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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. Moreover, these impacts are not concurrently assessed in well-established agricultural areas and new deforestations hotspots. 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 changes were the greatest in total inorganic carbon in the Amazon and in potassium in the Cerrado, representing a 5.0- and 5.5-fold increase in the fluxes of each biome, respectively. We found that stormflow, which is often neglected in studies on stream hydrochemistry in the tropics, 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). These processes are 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 stream hydrochemistry (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 the water quantity and quality that sustain aquatic biodiversity and mitigates eutrophication of water bodies (Coe et al., 2013; Davidson et al., 2012; Neary, 2016; Penaluna et al., 2017). 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) despite being a biodiversity hotspot for conservation comprised of dry forests, woodland savannas and grasslands (Spera et al., 2016; Strassburg et al., 2017). The conversion of native vegetation to crops and pastures has removed ca. 50% of the original 2 million km² in the Cerrado, which is greater than the forest loss in the Amazon biome (Klink and Machado, 2005; Lambin et al., 2013).

The negative impacts on water quality due to LULC change are reported to be a result of interrelated processes (i.e., changes in vegetation, soil and hydrology) that negatively disturbs its land capability, which is the ability of the land to sustain its use (Valle et al., 2014; Valle Junior et al., 2015). On the AAF, soil and hydrological changes 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). Even though rain and dry forests account for ca. 60% of the net primary production of global terrestrial ecosystems (Grace et al., 2006; Potter et al., 2012), the effects of the impacts of LULC change in these systems are not well studied as they are for other regions of the world (Luke et al., 2017).

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). Although many studies have evaluated the dynamics of carbon and nutrients in streams in several regions of the world (e.g. Southeastern USA (Marchman et al., 2015), subtropical China (Yan et al., 2015), Germany (Strohmeier et al., 2013) and Canada (Jollymore et al., 2012)), studies of carbon export dynamics in low-order tropical catchments are still scarce (de Paula et al., 2016). There is increasing research interest in high-temporal-resolution data collection in low-order fluvial systems that should also be taken into account in hydrochemistry studies (Hughes et al., 2005; Richey et al., 2011; Wohl et al., 2012) due to their importance to the global carbon dynamics (Bass et al., 2014).

The dynamics of stream hydrochemistry that have remained largely invisible due to the monitoring schemes that only consider weekly or monthly sampling (Kirchner and Neal, 2013), have been gradually unveiled due to approaches that use subdaily sampling

intervals (Tang et al., 2008). However, the high-frequency water sampling approach that has been shown to be useful for these studies in temperate regions (Clark et al., 2007) has been discredited in tropical regions (Chaussê et al., 2016). Moreover, findings in Amazonian headwater streams that have used subhourly sampling routines have found that the conversion of forests to fertilized agricultural lands changed neither the stream water chemistry nor nutrient output per unit of catchment area (Neill et al., 2017; Riskin et al., 2017).

Our study aims to identify the differences in stream carbon and nutrient (CAN) concentrations and output fluxes during prevalent baseflow and stormflow conditions in headwater catchments under contrasting LULC (native vegetation vs. pasture), thereby contributing to the understanding of CAN drivers in low-order streams on the AAF. Our hypothesis is that LULC change is impacting stream hydrochemistry in active deforestation zones of the Amazon and Cerrado biomes, with the stormflow, which is often neglected in studies in these regions, as a substantial contributor to the total CAN fluxes.

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.

The Amazonian catchments consist of one catchment covered with evergreen rainforest, with sings of logging and tree regrowth (AFOR), and another catchment 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 one catchment covered with cerrado sensu stricto vegetation (CCER) and another 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, $CaCO_3$) 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. (2018), 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, whose main characteristics are shown in Table 1. We instrumented these catchments during the dry season of 2012 and continuously monitored them from October of 2012 until the September of 2014.

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 topsoil of these catchments was chosen because it has a strong synergy with the surface waters and it is the soil layer under most direct influence of the LULC change (Lamparter et al., 2018). 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), aluminum (Al), calcium (Ca), iron (Fe), potassium (K), magnesium (Mg), sodium (Na), phosphorus (P), sulfur (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 for the Cerrado catchments 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, both at the 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 1–3 days using an extraction of 200 mL from the stream at equal intervals. The stormflow sampling was determined suing a subhourly routine activated by water-level increase and 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 with prior preparation at a field facility ca. 5 km from the catchments and stored in light-free freezers until their transportation to 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). Fluorine (F), chlorine (Cl), nitrate (NO_3) and sulfate (SO_4) 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 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 at 10 or 15-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:

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

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

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).

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

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 Kolmogorov-Smirnov test of normality for each dataset to determine the adequate statistical test, i.e., parametric or nonparametric, for comparison of catchments within the same biome. We used the two-sample t-test to compare the soil chemistry and the Mann–Whitney (MW) U-test to compare the CAN concentrations by means of sample ranks to determine whether S_b and S_s were significantly different between the native vegetation and pasture catchments. Additionally to the MW test, we used Mood's median test, given its robustness for outliers to detect differences in the median. We used the language and environment R (R Core Team, 2017) and the significance threshold at .05 for all statistical analyses.

4. Results

4.1. Soil physical and chemical properties

The soils exhibited textural similarities within each pair of catchments, with mostly sandy clay loams in the Amazonian and loamy sand textures in the Cerrado catchments (Table 2). The soil pH was between 10 to 25% higher in the pasture catchments, being significantly different ($p < .01$) between the CCER and CPAS catchments. The soils from all catchments have a high content of Al and Fe and low nutrient contents (Table 2). 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}).

4.2. Hydrochemistry results

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, Na, Ca and Mg (< 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 had the lowest concentrations in all catchments, with most values less than the limit of detection (Tables A.1 and A.2).

The varimax rotation applied to the PCA on the water quality parameