a total digestion of 100–150 mg of soil was created with $HClO_4$, HF and HNO_3 in 30-mL polytetrafluoroethylene (PTFE) vessels (Pressure Digestion System DAS 30, PicoTrace GmbH), and chemical concentrations were determined using inductively coupled plasma atomic emission spectroscopy (ICP-OES, Optima 4300™ DV and ICP-OES Optima 5300™ for the Amazonian catchments, PerkinElmer, Germany). Chemical analyses of soils from the Amazonian catchments were conducted at the Laboratory of the Department of Plant Ecology and Ecosystems Research and those of the Cerrado catchments were conducted at the Laboratory of the Department of Landscape Ecology, University of Goettingen, Germany.

3.2 Water-sampling design and analysis

An automatic water sampler (BL2000®, Hach-Lange GmbH) was installed at the outlet of each catchment to collect stream water ca. 20 cm below the water surface and 2–4 m upstream from the catchment weir. The sampling procedure was simultaneously based on both time intervals and water-level variations to characterize the streamflow hydrochemistry during baseflow- and stormflow-prevailing conditions, respectively. The time sampling routine was based on filling a 1-L sample bottle over 3 days using an extraction of 200 mL from the stream at 14.4-h intervals. The stormflow sampling was determined suing a subhourly routine activated by a water-level increase detected by a pressure bell switch (FD-01, Profimess GmbH). The pressure bell switches and the automatic samplers were calibrated throughout the year according to the water-level variation to maximize the coverage of the catchment stormflows, which considered the time of every sampling procedure and its respective hydrograph.

The samples from the Cerrado catchments were transported to the *Ecofisiologia Vegetal* Laboratory (EVL) at the Federal University of Mato Grosso (UFMT) in Cuiabá, Mato Grosso. The samples from the Amazonian catchments were also brought to this laboratory and included prior preparation at a field facility ca. 5 km from the catchments for appropriate storage until their processing at the EVL. Transport of all water samples to the EVL was made using light-free coolers packed with ice. After transportation, the water in each bottle was used to fill two 50-mL aliquots in high-density polyethylene bottles prewashed with deionized water. One aliquot was used for the analysis of TC, total organic carbon (TOC), total inorganic carbon (TIC) and TN, and the other was filtered with pre-ashed glass fiber filters (0.7-µm nominal pore size, Whatman GF/F) prewashed with 20 mL of water sample for the remaining analyses. The samples were then frozen and shipped in Styrofoam coolers for analysis at the Laboratory of the Department of Landscape Ecology, University of Goettingen, Germany (total travel time of ca. 22 h).

TC, TIC, TOC, total dissolved carbon (DC), dissolved inorganic carbon (DIC) and DOC contents were determined using high-temperature catalytic oxidation (TC-Analyzer, DIMATOC 100 (R), Dimatec GmbH). TN and DN were quantified using the chemiluminescence detection method (DIMA_N module (CLD), Dimatec GmbH). F, Cl, NO_3^- and SO_4^{2-} concentrations were determined using ion chromatography (761 Compact IC, Metrohm, Switzerland). Dissolved Ca, Fe, K, Mg, Na, P and S concentrations were quantified using atomic spectroscopy (ICP-OES, Optima 4300™ DV, PerkinElmer). Prior to the analyses of the dissolved solutes, the water samples were filtered through membrane filters (0.45-µm nominal pore size, cellulose acetate, Sartorius Stedim Biotech GmbH). These filters were prewashed with ultrapure water and transferred to high density polyethylene (HDPE) bottles that were prewashed with nitric acid solution (2.6% HNO_3) and rinsed with ultrapure water.

For quality control, during the entire study period, approximately 20% of the water samples were previously analyzed for DOC within 12 hours after collection using a UV-Vis spectrometric device (spectro::lyser™ UV-Vis, s::can Messtechnik GmbH) to cross-check with the final DOC results. This comparison indicated a linear correlation (r = .96, *n* = 200, *p* < .001, Pearson's correlation), which is considered adequate because of the insignificant differences in DOC estimation by the spectrometric device calibration (Avagyan et al., 2014; Bass et al., 2011). Additionally, a 1-L water sample was manually collected in an automatic sampler bottle and kept in a separate automatic water sampler unit at the EVL to check DOC fluctuations resulting from the storage of the samples in this instrument. This water sample was analyzed using the spectrometric device up to 8 days after sampling, which was the average time interval of the field trips for sample collection. This procedure was conducted during the first wet season (January–May of 2013) and did not indicate any significant changes in the DOC concentrations.

3.3. Streamflow and CAN output fluxes

At the outlet of each catchment, an adjustable weir was installed. During the rainy season, the weirs were rectangular, whereas a v-notch contraction section was inserted during the dry season. A multiparameter probe (DS 5X, OTT) was installed 2–4 m upstream of each catchment's weir to obtain data on water level, pH and temperature at 10-min intervals. To quantify catchment discharge (flow rate), we used the standard flow equation (Eq. (1)) based on the Bernoulli equation for the rectangular weir, and the Kindsvater-Shen equation (Eq. (2)) together with calibration adjustment functions (Eqs. (3) and (4)) for the v-notch weir (Shen, 1981), as follows:

$$Q = \frac{2}{3} C_{dR} b \sqrt{2g} h^{\frac{3}{2}}, \quad (1)$$

$$Q = \frac{8}{15} C_e \sqrt{2g} \tan\left(\frac{\theta}{2}\right) h_e^{\frac{5}{2}}, \quad (2)$$

$$K_h = 0.001[\theta(1.395\theta - 4.296) + 4.135], \quad (3)$$

$$C_e = \theta(0.02286\theta - 0.05734) + 0.6115, \quad (4)$$

where Q is the discharge over the weir (m^3 s^{-1}); C_{dR} and Ce are the effective dimensionless discharge coefficients for the rectangular and v-notch weirs, respectively; b is the weir length (m); θ is the angle of the v-notch (radians); h is the upstream head above the crest of the weir (m); h_e is the effective head (h + K_h); and K_h is the head-adjustment factor. For the Amazonian catchments, we adopted a C_{dR} of 0.62 based on the geometric characteristics of the weirs (Kindsvater and Carter, 1957). For the Cerrado catchments, we conducted discharge calibration measurements using an acoustic digital current meter (ADC, OTT) and estimated C_{dR} values of 0.74 for the CCER catchment and 0.65 for the APAS catchment.

We classified the streamflow as base streamflow (S_b) and storm streamflow (S_s), which represent the total stream discharge during baseflow- and stormflow-prevailing conditions, respectively. S_s was computed as the flow change in response to event precipitation and ending at the point separating the stormflow components, i.e. the surface and subsurface stormflow, from the baseflow recession. These flows were determined using a recursive digital filter (Eckhardt, 2005) implemented in the Web GIS-based Hydrograph Analysis Tool (WHAT) for baseflow separation (Lim et al., 2010, 2005). Using this information, we calculated the ratio of S_s to total streamflow (S_t) discharge.

The annual CAN stream output fluxes for each catchment were calculated multiplying the annual mean CAN concentration by the respective annual S_b and S_s volumes (Eqs. 5 and 6) as follows:

$$F_{TS_b} = \frac{C_{S_b} \times V_{S_b}}{A \times 10^6}, \tag{5}$$

$$F_{TS_s} = \frac{C_{Ss} \times V_{S_s}}{A \times 10^6}, \tag{6}$$

where F_{TSb} and F_{TSs} are, respectively, the annual CAN output fluxes of S_b and S_s (kg ha^{-1} yr^{-1}); C_{Sb} is the mean CAN concentration in S_b (mg L^{-1}); C_{Ss} is the volume-weighted mean CAN concentration obtained using Eq. 7 (mg L^{-1}); V_{Sb} and V_{Ss} are the mean annual S_b and S_s discharges (L yr^{-1}), respectively; and A is the catchment area (ha).

$$C_{Ss} = \frac{\sum_{j=1}^{m}\left(\sum_{i=1}^{n}\frac{C_{S_{S(i)}}}{n}\right) \times Vj}{\sum_{j=1}^{m} Vj}, \tag{7}$$

where $C_{Ss(i)}$ is the CAN concentration per S_s event interval *i* for the number of event intervals *n* (mg L^{-1}) and V_j is the volume per event *j* for the number of S_s events *m* (L).

3.4. Statistical analysis

We used principal component analysis (PCA) to identify the most representative hydrochemical parameters causing most of the total variance in S_b and S_s. PCA is commonly used to identify the variables that contain the most information and to provide future data collection criteria in ecological studies (King and Jackson, 1999; Zhang et al., 2009). It is useful for the identification of important surface water-quality parameters (Ouyang, 2005; Zeinalzadeh and Rezaei, 2017).

We conducted PCAs separately for each biome (Amazon and Cerrado) and flow condition (S_b and S_s) in order to avoid the dominance of the PCA by the data variance of only one specific region or streamflow condition. We used the Kaiser-Meyer-Olkin (KMO) test (Kaiser, 1974) as a measure of quality control in the PCAs. The KMO test measures the sampling adequacy of each variable for the complete analysis. We only considered CAN parameters with individual KMO values greater than the bare minimum of .5; therefore we repeated the PCAs, excluding the unacceptable CAN parameters from the analyses, until we obtained acceptable individual KMO results. We applied the orthogonal rotation varimax with Kaiser normalization to the PCAs to maximize the dispersion of loadings within the factors and considered the results with the most significant components (eigenvalues > 1).

We used the two-sample t-test to compare temperature and pH between the catchments, with the latter converted to H_3O^+ for statistical comparison because of the non-linearity of the pH values. Because of the solute concentration’s non-normal distribution, we used the Mann-Whitney (MW) U-test to compare these data by means of sample ranks to determine whether S_b and S_s were significantly different between the native vegetation and pasture catchments. Additionally, we used Mood’s median test given its robustness for outliers to detect differences in the median. The significance threshold was set at .05.

4. Results

4.1. Soil physical and chemical properties

Table 2 shows soil pH, C and N contents and texture results. The soil exhibited textural similarities within each pair of catchments, with mostly sandy clay loams in the Amazonian and loamy sand textures in the Cerrado catchments. The soil pH was significantly different ($p < .01$) between the native vegetation and the pasture catchments in each biome. Soil pH values ranging between 5 and 7 have also been reported in the Amazon (Mazzetto et al., 2016; Quesada et al., 2010); similarly, Carvalho et al. (2007) observed soil pH values between 3 and 5 in a Cerrado landscape. The results of C content and C:N ratios for the Amazonian catchments are in accordance with studies on primary forests and old pastures in the Amazon (McGrath et al., 2001). For the Cerrado catchments, the C:N ratios are also similar to other results for topsoil in areas with cerrado vegetation and pasture in this biome (Figueiredo et al., 2010; Neufeldt et al., 2002).

Table 2. Mean, one standard deviation and *n* of soil physical properties and C and N contents.

Soil attributes	**Amazonian catchments**		**Cerrado catchments**	
	AFOR	APAS	CCER	CPAS
Sand (%)	67.2 ± 6.0 (8)	57.6 ± 6.4 (8)	81.1 ± 20.5 (6)	93.3 ± 1.0 (8)
Silt (%)	9.1 ± 3.9 (8)	22.8 ± 6.0 (8)	6.1 ± 7.3 (6)	1.5 ± 0.4 (8)
Clay (%)	23.7 ± 6.1 (8)	19.6 ± 5.5 (8)	14.0 ± 13.4 (6)	5.2 ± 0.7 (8)
pH	5.7 ± 0.3 (3)	6.4 ± 0.7 (3)	3.6 ± 0.3 (6)	4.4 ± 0.5 (8)
C (%)	3.19 ± 2.54 (5)	1.47 ± 0.45 (6)	3.41 ± 3.88 (6)	1.33 ± 1.01 (8)
N (%)	0.27 ± 0.22 (5)	0.12 ± 0.04 (6)	0.18 ± 0.20 (6)	0.07 ± 0.05 (8)
C:N ratio	11.9 ± 1.8	11.8 ± 0.5	17.9 ± 2.4	18.3 ± 3.3

Figure 2 shows the soil chemical results. The soils from all catchments have a high content of Al and Fe, a characteristic often found in Amazon (dos Santos and Alleoni, 2013; Quesada et al., 2011) and Cerrado soils (Buol, 2009). Furthermore, we found low nutrient contents in the soils of all catchments. K, Mg and Mn contents exhibited significant differences ($p < .05$) between the Amazonian catchments, with higher Mn content in the AFOR than that of the APAS catchment. In the Cerrado catchments, Ca was the only element to exhibit significant differences ($p < .01$) between the CCER (0.03 g kg^{-1}) and CPAS catchments (0.18 g kg^{-1}).

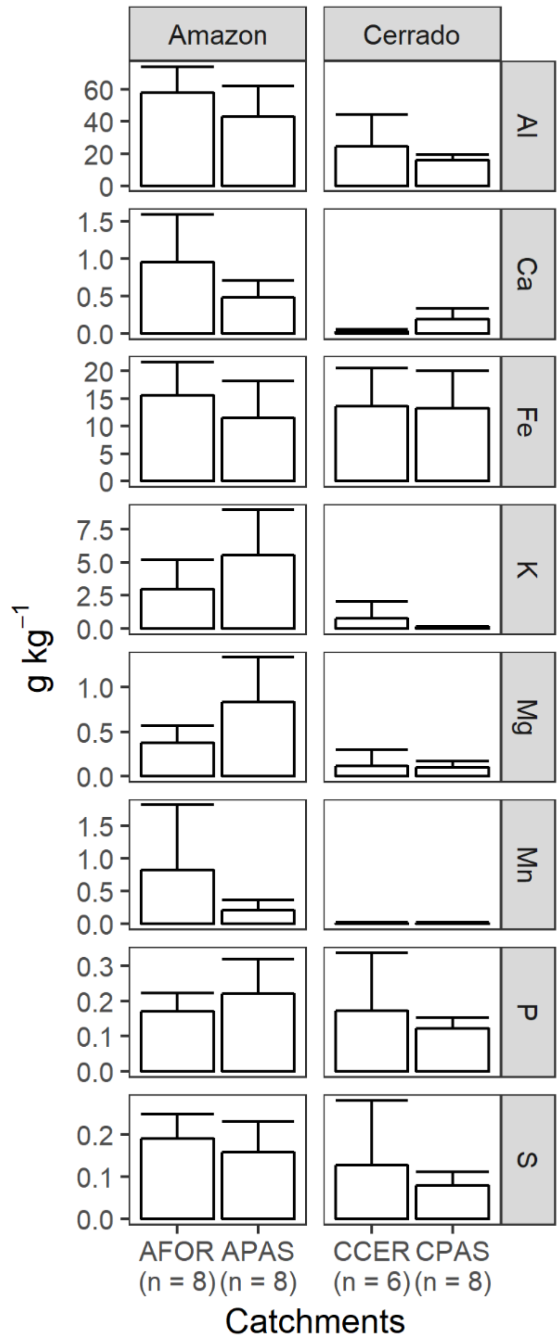

Figure 2. Total element contents in soils at a depth of 0–10 cm.

4.2. Hydrochemistry results

Figure 3 shows the results of stream water pH and temperature measurements of the four catchments. pH was significantly higher ($p < .001$) in the AFOS catchment (6.8 ± 0.58, n = 46,652) compared to that in the APAS catchment (6.4 ± 0.90, n = 83,488). Similarly, pH was significantly higher in the CCER catchment (5.3 ± 0.50, n = 38,397) compared to that in the CPAS catchment (5.1 ± 0.70, n = 57,361). Our findings also show that temperature was significantly lower ($p < .001$) in the AFOS catchment (24.6 ± 0.6 °C, n = 46,652) compared to that in the APAS catchment (26.4 ± 1.8 °C, n = 83,488), and in the CCER catchment (23.1 ± 0.8 °C, n = 46,884) compared to that in the CPAS catchment (24.7 ± 0.5 °C, n = 59,623). pH values measured in the Amazonian catchments were similar to those of other studies of small catchments in the Amazon (de Paula et al., 2016; Thomas et al., 2004). In the Cerrado, studies have also reported stream pH values ranging between 5 and 6 (Markewitz et al., 2006; Silva et al., 2007).

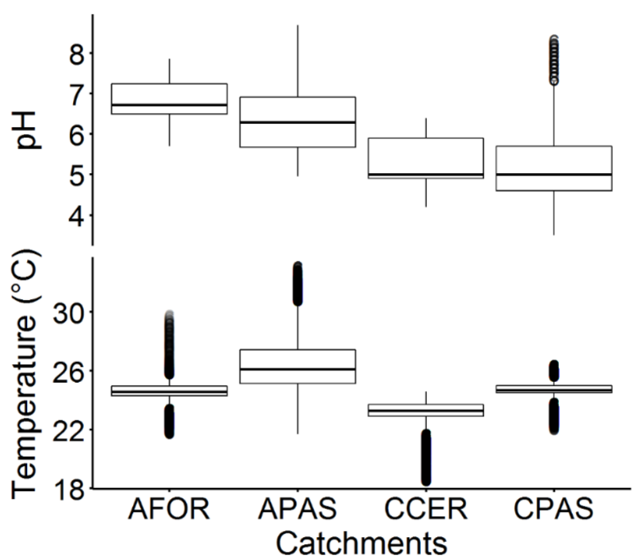

Figure 3. Streamflow pH and temperature.

Tables A.1 and A.2 show the descriptive statistics for the water quality results of S_b and S_s, respectively. TOC, DOC, K and NO_3^- exhibited the highest mean concentrations (> 1 mg L^{-1}) in the Amazonian catchments under both flow conditions.

For these catchments, our results indicate low mean streamflow concentrations for Cl, SO_4^{-2}, Na, Ca and Mg, which were all low (< 0.4 mg L^{-1}). In the Cerrado catchments, TOC, DOC, NO_3^- and Ca showed the highest mean concentrations. Other elements, such as Mg and Na, exhibited relatively low concentrations in the CCER catchment. Fe, F, P, S and SO_4^{-2} had the lowest concentrations, with most values less than the limit of detection. Although stream hydrochemistry data are scarce in these regions, studies have reported low stream concentrations for nutrients in a forested catchment in the central Amazon (Zanchi et al., 2015) as well in natural and disturbed catchments in the central and southwestern Cerrado (Silva et al., 2012, 2011).

The varimax rotation applied to the PCA on the water quality parameters exhibited individual KMO values greater than .5 (Table 3). The KMO was .70 for S_b and .63 for the S_s PCAs in the Amazonian catchments, and .68 for both the S_b and S_s PCAs in the Cerrado catchments, which are acceptable values of sampling adequacy for PCA (Kaiser, 1974). Bartlett's test of sphericity for the parameters indicated that correlations between items were sufficiently great for PCA (p < .001). Kaiser's criterion of eigenvalues greater than 1 was met by two components in the S_b PCAs and by three components in the stormflow PCAs for the Amazonian and Cerrado catchments. In combination, these components explained 80% and 86% of the variance in the S_b and S_s values in the Amazonian catchments, and 83% and 88% of the variance in the S_b and S_s values in the Cerrado catchments, respectively. Some parameters, such as TC, TOC, DC and DOC, cluster in the same components in all PCAs with high factor loadings.

In all of the PCAs, the first two components account for more than 60% of the total variance (Fig. 4). For the Amazonian catchments, the first component of the S_b PCA (Fig 4a) was mostly correlated with nitrogen and organic carbon, which showed the highest standard deviations. The items that cluster in the second component represent the inorganic carbon and cations (Ca and K). The main difference between the S_b and S_s PCAs (Fig. 4b) is the clustering of NO_3^-, TN and DN in the third component of the S_s PCA, suggesting that during stormflow events, nitrogen fluxes have a distinct dynamic from that of the other nutrients. For the Cerrado catchments, the first component of the S_b PCA (Fig. 4c) groups carbon and Ca, and the second component groups TN, DN and NO_3^-. This is the only PCA where the organic and inorganic carbon compounds cluster in the same component. The S_s PCA (Fig. 4d) shows that the first component groups DOC with DN, NO_3^- and K, and the second component shows a high factor loading grouping of TIC, DIC and Ca. The third component of this PCA groups TC, TOC and TN. This is the only PCA where TOC does not group together with DOC, which indicates the importance of particulate organic carbon (POC) in these catchments. We did not directly measure POC in our study, but the differences between TOC and DOC, which could be interpreted as POC (Zhou et al., 2013), were the highest in the Cerrado catchments, representing an average of 19% of the TOC.

Table 3. Factor loadings after varimax rotation.

	Amazonian catchments					Cerrado catchments				
	S_b		S_s			S_b		S_s		
	C1	C2	C1	C2	C3	C1	C2	C1	C2	C3
TC	**.92**	.27	**.99**	.07	.07	**.98**	-.02	.32	.25	**.90**
TIC	.12	**.88**	.07	**.95**	-.17	**.94**	-.12	.00	**.99**	.05
TOC	**.95**	.05	**.99**	.02	.08	**.77**	.11	.33	.06	**.92**
TN	**.81**	.30	.12	.10	**.92**	-.04	**.96**	.49	.01	**.75**
DC	**.88**	.19	**.99**	.12	.01	**.96**	-.24	**.74**	.36	.41
DIC	.01	**.93**	.07	**.95**	-.25	**.94**	-.12	.01	**.99**	.07
DOC	**.91**	-.05	**1.00**	.07	.03	**.79**	-.35	**.79**	.01	.41
DN	**.85**	.19	.09	-.14	**.95**	-.03	**.92**	**.77**	-.05	.33
NO_3^-	-	-	-.12	-.40	**.56**	-.16	**.74**	**.87**	.03	.12
Ca	.22	**.82**	-.02	**.92**	-.01	**.93**	-.06	.12	**.97**	.13
K	.20	**.79**	.17	**.56**	.37	-	-	**.87**	.05	.29
Eigenvalue	5.5	2.5	4.3	3.2	2.0	6.0	2.3	5.8	2.9	1.0
Cumulative Variability (%)	48.2	79.9	36.6	65.4	86.3	57.7	83.1	34.0	62.4	87.8

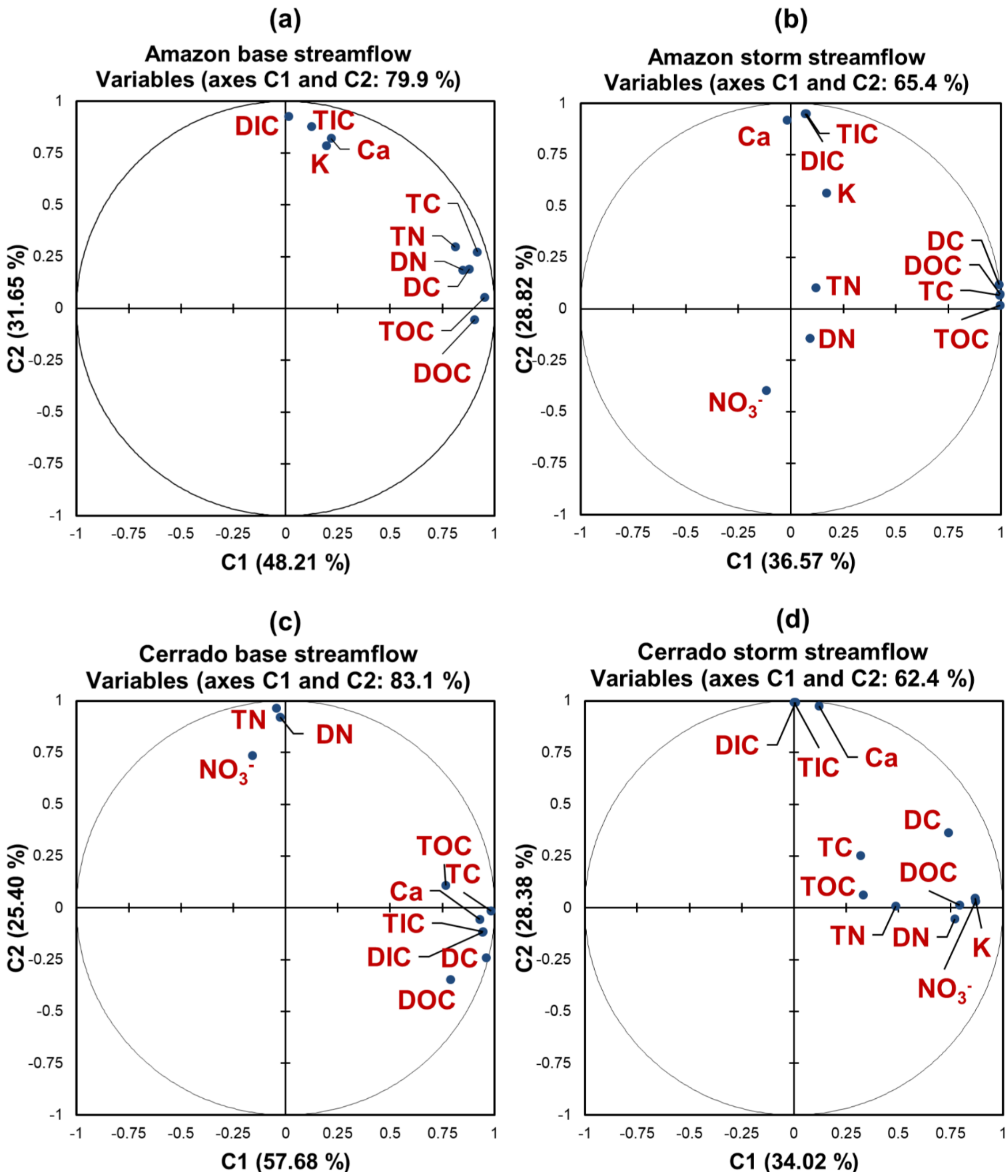

Figure 4. PCAs after varimax rotation: a) Amazon S_b; b) Amazon S_s; c) Cerrado S_b; and d) Cerrado S_s.

Based on the results of the PCAs, we compared TOC, DOC, TIC, DIC, TN and DN (Fig. 5), and NO_3^-, Ca and K (Fig. 6). Our DOC results for the Amazonian streams are in accordance with other studies of S_b of major tributaries of the Amazon River (Moreira-Turcq et al., 2003; Tardy et al., 2005) and in S_s of small Amazonian streams (Johnson et al., 2006). With the exception of higher TOC in the APAS catchment, the S_s, carbon concentrations between the Amazonian catchments did not exhibit significant differences.

In the Cerrado catchments, the highest differences were found in S_s, with higher TOC and DOC concentrations in the CPAS catchment compared to those of the CCER (Fig. 5a–b). For DIC, the differences in concentration between the Amazonian catchments in S_b and between the Cerrado catchments in S_s (Fig. 5c–d) were significant.

Except for DN in S_b of the Amazonian catchments, the pasture catchments exhibited higher TN and DN concentrations than those of the native vegetation catchments. The differences in NO_3^- were significant between the Cerrado catchments, with higher concentrations in the CPAS catchment, whereas there was no significant difference in the Amazonian catchments (Fig. 6a). In fact, the increase in NO_3^- concentrations due to deforestation in Amazonian streams are not as clear (Figueiredo et al., 2010; Silva et al., 2007; Williams and Melack, 1997) as they are in the Cerrado (Silva et al., 2011). Differences in Ca concentrations (Fig. 6b) were significant in the catchments of both biomes, but not for the same flow conditions. While the difference in Ca was significant only in S_b of the Amazonian catchments, this was only observed in S_s of the Cerrado catchments. The pasture catchments exhibited significantly higher Ca concentrations, which were also found in other studies in the Amazon (Biggs et al., 2002; Figueiredo et al., 2010) and Cerrado (Markewitz et al., 2011; Silva et al., 2011). The pastures for both S_b and S_s also exhibited significantly higher K concentrations (Fig. 6c).

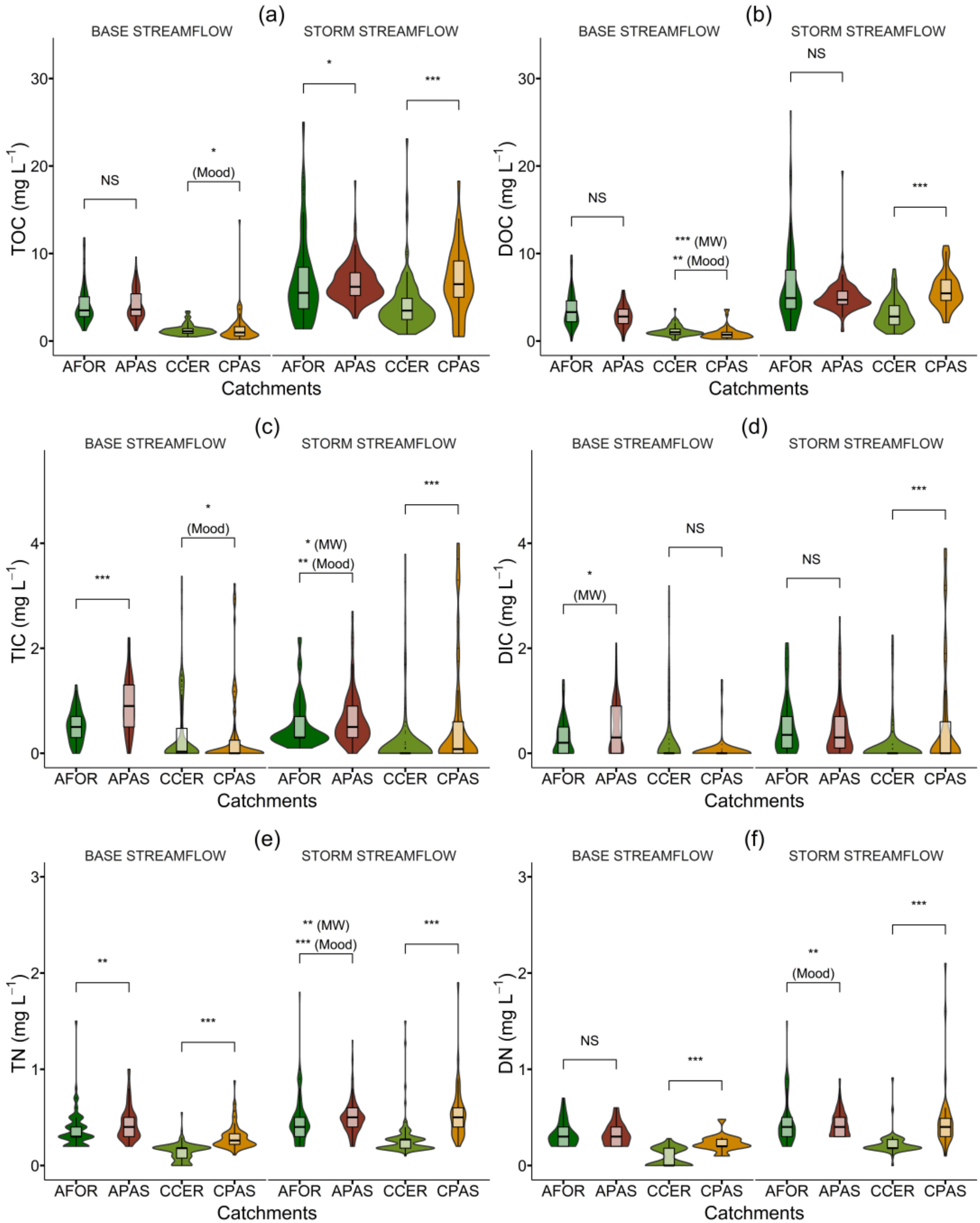

Figure 5. Boxplot and violin plots of non-flow weighted carbon and nitrogen concentrations in base streamflow and storm streamflow. The violin plots indicate the density of the sample distribution across the y-values. The y-axis was limited to exclude some outliers (only graphically) for better

visualization of the results. NS stands for not significant and *, ** and *** indicate statistical significance at the .05, .01 and .001 probability levels, respectively. The significance of the results was based on the MW and Mood tests. When the test type is not indicated, the result is valid for both tests.

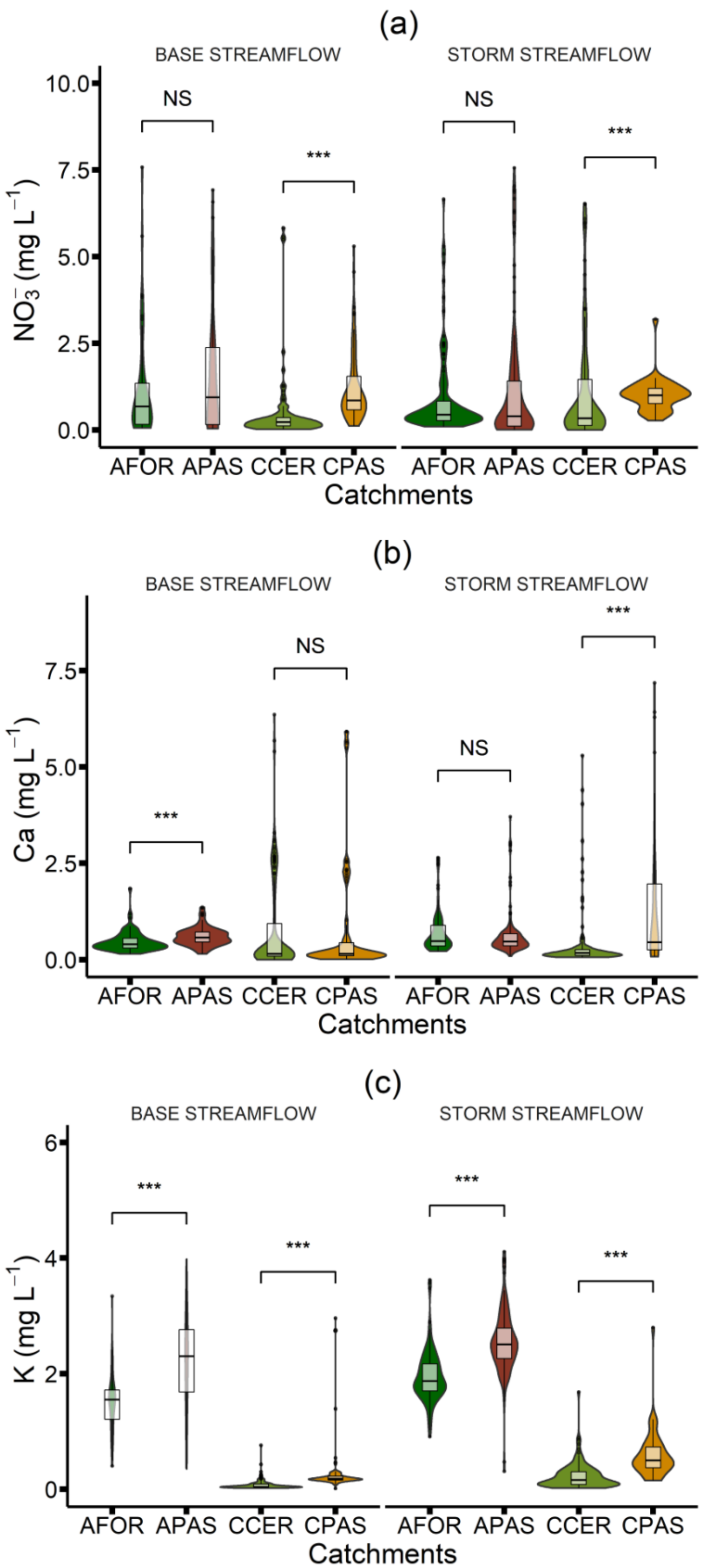

Figure 6. Boxplot and violin plots of NO_3^-, Ca and K non-flow weighted concentrations in base streamflow and storm streamflow. The violin plots indicate the density of the sample distribution

across the y-values. The y-axis was limited to exclude some outliers (only graphically) for better visualization of the results. NS stands for not significant and *, ** and *** indicate the statistical significance at the .05, .01 and .001 probability levels, respectively. The significance results were based on the MW and Mood tests. When the test type is not indicated, the result is valid for both tests.

4.3. CAN output fluxes

Table 4. Annual carbon and nutrient output fluxes of base streamflow, storm streamflow and total streamflow.

	Output fluxes (kg ha^{-1} yr^{-1})								
	Base streamflow (S_b)								
Catchment	**TOC**	**TIC**	**TN**	**DOC**	**DIC**	**DN**	**NO_3^-**	**Ca**	**K**
AFOR	27.43	3.36	2.31	23.35	1.91	2.04	7.65	3.10	9.96
APAS	77.29	16.93	7.91	52.63	8.65	5.70	29.81	11.04	40.49
CCER	5.69	1.69	0.62	5.07	0.89	0.40	2.22	3.51	0.31
CPAS	10.02	2.45	2.03	6.24	0.35	1.61	8.41	6.45	2.10
	Storm streamflow (S_s)								
AFOR	9.54	1.04	0.68	8.94	0.88	0.61	0.60	1.24	3.04
APAS	54.94	5.18	3.15	52.02	4.21	2.72	2.26	5.64	17.25
CCER	1.96	0.06	0.10	1.11	0.06	0.06	0.09	0.05	0.10
CPAS	1.86	0.04	0.12	1.24	0.04	0.10	0.25	0.15	0.14
	Total streamflow (S_t)								
AFOR	36.98	4.40	2.98	32.29	2.79	2.66	8.25	4.34	13.00
APAS	132.23	22.11	11.06	104.65	12.86	8.42	32.07	16.68	57.74
CCER	7.65	1.75	0.72	6.18	0.95	0.46	2.31	3.57	0.41
CPAS	11.88	2.50	2.16	7.48	0.39	1.71	8.66	6.60	2.24

The annual S_b and S_s CAN output fluxes are shown in Table 4. In the Amazonian catchments, TOC total output fluxes were between 35 and 135 kg ha^{-1} yr^{-1}, and K and NO_3^- values ranged from 8 to 60 kg ha^{-1} yr^{-1}. In the Cerrado catchments, TOC, Ca and NO_3^- had total output fluxes between 2 and 12 kg ha^{-1} yr^{-1}, and DIC and DN had output fluxes less than 2 kg ha^{-1} yr^{-1}. Although the two biomes show different magnitudes of CAN fluxes with higher fluxes in the Amazonian catchments, the S_b CAN fluxes were higher than those of the S_s CAN fluxes in all catchments. Furthermore, the fluxes in the pasture catchments were generally higher compared to those of the native vegetation catchments. Nutrients, especially K and Ca, have also been shown to have higher stream fluxes in pastures than in forests in the Amazon (Germer et al., 2009; Williams and Melack, 1997) and Cerrado (Figueiredo et al., 2010; Silva et al., 2011).

5. Discussion

5.1. Stream hydrochemistry

Our results showed significantly higher CAN concentrations in the pasture catchments compared to those of the native vegetation catchments, especially for TIC, TN and K. Some other macronutrients (Mg, P and S) and micronutrients (F, Cl, Fe and Na) exhibited concentrations of < 1 mg L^{-1} in all of the studied catchments. For some nutrients, i.e. F and Fe, we attributed this to the absence of fertilizer application in the pasture catchments and the poor soil nutrient conditions in both regions, which is typical of Lixisols (Driessen and Deckers, 2001) and Arenosols (Markewitz et al., 2006) because of their strongly weathered substrate. Additionally, the highly weathered soils fix available nutrients, especially P, in the form of Fe and Al sesquioxides (Uehara and Gillman, 1981).

In contrast to our findings, stream pH increased with the clearing of native vegetation cover in studies in the eastern Amazon (Figueiredo et al., 2010a) and in the central and southern Cerrado (Silva et al., 2011, 2007). However, our observations agree with studies that show that stream temperature could be an indicator of deforestation in both biomes. In fact, the influence of LULC change on stream temperature has been reported in other studies (e.g., Brion et al., 2011; Daraio et al., 2014). In the Amazon and Cerrado, Macedo et al. (2013) found that temperature could be an indicator of LULC change and found lower stream temperatures in areas covered with native vegetation than those areas covered with pasture. There are several explanations that can associate increased stream temperature to deforestation, such as higher concentrations of suspended solids and greater contribution of direct runoff into the stream. Based on our field observations, we attribute this to the degradation of the riparian vegetation in the pasture catchments, reducing shade and increasing incident sunlight and, consequently, water temperature in small streams (Bojsen and Barriga, 2002; Castello and Macedo, 2016).

We found that the soil pH relationship between the pasture and native vegetation catchments contrasted with that of streamflow pH. Soil pH in the pasture catchments was higher than that in the native vegetation catchments, which has also been reported in other studies in other regions of the Amazon (Mazzetto et al., 2016) and Cerrado (Carvalho et al., 2007; Hunke et al., 2015b; Neufeldt et al., 2002). This is owing to liming practices in the pasture catchments. Lime ($CaCO_3$) is often applied to acidic soils in these regions to increase soil pH (Couto et al., 1997; Jepson et al., 2010; Moreira and Fageria, 2010). Therefore, Ca content was higher in the soils of the pasture catchments than in the soils of the native vegetation catchments.

The significantly higher Ca S_s concentrations exhibited in the CPAS catchment compared to those of the CCER catchment indicates that liming practices are increasing Ca content in the topsoil of the CPAS catchment and facilitating the leaching of this element to the stream during stormflow events. Other studies have already reported that the high rainfall rates in the Cerrado are sufficient to solubilize and leach fertilizers such as Ca (Hunke et al., 2015a; Villela and Haridasan, 1994). Conversely, between the Amazonian catchments, the Ca concentrations in stream water were significantly higher in the APAS, but only in S_b. Such an enrichment of Ca in the S_b has been observed in other studies in Brazil (Da Silva et al., 1998; Gonzatto, 2014), and we attribute this to the slow percolation of the residual lime through the soil profile (Rowe, 1982). Because Lixisols are in an advanced weathering stage (Quesada et al., 2011) and characterized by a low cation exchange capacity (Driessen and Deckers, 2001), the percolating soil water carries the residual Ca, thereby increasing its concentration in the S_b. In contrast, during storm events, the surface runoff dilutes the Ca concentration in the S_b, resulting in similar concentrations between the Amazonian catchments. Biggs et al. (2002) found strong correlations between the soil exchangeable cation content and the concentration of stream solutes and suggested that pasture age may help explain the substantial variation in solute concentration responses to deforestation, especially for Ca. DIC presented dynamics similar to Ca; its differences within the Amazonian and Cerrado catchments occur in the same flow types, and they are grouped in the same components in all PCAs. We ascribe this to be a consequence of liming practices. As lime is applied, the $CaCO_3$ reacts with water, increasing the soil pH and producing HCO_3^-, which is one of the main

DIC components and has been identified as a main driver of DIC fluxes in small streams in the Amazon (Cak et al., 2015; Johnson et al., 2006).

We found NO_3^- concentrations to be significantly different only between the Cerrado catchments, with higher values in the CPAS catchment. It has been reported that the high percentage of mineralized N nitrified in forests is the cause of a high potential for NO_3^- loss in soil solution and streamwater when these forests are cleared and burned (Neill et al., 2006; Vourlitis and Hentz, 2016), which has occurred in small catchments under recent or ongoing deforestation (Williams and Melack, 1997). The fact that we could not find this same relationship between the NO_3^- concentrations of the Amazonian catchments is consistent with patterns of N cycling and N availability, which shows high soil solution NO_3^- concentrations in Amazonian forests (Neill et al., 2001). The Amazonian forest behaves rather similar to old and temperate forests, which present high nitrification rates and NO_{3-} pool losses that occur under normal conditions (Aber et al., 1989; Neill et al., 2001; Stevens et al., 1994). These forests may become net sources of nitrogen, thereby causing NO_3^- leaching to streams (Aber et al., 1995).

5.2. Stream CAN output fluxes

Table 5. Base streamflow, storm streamflow and total streamflow ratios of stream output fluxes for each pair of catchments.

Ratio	Flow type	TOC	TIC	TN	DOC	DIC	DN	NO_3^-	Ca	K
APAS:AFOR	Base streamflow	2.8	5.0	3.4	2.3	4.5	2.8	3.9	3.6	4.1
APAS:AFOR	Storm streamflow	5.8	5.0	4.7	5.8	4.8	4.4	3.8	4.6	5.7
APAS:AFOR	Total streamflow	3.6	5.0	3.7	3.2	4.6	3.2	3.9	3.8	4.4
CPAS:CCER	Base streamflow	1.8	1.5	3.3	1.2	0.4	4.0	3.8	1.8	6.8
CPAS:CCER	Storm streamflow	1.0	0.7	1.2	1.1	0.6	1.7	2.7	2.8	1.4
CPAS:CCER	Total streamflow	1.6	1.4	3.0	1.2	0.4	3.7	3.7	1.8	5.5

Except for DIC and NO_3^- in the Cerrado catchments, the CAN fluxes were greater in the pasture catchments (Table 5). The Amazonian catchments exhibited the greatest differences in CAN fluxes. In these catchments, S_b showed a more substantial contribution to the total S_t CAN fluxes, with an average CAN flux 37% higher than that in S_b. Conversely, for the Cerrado catchments, the CPAS:CCER CAN ratios were, on average, 56% less in S_s than in S_b.

The total and dissolved carbon stream outputs were higher from the pasture catchments. Strey et al. (2016) found that degraded pasture areas exhibit lower organic carbon (OC) content than that of areas with native vegetation in the Cerrado and Amazon biomes, which is likely connected to larger losses of forest-derived OC after deforestation. In these biomes, the reduced organic carbon due to native vegetation clearing for pasture has been shown to be associated with reduced aggregate stability (Longo et al., 1999), which, in turn, has resulted in degraded pasture soils storing less carbon than soils covered with natural vegetation (Fonte et al., 2014). This facilitates carbon leaching and, consequently, increases the TOC and DOC fluxes. Kindler et al. (2011) affirmed that the quantification of DOC leaching from soil is crucial for the carbon balance. These authors found that losses of biogenic carbon from grasslands account for ca. 22% of the net ecosystem exchange, whereas leaching from forest sites hardly affects net ecosystem carbon balances. In the Amazon, the decreased soil carbon storage as a consequence of forest conversion to pastures has been reported to be directly correlated with pasture age (Asner et al., 2004). In the Cerrado, while well-managed pastures may sustain soil carbon content, most pastures in this biome are in advanced stages of degradation (Davidson et al., 2012).

Similar to C, N output fluxes were higher in the pasture catchments. In comparison to the Cerrado catchments, the Amazonian catchments exhibited a lower C:N ratio, which is typical for Oxisols in the uppermost horizon (Tardy et al., 2005), and has been identified as an important controlling factor of total ecosystem N retention. High C:N promotes N immobilization, reduces net nitrification and consequently contributes to greater N retention (Templer et al., 2012). This has direct implications for the net N fluxes in this region, as the atmospheric deposition of N (3.5–10 kg N ha^{-1} $year^{-1}$ (Bobbink et al., 2010; Salemi et al., 2015)) is exceeded by N output via streamflow in the APAS catchment. This indicates that the pastures in this region might be a sink for N, as has been found in other studies in the Amazon (e.g., Germer et al., 2009 and Salemi et al., 2015).

Our results reaffirm the importance of S_s as a significant contributor to S_t CAN fluxes in catchments of the Amazon and Cerrado biomes. To illustrate this, we provide the ratios between the short-lived events (S_s) to the S_t duration, volume and CAN fluxes in Table 6.

The S_s:S_t duration ratios were only 4.9–5.3% in the Amazonian catchments and 1.7–2.1% in the Cerrado catchments. Nevertheless, the relatively small durations of the S_s events caused an increase of 15.9–26.5% and 2.8–5.5% in the S_t volume in the Amazonian and Cerrado catchments, respectively. Moreover, in nearly all cases the S_s contribution to the S_t CAN output fluxes was greater than its contribution to the S_t volume. In the APAS catchment, 50% of the S_t DOC output fluxes were caused by S_s. In the Cerrado catchments, S_s fluxes accounted for 16–26% of the TOC total streamflow output fluxes, despite the S_s contribution to S_t volume of only approximately 2–5%. This shows that S_s is especially important as a rapid hydrological pathway for CAN losses in areas on the AAF where deforestation reduces the infiltration capacity rates, which are in turn exceeded by the rainfall intensities, causing greater stormflow contributions (Zimmermann et al., 2006). The substantial contribution exhibited by S_s to S_t CAN fluxes is mainly owing to their higher CAN concentrations compared to those of S_b. These concentrations may be higher in S_s because of the rapid subsurface response in streams dominated by pre-event water, where a rapid mobilization of old water occurs (Kirchner, 2003), and to surface flow paths that contribute to increased CAN concentrations (Johnson et al., 2006).

Table 6. Percentage ratio of the storm streamflow duration, volume and fluxes to the total streamflow.

			S_s:S_t (CAN fluxes)								
Catchment	S_s:St (duration)	S_s:S_t (volume)	TOC	TIC	TN	DOC	DIC	DN	NO_3^-	Ca	K
AFOR	4.9%	15.9%	26%	24%	23%	28%	31%	23%	7%	29%	23%
APAS	5.3%	26.5%	42%	23%	28%	50%	33%	32%	7%	34%	30%
CCER	2.0%	5.2%	26%	3%	14%	18%	6%	12%	4%	2%	24%
CPAS	1.6%	2.8%	16%	2%	6%	17%	10%	6%	3%	2%	6%

DIC also exhibits a rapid response during stormflows in wet tropical catchments under pristine rainforest and agriculture LULC (Bass et al., 2014). In the Amazonian catchments, we found that S_s represented slightly more than 30% of S_t DIC fluxes, with similar S_s:S_t DIC fluxes between these catchments. In contrast, DIC S_s fluxes represented only 6% of the total output fluxes in the CCER catchment and 10% in the CPAS catchment.

6. Conclusions

We analyzed the role of stream discharge in carbon and nutrient dynamics and fluxes in catchments under contrasting land use and land cover on the Amazon agricultural frontier. Our research supplements existing studies in the Amazon and Cerrado biomes in demonstrating how the conversion of natural vegetated landscapes (forest and cerrado) to pasture increases hydrochemical fluxes, which can disturb the natural carbon and nutrient balance in both regions.

Stream carbon and nutrient concentrations were significantly higher in catchments where the native vegetation was replaced by pastures. These higher concentrations underlie further implications for carbon and nutrient fluxes as streamflow increase occurs, which is widely reported in this region as a consequence of the conversion of native vegetation into agricultural lands. We found that most of the carbon and nutrient flux contributions of stormflow to total streamflow is proportionately greater than its respective volumetric contribution to stream discharge. This shows that stormflow is a substantial hydrological pathway for carbon and nutrient losses, including areas with small stormflow contribution, as shown in the Cerrado catchments. Although the acquisition of such detailed data in tropical forests is often limited by logistical restraints, we recommend that further studies use novel monitoring techniques such as automatic overland flow sampling and real-time water-quality sensors to improve the understanding of hydrochemical pathways and fluxes in forest ecosystems under anthropogenic changes such as the Amazonian agricultural frontier.

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References

Aber, J.D., Magill, A., Mcnulty, S.G., Boone, R.D., Nadelhoffer, K.J., Downs, M., Hallett, R., 1995. Forest biogeochemistry and primary production altered by nitrogen saturation. Water, Air, Soil Pollut. 85, 1665–1670. doi:10.1007/BF00477219

Aber, J.D., Nadelhoffer, K.J., Steudler, P., Melillo, J.M., 1989. Nitrogen Saturation in Northern Forest EcosystemsExcess nitrogen from fossil fuel combustion may stress the biosphere. Bioscience 39, 378–386. doi:10.2307/1311067

Alexander, R.B., Smith, R. a, Schwarz, G.E., 2000. Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. Nature 403, 758–761. doi:10.1038/35001562

Andreae, M.O., Acevedo, O.C., Araùjo, A., Artaxo, P., Barbosa, C.G.G., Barbosa, H.M.J., Brito, J., Carbone, S., Chi, X., Cintra, B.B.L., da Silva, N.F., Dias, N.L., Dias-Júnior, C.Q., Ditas, F., Ditz, R., Godoi, A.F.L., Godoi, R.H.M., Heimann, M., Hoffmann, T., Kesselmeier, J., Könemann, T., Krüger, M.L., Lavric, J. V., Manzi, A.O., Lopes, A.P., Martins, D.L., Mikhailov, E.F., Moran-Zuloaga, D., Nelson, B.W., Nölscher, A.C., Santos Nogueira, D., Piedade, M.T.F., Pöhlker, C., Pöschl, U., Quesada, C.A., Rizzo, L. V., Ro, C.-U., Ruckteschler, N., Sá, L.D.A., de Oliveira Sá, M., Sales, C.B., dos Santos, R.M.N., Saturno, J., Schöngart, J., Sörgel, M., de Souza, C.M., de Souza, R.A.F., Su, H., Targhetta, N., Tóta, J., Trebs, I., Trumbore, S., van Eijck, A., Walter, D., Wang, Z., Weber, B., Williams, J., Winderlich, J., Wittmann, F., Wolff, S., Yáñez-Serrano, A.M., 2015. The Amazon Tall Tower Observatory (ATTO): overview of pilot measurements on ecosystem ecology, meteorology, trace gases, and aerosols. Atmos. Chem. Phys. 15, 10723–10776. doi:10.5194/acp-15-10723-2015

Armenteras, D., Rodríguez, N., Retana, J., 2013. Landscape Dynamics in Northwestern Amazonia: An Assessment of Pastures, Fire and Illicit Crops as Drivers of Tropical Deforestation. PLoS One 8, e54310. doi:10.1371/journal.pone.0054310

Asner, G.P., Townsend, A.R., Bustamante, M.M.C., Nardoto, G.B., Olander, L.P., 2004. Pasture degradation in the central Amazon: linking changes in carbon and nutrient cycling with remote sensing. Glob. Chang. Biol. 10, 844–862. doi:10.1111/j.1529-8817.2003.00766.x

Avagyan, A., Runkle, B.R.K., Kutzbach, L., 2014. Application of high-resolution spectral absorbance measurements to determine dissolved organic carbon concentration in remote areas. J. Hydrol. 517, 435–446. doi:10.1016/j.jhydrol.2014.05.060

Barona, E., Ramankutty, N., Hyman, G., Coomes, O.T., 2010. The role of pasture and soybean in deforestation of the Brazilian Amazon. Environ. Res. Lett. 5, 24002.

doi:10.1088/1748-9326/5/2/024002

Bass, A.M., Bird, M.I., Liddell, M.J., Nelson, P.N., 2011. Fluvial dynamics of dissolved and particulate organic carbon during periodic discharge events in a steep tropical rainforest catchment. Limnol. Oceanogr. 56, 2282–2292. doi:10.4319/lo.2011.56.6.2282

Bass, A.M., Munksgaard, N.C., Leblanc, M., Tweed, S., Bird, M.I., 2014. Contrasting carbon export dynamics of human impacted and pristine tropical catchments in response to a short-lived discharge event. Hydrol. Process. 28, 1835–1843. doi:10.1002/hyp.9716

Biggs, T.W., Dunne, T., Domingues, T.F., Martinelli, L.A., 2002. Relative influence of natural watershed properties and human disturbance on stream solute concentrations in the southwestern Brazilian Amazon basin. Water Resour. Res. 38, 25-1-25–16. doi:10.1029/2001WR000271

Biggs, T.W., Dunne, T., Muraoka, T., 2006. Transport of water, solutes and nutrients from a pasture hillslope, southwestern Brazilian Amazon. Hydrol. Process. 20, 2527–2547. doi:10.1002/hyp.6214

Bobbink, R., Hicks, K., Galloway, J., Spranger, T., Alkemade, R., Ashmore, M., Bustamante, M., Cinderby, S., Davidson, E., Dentener, F., Emmett, B., Erisman, J.-W., Fenn, M., Gilliam, F., Nordin, A., Pardo, L., De Vries, W., 2010. Global assessment of nitrogen deposition effects on terrestrial plant diversity: a synthesis. Ecol. Appl. 20, 30–59. doi:10.1890/08-1140.1

Bojsen, B.H., Barriga, R., 2002. Effects of deforestation on fish community structure in Ecuadorian Amazon streams. Freshw. Biol. 47, 2246–2260. doi:10.1046/j.1365-2427.2002.00956.x

Brannstrom, C., Jepson, W., Filippi, A.M., Redo, D., Xu, Z., Ganesh, S., 2008. Land change in the Brazilian Savanna (Cerrado), 1986–2002: Comparative analysis and implications for land-use policy. Land use policy 25, 579–595. doi:10.1016/j.landusepol.2007.11.008

Brion, G., Brye, K.R., Haggard, B.E., West, C., Brahana, J.V., 2011. Land-use effects on water quality of a first-order stream in the Ozark Highlands, mid-southern United States. River Res. Appl. 27, 772–790. doi:10.1002/rra.1394

Brown, A.E., Zhang, L., McMahon, T.A., Western, A.W., Vertessy, R.A., 2005. A review of paired catchment studies for determining changes in water yield resulting from alterations in vegetation. J. Hydrol. 310, 28–61. doi:10.1016/j.jhydrol.2004.12.010

Buol, S.W., 2009. Soils and agriculture in central-west and north Brazil. Sci. Agric. 66, 697–707. doi:10.1590/S0103-90162009000500016

Cak, A.D., Moran, E.F., Figueiredo, R.D.O., Lu, D., Li, G., Hetrick, S., 2015. Urbanization and small household agricultural land use choices in the Brazilian Amazon and the role for the water chemistry of small streams. J. Land Use Sci. 4248, 1–19. doi:10.1080/1747423X.2015.1047909

Canadell, J., Jackson, R.B., Ehleringer, J.B., Mooney, H. a., Sala, O.E., Schulze, E.-D., 1996. Maximum rooting depth of vegetation types at the global scale. Oecologia 108, 583–595. doi:10.1007/BF00329030

Carvalho, J.L.N., Cerri, C.E.P., Cerri, C.C., Feigl, B.J., Píccolo, M.C., Godinho, V.P., Herpin, U., 2007. Changes of chemical properties in an oxisol after clearing of native Cerrado vegetation for agricultural use in Vilhena, Rondonia State, Brazil. Soil Tillage Res. 96, 95–102. doi:10.1016/j.still.2007.04.001

Castello, L., Macedo, M.N., 2016. Large-scale degradation of Amazonian freshwater ecosystems. Glob. Chang. Biol. 22, 990–1007. doi:10.1111/gcb.13173

Christophersen, N., Clair, T.A., Driscoll, C.T., Jeffries, D.S., Neal, C., Semkin, R.G., 1994. Hydrochemical Studies, in: Moldan, B., Cerny, J. (Eds.), Biogeochemistry of Small Catchments: A Tool for Environmental Research. J. Wiley, Chichester, West Sussex, England, pp. 285–297.

Clark, J.M., Lane, S.N., Chapman, P.J., Adamson, J.K., 2007. Export of dissolved organic carbon from an upland peatland during storm events: Implications for flux estimates. J. Hydrol. 347, 438–447. doi:10.1016/j.jhydrol.2007.09.030

Coe, M.T., Marthews, T.R., Costa, M.H., Galbraith, D.R., Greenglass, N.L., Imbuzeiro, H.M. a, Levine, N.M., Malhi, Y., Moorcroft, P.R., Muza, M.N., Powell, T.L., Saleska, S.R., Solorzano, L. a, Wang, J., 2013. Deforestation and climate feedbacks threaten the ecological integrity of south-southeastern Amazonia. Philos. Trans. R. Soc. Lond. B. Biol. Sci. 368, 20120155. doi:10.1098/rstb.2012.0155

Cohn, A.S., Gil, J., Berger, T., Pellegrina, H., Toledo, C., 2016. Patterns and processes of pasture to crop conversion in Brazil: Evidence from Mato Grosso State. Land use policy 55, 108–120. doi:10.1016/j.landusepol.2016.03.005

Couto, E.G., Stein, a, Klamt, E., 1997. Large area spatial variability of soil chemical properties in central Brazil. Agric. Ecosyst. Environ. 66, 139–152. doi:Doi 10.1016/S0167-8809(97)00076-5

Crossman, J., Futter, M.N., Whitehead, P.G., Stainsby, E., Baulch, H.M., Jin, L., Oni, S.K., Wilby, R.L., Dillon, P.J., 2014. Flow pathways and nutrient transport mechanisms drive hydrochemical sensitivity to climate change across catchments with different geology and topography. Hydrol. Earth Syst. Sci. 18, 5125–5148. doi:10.5194/hess-18-5125-2014

Cuo, L., Zhang, Y., Gao, Y., Hao, Z., Cairang, L., 2013. The impacts of climate change and land cover/use transition on the hydrology in the upper Yellow River Basin, China. J. Hydrol. 502, 37–52. doi:10.1016/j.jhydrol.2013.08.003

Da Silva, N.M., Van Raij, B., De Carvalho, L.H., Bataglia, O.C., Kondo, J.I., 1998. Efeitos do calcário e do gesso nas características químicas do solo e na cultura do algodão. Bragantia 56, 389–401. doi:10.1590/S0006-87051997000200018

Daraio, J. a., Bales, J.D., Pandolfo, T.J., 2014. Effects of Land Use and Climate Change on Stream Temperature II: Threshold Exceedance Duration Projections for

Freshwater Mussels. JAWRA J. Am. Water Resour. Assoc. 2, n/a-n/a. doi:10.1111/jawr.12178

Davidson, E.A., de Araújo, A.C., Artaxo, P., Balch, J.K., Brown, I.F., C. Bustamante, M.M., Coe, M.T., DeFries, R.S., Keller, M., Longo, M., Munger, J.W., Schroeder, W., Soares-Filho, B.S., Souza, C.M., Wofsy, S.C., 2012. The Amazon basin in transition. Nature 481, 321–328. doi:10.1038/nature10717

de Moraes, J.M., Schuler, A.E., Dunne, T., Figueiredo, R. de O., Victoria, R.L., 2006. Water storage and runoff processes in plinthic soils under forest and pasture in eastern Amazonia. Hydrol. Process. 20, 2509–2526. doi:10.1002/hyp.6213

de Paula, J.D., Luizão, F.J., Piedade, M.T.F., 2016. The size distribution of organic carbon in headwater streams in the Amazon basin. Environ. Sci. Pollut. Res. 23, 11461–11470. doi:10.1007/s11356-016-6041-6

Dias, L.C.P., Macedo, M.N., Costa, M.H., Coe, M.T., Neill, C., 2015. Effects of land cover change on evapotranspiration and streamflow of small catchments in the Upper Xingu River Basin, Central Brazil. J. Hydrol. Reg. Stud. 4, 108–122. doi:10.1016/j.ejrh.2015.05.010

DIN ISO 11277:2002-08, 2002. Bodenbeschaffenheit – Bestimmung der Partikelgrößenverteilung in Mineralböden – Verfahren mittels Siebung und Sedimentation. ISO 11277: 1998/Cor.1:2002. Beuth Verlag, Berlin, Germany.

Do Vale, I., Miranda, I.S., Mitja, D., Grimaldi, M., Nelson, B.W., Desjardins, T., Costa, L.G.S., 2015. Tree Regeneration Under Different Land-Use Mosaics in the Brazilian Amazon's "Arc of Deforestation." Environ. Manage. 56, 342–354. doi:10.1007/s00267-015-0500-6

dos Santos, S.N., Alleoni, L.R.F., 2013. Reference values for heavy metals in soils of the Brazilian agricultural frontier in Southwestern Amazônia. Environ. Monit. Assess. 185, 5737–5748. doi:10.1007/s10661-012-2980-7

Driessen, P., Deckers, J., 2001. Lecture notes on the major soils of the world, World Soil Resources Reports. Rome.

Durieux, L., 2003. The impact of deforestation on cloud cover over the Amazon arc of deforestation. Remote Sens. Environ. 86, 132–140. doi:10.1016/S0034-4257(03)00095-6

Eckhardt, K., 2005. How to construct recursive digital filters for baseflow separation. Hydrol. Process. 19, 507–515. doi:10.1002/hyp.5675

El-Khoury, a., Seidou, O., Lapen, D.R., Que, Z., Mohammadian, M., Sunohara, M., Bahram, D., 2015. Combined impacts of future climate and land use changes on discharge, nitrogen and phosphorus loads for a Canadian river basin. J. Environ. Manage. 151, 76–86. doi:10.1016/j.jenvman.2014.12.012

Fearnside, P.M., 2001. Soybean cultivation as a threat to the environment in Brazil. Environ. Conserv. doi:10.1017/S0376892901000030

Figueiredo, R.O., Markewitz, D., Davidson, E.A., Schuler, A.E., Dos S. Watrin, O., De Souza Silva, P.P., 2010. Land-use effects on the chemical attributes of low-order streams in the eastern Amazon. J. Geophys. Res. 115, G04004. doi:10.1029/2009JG001200

Figueiredo, C.C. De, Resck, D.V.S., Carneiro, M.A.C., 2010. Labile and stable fractions of soil organic matter under management systems and native cerrado. Rev. Bras. Ciência do Solo 34, 907–916. doi:10.1590/S0100-06832010000300032

Fonte, S.J., Nesper, M., Hegglin, D., Velásquez, J.E., Ramirez, B., Rao, I.M., Bernasconi, S.M., Bünemann, E.K., Frossard, E., Oberson, A., 2014. Pasture degradation impacts soil phosphorus storage via changes to aggregate-associated soil organic matter in highly weathered tropical soils. Soil Biol. Biochem. 68, 150–157. doi:10.1016/j.soilbio.2013.09.025

Furley, P.A., 1999. The nature and diversity of neotropical savanna vegetation with particular reference to the Brazilian cerrados. Glob. Ecol. Biogeogr. 8, 223–241. doi:10.1046/j.1466-822X.1999.00142.x

Germer, S., Neill, C., Krusche, A. V., Elsenbeer, H., 2010. Influence of land-use change on near-surface hydrological processes: Undisturbed forest to pasture. J. Hydrol. 380, 473–480. doi:10.1016/j.jhydrol.2009.11.022

Germer, S., Neill, C., Vetter, T., Chaves, J., Krusche, A. V., Elsenbeer, H., 2009. Implications of long-term land-use change for the hydrology and solute budgets of small catchments in Amazonia. J. Hydrol. 364, 349–363. doi:10.1016/j.jhydrol.2008.11.013

Gonzatto, R., 2014. Aplicação superficial de calcário: até onde migram e até quando persistem os efeitos no perfil do solo? Master Thesis. Federal University of Santa Maria.

Goodland, R., 1971. A physiognomic analysis of the Cerrado vegetation of Central Brasil. J. Ecol. 59, 411–419. doi:10.2307/2258321

Goodland, R., Pollard, R., 1973. The Brazilian Cerrado Vegetation: A Fertility Gradient. J. Ecol. 61, 219–224. doi:10.2307/2258929

Guzha, A.C., Nobrega, R.L.B., Kovacs, K., Rebola-Lichtenberg, J., Amorim, R.S.S., Gerold, G., 2015. Characterizing rainfall-runoff signatures from micro-catchments with contrasting land cover characteristics in southern Amazonia. Hydrol. Process. 29, 508–521. doi:10.1002/hyp.10161

Hope, D., Palmer, S.M., Billett, M.F., Dawson, J.J.C., 2004. Variations in dissolved CO2 and CH4 in a first-order stream and catchment: an investigation of soil-stream linkages. Hydrol. Process. 18, 3255–3275. doi:10.1002/hyp.5657

Hughes, F.M.R., Colston, A., Mountford, J.O., 2005. Restoring riparian ecosystems: The challenge of accommodating variability and designing restoration trajectories. Ecol. Soc. 10, 12.

Hunke, P., Mueller, E.N., Schröder, B., Zeilhofer, P., 2015a. The Brazilian Cerrado:

assessment of water and soil degradation in catchments under intensive agricultural use. Ecohydrology 8, 1154–1180. doi:10.1002/eco.1573

Hunke, P., Roller, R., Zeilhofer, P., Schröder, B., Mueller, E.N., Nora, E., 2015b. Soil changes under different land-uses in the Cerrado of Mato Grosso, Brazil. Geoderma Reg. 4, 31–43. doi:10.1016/j.geodrs.2014.12.001

IUSS Working Group WRB, 2015. World Reference Base for Soil Resources 2014, update 2015. International soil classification system for naming soils and creating legends for soil maps., World Soil Resources Reports No. 106. Rome.

Jepson, W., Brannstrom, C., Filippi, A., 2010. Access Regimes and Regional Land Change in the Brazilian Cerrado, 1972–2002. Ann. Assoc. Am. Geogr. 100, 87–111. doi:10.1080/00045600903378960

Johnson, M.S., Lehmann, J., Couto, E.G., Filho, J.P.N., Riha, S.J., 2006. DOC and DIC in Flowpaths of Amazonian Headwater Catchments with Hydrologically Contrasting Soils. Biogeochemistry 81, 45–57. doi:10.1007/s10533-006-9029-3

Jordan, T.E., Correll, D.L., Weller, D.E., 1997. Relating nutrient discharges from watersheds to land use and streamflow variability. Water Resour. Res. 33, 2579–2590. doi:10.1029/97WR02005

Kaiser, H.F., 1974. An index of factorial simplicity. Psychometrika 39, 31–36. doi:10.1007/BF02291575

Kindler, R., Siemens, J., Kaiser, K., Walmsley, D.C., Bernhofer, C., Buchmann, N., Cellier, P., Eugster, W., Gleixner, G., Grũnwald, T., Heim, A., Ibrom, A., Jones, S.K., Jones, M., Klumpp, K., Kutsch, W., Larsen, K.S., Lehuger, S., Loubet, B., Mckenzie, R., Moors, E., Osborne, B., Pilegaard, K., Rebmann, C., Saunders, M., Schmidt, M.W.I., Schrumpf, M., Seyfferth, J., Skiba, U., Soussana, J.-F., Sutton, M.A., Tefs, C., Vowinckel, B., Zeeman, M.J., Kaupenjohann, M., 2011. Dissolved carbon leaching from soil is a crucial component of the net ecosystem carbon balance. Glob. Chang. Biol. 17, 1167–1185. doi:10.1111/j.1365-2486.2010.02282.x

Kindsvater, C.E., Carter, R.W.C., 1957. Discharge Characteristics of Rectangular Thin Plate Weirs. JProceedings Am. Soc. Civ. Eng. J. Hydraul. Div. 83, 1453/1-1453/36.

King, J.R., Jackson, D. a, 1999. Variable selection in large environmental data sets using principal components analysis. Environmetrics 10, 67–77. doi:10.1002/(SICI)1099-095X(199901/02)10:1<67::AID-ENV336>3.0.CO;2-0

Kirchner, J.W., 2003. A double paradox in catchment hydrology and geochemistry. Hydrol. Process. 17, 871–874. doi:10.1002/hyp.5108

Klink, C.A., Machado, R.B., 2005. Conservation of the Brazilian Cerrado. Conserv. Biol. 19, 707–713. doi:10.1111/j.1523-1739.2005.00702.x

Lahsen, M., Nobre, C.A., 2007. Challenges of connecting international science and local level sustainability efforts: the case of the Large-Scale Biosphere–Atmosphere Experiment in Amazonia. Environ. Sci. Policy 10, 62–74. doi:10.1016/j.envsci.2006.10.005

Lamparter, G., Nobrega, R.L.B., Kovacs, K., Amorim, R.S., Gerold, G., 2018. Modelling hydrological impacts of agricultural expansion in two macro-catchments in Southern Amazonia, Brazil. Reg. Environ. Chang. 18, 91–103. doi:10.1007/s10113-016-1015-2

Lim, K.J., Engel, B.A., Tang, Z., Choi, J., Kim, K.-S., Muthukrishnan, S., Tripathy, D., 2005. Automated Web GIS based hydrograph analysis tool, WHAT. J. Am. Water Resour. Assoc. 41, 1407–1416. doi:10.1111/j.1752-1688.2005.tb03808.x

Lim, K.J., Park, Y.S., Kim, J., Shin, Y.-C., Kim, N.W., Kim, S.J., Jeon, J.-H., Engel, B.A., 2010. Development of genetic algorithm-based optimization module in WHAT system for hydrograph analysis and model application. Comput. Geosci. 36, 936–944. doi:10.1016/j.cageo.2010.01.004

Longo, R.M., Espíndola, C.R., Ribeiro, A.Í., 1999. Modificações Na Estabilidade De Agregados No Solo Decorrentes Da Introdução De Pastagens Em Áreas De Cerrado E Floresta Amazônica Introduction of Pasture Areas in “ Cerrado ” and Amazon Forest. Rev. Bras. Eng. Agrícola e Ambient. 3, 276–280. doi:10.1590/1807-1929/agriambi.v3n3p276-280

Macedo, M.N., Coe, M.T., DeFries, R., Uriarte, M., Brando, P.M., Neill, C., Walker, W.S., 2013. Land-use-driven stream warming in southeastern Amazonia. Philos. Trans. R. Soc. Lond. B. Biol. Sci. 368, 20120153. doi:10.1098/rstb.2012.0153

Markewitz, D., Lamon, E.C., Bustamante, M.C., Chaves, J., Figueiredo, R.O., Johnson, M.S., Krusche, A., Neill, C., Silva, J.S.O., 2011. Discharge–calcium concentration relationships in streams of the Amazon and Cerrado of Brazil: soil or land use controlled. Biogeochemistry 105, 19–35. doi:10.1007/s10533-011-9574-2

Markewitz, D., Resende, J.C.F., Parron, L., Bustamante, M., Klink, C.A., Figueiredo, R. de O., Davidson, E.A., 2006. Dissolved rainfall inputs and streamwater outputs in an undisturbed watershed on highly weathered soils in the Brazilian cerrado. Hydrol. Process. 20, 2615–2639. doi:10.1002/hyp.6219

Mazzetto, A.M., Feigl, B.J., Cerri, C.E.P., Cerri, C.C., 2016. Comparing how land use change impacts soil microbial catabolic respiration in Southwestern Amazon. Brazilian J. Microbiol. 47, 63–72. doi:10.1016/j.bjm.2015.11.025

McGrath, D.A., Smith, C.K., Gholz, H.L., Oliveira, F.D.A., 2001. Effects of land-use change on soil nutrient dynamics in Amaz??nia. Ecosystems 4, 625–645. doi:10.1007/s10021-001-0033-0

Moreira-Turcq, P., Seyler, P., Guyot, J.L., Etcheber, H., 2003. Exportation of organic carbon from the Amazon River and its main tributaries. Hydrol. Process. 17, 1329–1344. doi:10.1002/hyp.1287

Moreira, A., Fageria, N.K., 2010. Liming influence on soil chemical properties, nutritional status and yield of alfalfa grown in acid soil. Rev. Bras. Ciência do Solo 34, 1231–1239. doi:10.1590/S0100-06832010000400022

Muñoz-Villers, L.E., McDonnell, J.J., 2013. Land use change effects on runoff generation in a humid tropical montane cloud forest region. Hydrol. Earth Syst. Sci. 17, 3543–3560. doi:10.5194/hess-17-3543-2013

Neill, C., Chaves, J.E., Biggs, T., Deegan, L.A., Elsenbeer, H., Figueiredo, R.O., Germer, S., Johnson, M.S., Lehmann, J., Markewitz, D., Piccolo, M.C., 2011. Runoff sources and land cover change in the Amazon: an end-member mixing analysis from small watersheds. Biogeochemistry 105, 7–18. doi:10.1007/s10533-011-9597-8

Neill, C., Coe, M.T., Riskin, S.H., Krusche, A. V, Elsenbeer, H., Macedo, M.N., McHorney, R., Lefebvre, P., Davidson, E.A., Scheffler, R., Figueira, A.M. e. S., Porder, S., Deegan, L.A., 2013. Watershed responses to Amazon soya bean cropland expansion and intensification. Philos. Trans. R. Soc. B Biol. Sci. 368, 20120425–20120425. doi:10.1098/rstb.2012.0425

Neill, C., Deegan, L.A., Thomas, S.M., Cerri, C.C., 2001. Deforestation for pasture alters nitrogen and phosphorus in small Amazonian streams. Ecol. Appl. 11, 1817–1828. doi:10.1890/1051-0761(2001)011[1817:DFPANA]2.0.CO;2

Neill, C., Germer, S., Neto, G., Krusche, A., Chaves, J., Neill, C., Germer, S., Neto, S.G., Krusche, A., Elsenbeer, H., 2008. Land management impacts on runoff sources in small Amazon watersheds. Hydrol. Process. 22, 1766–1775. doi:10.1002/hyp.6803

Neill, C., Piccolo, M.C., Cerri, C.C., Steudler, P.A., Melillo, J.M., 2006. Soil solution nitrogen losses during clearing of lowland Amazon forest for pasture. Plant Soil 281, 233–245. doi:10.1007/s11104-005-4435-1

Neufeldt, H., Resck, D.V.S., Ayarza, M.A., 2002. Texture and land-use effects on soil organic matter in Cerrado Oxisols, Central Brazil. Geoderma 107, 151–164. doi:10.1016/S0016-7061(01)00145-8

Nóbrega, R.L.B., Guzha, A.C., Torres, G.N., Kovacs, K., Lamparter, G., Amorim, R.S.S., Couto, E., Gerold, G., 2017. Effects of conversion of native cerrado vegetation to pasture on soil hydro-physical properties, evapotranspiration and streamflow on the Amazonian agricultural frontier. PLoS One 12, e0179414. doi:10.1371/journal.pone.0179414

Ogden, F.L., Crouch, T.D., Stallard, R.F., Hall, J.S., 2013. Effect of land cover and use on dry season river runoff, runoff efficiency, and peak storm runoff in the seasonal tropics of Central Panama. Water Resour. Res. 49, 8443–8462. doi:10.1002/2013WR013956

Oliveira, P.T.S., Wendland, E., Nearing, M. a., Scott, R.L., Rosolem, R., da Rocha, H.R., 2015. The water balance components of undisturbed tropical woodlands in the Brazilian cerrado. Hydrol. Earth Syst. Sci. 19, 2899–2910. doi:10.5194/hess-19-2899-2015

Oni, S.K., Futter, M.N., Molot, L.A., Dillon, P.J., 2014. Adjacent catchments with similar patterns of land use and climate have markedly different dissolved organic carbon concentration and runoff dynamics. Hydrol. Process. 28, 1436–1449. doi:10.1002/hyp.9681

Ouyang, Y., 2005. Evaluation of river water quality monitoring stations by principal component analysis. Water Res. 39, 2621–2635. doi:10.1016/j.watres.2005.04.024

Öztürk, M., Copty, N.K., Saysel, A.K., 2013. Modeling the impact of land use change on the hydrology of a rural watershed. J. Hydrol. 497, 97–109. doi:10.1016/j.jhydrol.2013.05.022

Pinheiro, T.F., Escada, M.I.S., Valeriano, D.M., Hostert, P., Gollnow, F., Müller, H., 2016. Forest Degradation Associated with Logging Frontier Expansion in the Amazon: The BR-163 Region in Southwestern Pará, Brazil. Earth Interact. 20, 1–26. doi:10.1175/EI-D-15-0016.1

Quesada, C.A., Lloyd, J., Anderson, L.O., Fyllas, N.M., Schwarz, M., Czimczik, C.I., 2011. Soils of Amazonia with particular reference to the RAINFOR sites. Biogeosciences 8, 1415–1440. doi:10.5194/bg-8-1415-2011

Quesada, C.A., Lloyd, J., Schwarz, M., Patiño, S., Baker, T.R., Czimczik, C., Fyllas, N.M., Martinelli, L., Nardoto, G.B., Schmerler, J., Santos, A.J.B., Hodnett, M.G., Herrera, R., Luizão, F.J., Arneth, A., Lloyd, G., Dezzeo, N., Hilke, I., Kuhlmann, I., Raessler, M., Brand, W.A., Geilmann, H., Moraes Filho, J.O., Carvalho, F.P., Araujo Filho, R.N., Chaves, J.E., Cruz Junior, O.F., Pimentel, T.P., Paiva, R., 2010. Variations in chemical and physical properties of Amazon forest soils in relation to their genesis. Biogeosciences 7, 1515–1541. doi:10.5194/bg-7-1515-2010

Ratter, J., Ribeiro, J.F., Bridgewater, S., 1997. The Brazilian Cerrado Vegetation and Threats to its Biodiversity. Ann. Bot. 80, 223–230. doi:10.1006/anbo.1997.0469

Recha, J.W., Lehmann, J., Walter, M.T., Pell, A., Verchot, L., Johnson, M., 2013. Stream water nutrient and organic carbon exports from tropical headwater catchments at a soil degradation gradient. Nutr. Cycl. Agroecosystems. doi:10.1007/s10705-013-9554-0

Recha, J.W., Lehmann, J., Walter, M.T., Pell, A., Verchot, L., Johnson, M., 2012. Stream Discharge in Tropical Headwater Catchments as a Result of Forest Clearing and Soil Degradation. Earth Interact. 16, 1–18. doi:10.1175/2012EI000439.1

Richey, J.E., Ballester, M.V., Davidson, E.A., Johnson, M.S., Krusche, A. V., 2011. Land-Water interactions in the amazon. Biogeochemistry 105, 1–5. doi:10.1007/s10533-011-9622-y

Richey, J.E., Wilhelm, S.R., Mcclain, M.E., Victoria, R.L., Melack, J.M., Araujo Lima, C., 1997. Organic matter and nutrient dynamics in river corridors of the Amazon Basin and their response to anthropogenic change. Cienc. e Cult. (Sao Paulo). doi:10.1029/20086M000728

Riskin, S.H., Porder, S., Neill, C., Figueira, A.M.E.S., Tubbesing, C., Mahowald, N., 2013. The fate of phosphorus fertilizer in Amazon soya bean fields. Philos. Trans. R. Soc. Lond. B. Biol. Sci. 368, 20120154. doi:10.1098/rstb.2012.0154

Roa-García, M.C., Brown, S., Schreier, H., Lavkulich, L.M., 2011. The role of land use and soils in regulating water flow in small headwater catchments of the Andes. Water

Resour. Res. 47, W05510. doi:10.1029/2010WR009582

Rodriguez, D.A., Tomasella, J., Linhares, C., 2010. Is the forest conversion to pasture affecting the hydrological response of Amazonian catchments? Signals in the Ji-Paraná Basin. Hydrol. Process. 24, 1254–1269. doi:10.1002/hyp.7586

Rowe, B.A., 1982. Effects of limestone on pasture yields and the ph of two krasnozems in north-western tasmania. Aust. J. Exp. Agric. 22, 100–105. doi:10.1071/EA9820100

Rufin, P., Müller, H., Pflugmacher, D., Hostert, P., 2015. Land use intensity trajectories on Amazonian pastures derived from Landsat time series. Int. J. Appl. Earth Obs. Geoinf. 41, 1–10. doi:10.1016/j.jag.2015.04.010

Salemi, L.F., Groppo, J.D., Trevisan, R., de Barros Ferraz, S.F., de Moraes, J.M., Martinelli, L.A., 2015. Nitrogen dynamics in hydrological flow paths of a small tropical pasture catchment. Catena 127, 250–257. doi:10.1016/j.catena.2015.01.009

Salemi, L.F., Groppo, J.D., Trevisan, R., de Moraes, J.M., de Barros Ferraz, S.F., Villani, J.P., Duarte-Neto, P.J., Martinelli, L.A., 2013. Land-use change in the Atlantic rainforest region: Consequences for the hydrology of small catchments. J. Hydrol. 499, 100–109. doi:10.1016/j.jhydrol.2013.06.049

Satinsky, B.M., Zielinski, B.L., Doherty, M., Smith, C.B., Sharma, S., Paul, J.H., Crump, B.C., Moran, M., 2014. The Amazon continuum dataset: quantitative metagenomic and metatranscriptomic inventories of the Amazon River plume, June 2010. Microbiome 2, 17. doi:10.1186/2049-2618-2-17

Schierhorn, F., Gittelson, A.K., Müller, D., 2016. How the Collapse of the Beef Sector in Post-Soviet Russia Displaced Competition for Ecosystem Services to the Brazilian Amazon, in: Land Use Competition. Springer International Publishing, Cham, pp. 165–182. doi:10.1007/978-3-319-33628-2_10

Schiesari, L., Waichman, a., Brock, T., Adams, C., Grillitsch, B., 2013. Pesticide use and biodiversity conservation in the Amazonian agricultural frontier. Philos. Trans. R. Soc. Lond. B. Biol. Sci. 368, 20120378. doi:10.1098/rstb.2012.0378

Shen, J., 1981. Discharge Characteristics of Triangular-notch Thin-plate Weirs, Geological Survey water-supply paper. Washington, USA.

Silva, D.M.L., Camargo, P.B., Mcdowell, W.H., Vieira, I., Salomão, M.S.M.B., Martinelli, L.A., 2012. Influence of land use changes on water chemistry in streams in the State of São Paulo, southeast Brazil. An. Acad. Bras. Cienc. 84, 919–930. doi:10.1590/S0001-37652012000400007

Silva, J.S.O., da Bustamante, M.M.C., Markewitz, D., Krusche, A.V., Ferreira, L.G., da Cunha Bustamante, M.M., Markewitz, D., Krusche, A.V., Ferreira, L.G., 2011. Effects of land cover on chemical characteristics of streams in the Cerrado region of Brazil. Biogeochemistry 105, 75–88. doi:10.1007/s10533-010-9557-8

Silva, M.E., Pereira, G., Rocha, R., 2013. Increasing deforestation at the Arc of Deforestation in Brazil, in: Geophysical Research Abstracts. Vienna, p. EGU2013-

12011-1.

Silva, D.M.L. da, Ometto, J.P.H.B., Lobo, G. de A., Lima, W.D.P., Scaranello, M.A., Mazzi, E., Rocha, H.R. da, 2007. Can land use changes alter carbon, nitrogen and major ion transport in subtropical brazilian streams? Sci. Agric. 64, 317–324. doi:10.1590/S0103-90162007000400002

Soil Survey Staff, 2015. Illustrated guide to soil taxonomy, version 2. Lincoln, Nebraska.

Stevens, P.A., Norris, D.A., Sparks, T.H., Hodgson, A.L., 1994. The impacts of atmospheric n inputs on throughfall, soil and stream water interactions for different aged forest and moorland catchments in Wales. Water, Air, Soil Pollut. 73, 297–317. doi:10.1007/BF00477994

Strey, S., Boy, J., Strey, R., Weber, O., Guggenberger, G., 2016. Response of soil organic carbon to land-use change in central Brazil: a large-scale comparison of Ferralsols and Acrisols. Plant Soil 408, 327–342. doi:10.1007/s11104-016-2901-6

Sun, J., Tang, C., Wu, P., Strosnider, W.H.J., Han, Z., 2013. Hydrogeochemical characteristics of streams with and without acid mine drainage impacts: A paired catchment study in karst geology, SW China. J. Hydrol. 504, 115–124. doi:10.1016/j.jhydrol.2013.09.029

Tardy, Y., Bustillo, V., Roquin, C., Mortatti, J., Victoria, R., 2005. The Amazon. Bio-geochemistry applied to river basin management: Part I. Hydro-climatology, hydrograph separation, mass transfer balances, stable isotopes, and modelling. Appl. Geochemistry 20, 1746–1829. doi:10.1016/j.apgeochem.2005.06.001

Templer, P.H., Mack, M.C., III, F.S.C., Christenson, L.M., Compton, J.E., Crook, H.D., Currie, W.S., Curtis, C.J., Dail, D.B., D'Antonio, C.M., Emmett, B.A., Epstein, H.E., Goodale, C.L., Gundersen, P., Hobbie, S.E., Holland, K., Hooper, D.U., Hungate, B.A., Lamontagne, S., Nadelhoffer, K.J., Osenberg, C.W., Perakis, S.S., Schleppi, P., Schimel, J., Schmidt, I.K., Sommerkorn, M., Spoelstra, J., Tietema, A., Wessel, W.W., Zak, D.R., 2012. Sinks for nitrogen inputs in terrestrial ecosystems: a meta-analysis of 15 N tracer field studies. Ecology 93, 1816–1829. doi:10.1890/11-1146.1

Thomas, S.M., Neill, C., Deegan, L.A., Krusche, A. V., Ballester, V.M., Victoria, R.L., 2004. Influences of land use and stream size on particulate and dissolved materials in a small Amazonian stream network. Biogeochemistry 68, 135–151. doi:10.1023/B:BIOG.0000025734.66083.b7

Tollefson, J., 2015. Stopping deforestation: Battle for the Amazon. Nature 520, 20–23. doi:10.1038/520020a

Troch, P.A., Lahmers, T., Meira, A., Mukherjee, R., Pedersen, J.W., Roy, T., Valdés-Pineda, R., 2015. Catchment coevolution: A useful framework for improving predictions of hydrological change? Water Resour. Res. 51, 4903–4922. doi:10.1002/2015WR017032

Uehara, G., Gillman, G., 1981. The Mineralogy, Chemistry, and Physics of Tropical Soils with Variable-Charge Clays. West-View Press, Buolder, Colorado.

Villela, D.M., Haridasan, M., 1994. Response of the ground layer community of a cerrado vegetation in central Brazil to liming and irrigation. Plant Soil 163, 25–31. doi:10.1007/BF00033937

Vogt, E., Braban, C.F., Dragosits, U., Durand, P., Sutton, M.A., Theobald, M.R., Rees, R.M., McDonald, C., Murray, S., Billett, M.F., 2015. Catchment land use effects on fluxes and concentrations of organic and inorganic nitrogen in streams. Agric. Ecosyst. Environ. 199, 320–332. doi:10.1016/j.agee.2014.10.010

Vourlitis, G.L., Hentz, C.S., 2016. Impacts of chronic N input on the carbon and nitrogen storage of a postfire Mediterranean-type shrubland. J. Geophys. Res. G Biogeosciences 121, 385–398. doi:10.1002/2015JG003220

Williams, M.R., Melack, J.M., 1997. Solute export from forested and partially deforested catchments in the central Amazon. Biogeochemistry 38, 67–102. doi:10.1023/A:1005774431820

Wohl, E., Barros, A., Brunsell, N., Chappell, N.A., Coe, M., Giambelluca, T., Goldsmith, S., Harmon, R., Hendrickx, J.M.H., Juvik, J., McDonnell, J., Ogden, F., 2012. The hydrology of the humid tropics. Nat. Clim. Chang. 2, 655–662. doi:10.1038/nclimate1556

Zanchi, F.B., Waterloo, M.J., Tapia, A.P., Alvarado Barrientos, M.S., Bolson, M. a., Luizão, F.J., Manzi, A.O., Dolman, A.J., 2015. Water balance, nutrient and carbon export from a heath forest catchment in central Amazonia, Brazil. Hydrol. Process. 3648, n/a-n/a. doi:10.1002/hyp.10458

Zeinalzadeh, K., Rezaei, E., 2017. Determining spatial and temporal changes of surface water quality using principal component analysis. J. Hydrol. Reg. Stud. 13, 1–10. doi:10.1016/j.ejrh.2017.07.002

Zhang, Y., Guo, F., Meng, W., Wang, X.-Q., 2009. Water quality assessment and source identification of Daliao river basin using multivariate statistical methods. Environ. Monit. Assess. 152, 105–121. doi:10.1007/s10661-008-0300-z

Zhao, M., Zeng, C., Liu, Z., Wang, S., 2010. Effect of different land use/land cover on karst hydrogeochemistry: A paired catchment study of Chenqi and Dengzhanhe, Puding, Guizhou, SW China. J. Hydrol. 388, 121–130. doi:10.1016/j.jhydrol.2010.04.034

Zhou, W., Zhang, Y., Schaefer, D.A., Sha, L., Deng, Y., 2013. The Role of Stream Water Carbon Dynamics and Export in the Carbon Balance of a Tropical Seasonal Rainforest , Southwest China 8. doi:10.1371/journal.pone.0056646

Zimmermann, B., Elsenbeer, H., De Moraes, J.M., 2006. The influence of land-use changes on soil hydraulic properties: Implications for runoff generation. For. Ecol. Manage. 222, 29–38. doi:10.1016/j.foreco.2005.10.070

Table A.1. Descriptive statistics of the base streamflow hydrochemistry.

Parameter ($mg\ L^{-1}$)	Amazonian catchments														Cerrado catchments													
	AFOR							APAS							CCER							CPAS						
	N	min	max	median	mean	sd	vc	n	min	max	median	mean	sd	vc	n	min	max	median	mean	sd	vc	n	min	max	median	mean	sd	vc
TC	75	1.18	12.62	4.04	4.67	2.29	0.49	96	1.17	10.27	4.67	5.12	1.90	0.37	126	0.48	5.46	1.19	1.65	1.17	0.70	86	0.19	13.81	1.04	1.78	1.89	1.06
TIC	75	< LOD	1.33	0.50	0.51	0.30	0.59	96	< LOD	2.21	0.86	0.92	0.51	0.56	126	< LOD	3.37	0.03	0.38	0.66	1.75	86	< LOD	3.23	< LOD	0.35	0.74	2.11
TOC	75	1.18	11.78	3.50	4.16	2.18	0.52	96	1.17	9.63	3.63	4.20	1.74	0.41	126	0.48	3.42	1.10	1.28	0.62	0.48	86	0.19	13.81	0.97	1.43	1.66	1.15
TN	75	0.18	1.55	0.27	0.35	0.21	0.58	96	0.18	1.00	0.36	0.43	0.19	0.45	126	< LOD	0.55	0.18	0.14	0.09	0.62	86	0.11	0.88	0.26	0.29	0.12	0.42
DC	73	0.48	9.76	3.54	3.83	1.99	0.51	95	0.70	6.51	3.12	3.33	1.34	0.40	82	0.01	5.58	1.00	1.37	1.13	0.82	53	0.20	4.23	0.71	0.97	0.88	0.89
DIC	73	< LOD	1.44	0.23	0.29	0.34	1.16	95	< LOD	2.08	0.25	0.47	0.49	1.06	101	< LOD	3.19	0.00	0.20	0.59	2.93	73	< LOD	1.40	< LOD	0.05	0.23	4.53
DOC	73	< LOD	9.76	3.29	3.54	1.95	0.55	95	< LOD	5.76	2.84	2.86	1.21	0.42	82	0.10	3.70	1.00	1.14	0.59	0.52	53	0.20	3.62	0.71	0.89	0.73	0.81
DN	41	0.18	0.73	0.27	0.31	0.14	0.43	37	0.18	0.65	0.27	0.31	0.11	0.37	62	< LOD	0.28	< LOD	0.09	0.09	1.08	16	0.10	0.48	0.20	0.23	0.09	0.37
F	75	0.01	0.09	0.02	0.02	0.01	0.43	95	0.01	0.20	0.04	0.04	0.02	0.53	114	< LOD	0.64	0.01	0.05	0.11	2.03	88	< LOD	1.18	0.03	0.12	0.21	1.82
Cl	75	0.17	0.79	0.43	0.45	0.15	0.32	95	0.10	2.03	0.44	0.55	0.32	0.57	119	0.04	2.81	0.19	0.39	0.48	1.22	88	0.10	5.18	0.27	0.62	0.81	1.30
NO_3^-	51	0.06	7.58	0.68	1.16	1.52	1.29	66	0.04	6.92	0.94	1.62	1.84	1.13	90	0.02	5.83	0.23	0.50	1.03	2.03	77	0.12	5.30	0.85	1.20	1.01	0.84
SO_4^{2-}	70	< LOD	0.63	0.04	0.08	0.10	1.29	87	< LOD	0.34	0.04	0.06	0.05	0.93	119	< LOD	0.50	0.06	0.08	0.08	0.95	88	< LOD	0.74	0.06	0.11	0.13	1.18
Ca	75	0.15	1.85	0.40	0.47	0.26	0.56	95	0.15	1.36	0.57	0.60	0.24	0.40	126	< LOD	6.36	0.15	0.79	1.26	1.58	87	0.01	15.54	0.15	0.92	2.13	2.29
Fe	75	< LOD	0.11	< 0.01	0.01	0.02	1.54	95	< LOD	0.06	< 0.01	0.01	0.01	1.73	126	< LOD	0.05	< 0.01	< 0.01	0.01	3.18	87	< LOD	0.09	< 0.01	< 0.01	0.01	4.78
K	75	0.40	3.34	1.55	1.51	0.50	0.33	95	0.35	3.98	2.30	2.20	0.81	0.36	126	0.02	0.76	0.04	0.07	0.09	1.16	87	0.01	2.96	0.18	0.30	0.50	1.64
Mg	75	0.03	0.40	0.10	0.12	0.06	0.50	95	0.03	0.42	0.15	0.16	0.07	0.42	126	0.01	0.56	0.05	0.07	0.07	0.98	87	0.01	0.35	0.06	0.07	0.06	0.81
Na	75	0.24	1.36	0.90	0.89	0.25	0.28	95	0.21	1.65	0.93	0.90	0.31	0.34	125	< LOD	0.73	0.10	0.16	0.13	0.86	87	< LOD	1.40	0.23	0.27	0.16	0.59
P	75	< LOD	0.11	0.04	0.04	0.03	0.78	95	< LOD	0.15	0.03	0.03	0.04	1.03	126	< LOD	0.09	< 0.01	0.01	0.02	1.92	87	< LOD	0.20	< 0.01	0.02	0.04	1.92
S	75	< LOD	0.27	0.03	0.05	0.05	1.07	95	< LOD	0.19	0.04	0.05	0.03	0.66	126	< LOD	0.06	< 0.01	0.01	0.01	1.63	87	< LOD	0.21	< 0.01	0.01	0.04	2.51

LOD = Limit of detection.

Table A.2. Descriptive statistics of the storm streamflow hydrochemistry.

Parameter ($mg\ L^{-1}$)	Amazonian catchments														Cerrado catchments													
	AFOR							APAS							CCER							CPAS						
	n	min	max	median	mean	sd	vc	n	min	max	median	mean	sd	vc	n	min	max	median	mean	sd	vc	n	min	max	median	mean	sd	vc
TC	108	1.56	25.80	6.08	7.39	4.91	0.66	160	2.63	96.80	7.04	8.59	9.71	1.13	119	0.77	24.90	3.57	4.27	3.16	0.74	43	0.50	20.02	7.00	7.47	3.98	0.53
TIC	108	0.08	2.20	0.35	0.53	0.47	0.87	160	< LOD	2.70	0.52	0.64	0.49	0.76	119	< LOD	3.79	< LOD	0.17	0.58	3.44	43	< LOD	4.00	0.08	0.64	1.11	1.73
TOC	108	1.38	25.01	5.50	6.86	4.81	0.70	160	2.63	95.50	6.29	7.95	9.66	1.21	119	0.77	23.10	3.47	4.10	3.00	0.73	43	0.50	18.27	6.50	6.84	3.88	0.56
TN	108	0.18	1.82	0.40	0.46	0.24	0.53	160	0.22	1.30	0.50	0.49	0.17	0.35	119	0.10	1.50	0.27	0.27	0.18	0.65	43	0.20	3.10	0.50	0.61	0.48	0.79
DC	93	1.94	27.30	5.35	6.73	4.41	0.65	148	1.12	98.60	5.18	6.94	10.58	1.52	119	0.80	10.20	2.90	3.26	1.73	0.53	38	3.30	11.40	6.21	6.50	1.96	0.30
DIC	46	< LOD	2.10	0.34	0.52	0.56	1.06	125	< LOD	2.60	0.30	0.45	0.51	1.14	115	< LOD	2.25	< LOD	0.12	0.40	3.43	41	< LOD	3.90	< LOD	0.62	1.10	1.75
DOC	93	1.21	26.30	4.87	6.13	4.33	0.70	148	1.12	97.60	4.73	6.47	10.49	1.61	119	0.80	8.22	2.80	3.13	1.62	0.51	38	2.10	10.90	5.45	5.81	2.03	0.34
DN	91	0.18	1.46	0.36	0.42	0.23	0.55	117	0.27	0.90	0.40	0.42	0.15	0.34	65	< LOD	0.91	0.18	0.22	0.11	0.49	35	0.10	2.10	0.40	0.49	0.37	0.75
F	109	0.01	3.62	0.02	0.07	0.35	5.03	159	0.01	0.10	0.03	0.03	0.01	0.42	119	< LOD	0.33	0.01	0.01	0.03	2.93	36	< LOD	1.23	0.04	0.19	0.30	1.51
Cl	109	0.35	16.05	0.53	0.81	1.53	1.88	159	0.08	4.95	0.60	0.63	0.40	0.64	119	0.06	4.20	0.17	0.28	0.42	1.50	36	0.20	3.65	0.59	0.93	0.90	0.96
NO_3^-	107	0.10	6.66	0.44	0.93	1.21	1.29	142	0.01	7.56	0.40	1.18	1.74	1.48	109	< LOD	6.53	0.34	1.09	1.62	1.48	35	0.27	3.20	1.00	1.02	0.50	0.48
SO_4^{2-}	107	0.01	1.03	0.07	0.12	0.16	1.26	159	0.01	0.55	0.07	0.09	0.07	0.82	117	0.02	0.62	0.05	0.07	0.07	0.97	36	0.04	0.38	0.11	0.14	0.09	0.67
Ca	109	0.22	2.65	0.48	0.70	0.53	0.77	160	0.09	3.71	0.47	0.61	0.54	0.88	118	0.06	5.30	0.17	0.41	0.84	2.02	42	0.08	7.18	0.45	1.43	1.88	1.30
Fe	109	< LOD	0.06	0.01	0.01	0.02	1.04	160	< LOD	0.23	0.03	0.03	0.03	1.02	119	< LOD	0.11	0.01	0.02	0.02	1.09	42	< LOD	0.05	< 0.01	0.01	0.02	1.75
K	109	0.91	3.62	1.87	1.96	0.46	0.23	160	0.31	4.11	2.51	2.54	0.53	0.21	118	0.02	1.68	0.16	0.23	0.23	0.98	42	0.15	2.80	0.50	0.60	0.45	0.73
Mg	109	0.04	0.30	0.12	0.14	0.06	0.40	160	0.02	0.26	0.12	0.14	0.05	0.35	118	0.03	2.36	0.08	0.12	0.22	1.81	42	0.04	0.42	0.08	0.11	0.07	0.65
Na	109	0.56	1.95	0.92	0.96	0.22	0.23	160	0.14	1.18	0.76	0.72	0.23	0.33	118	0.05	1.57	0.11	0.22	0.22	1.01	42	0.15	1.62	0.27	0.41	0.30	0.72
P	109	< LOD	0.11	< LOD	0.02	0.03	1.45	160	< LOD	0.14	0.01	0.04	0.04	1.13	119	< LOD	0.11	< 0.01	0.02	0.03	1.39	42	< LOD	0.09	< 0.01	0.02	0.03	1.82
S	109	< LOD	0.52	0.05	0.07	0.08	1.18	160	< LOD	0.21	0.07	0.07	0.05	0.78	119	< LOD	0.26	0.02	0.03	0.03	1.18	42	< LOD	0.09	< 0.01	0.01	0.03	1.76

LOD = Limit of detection.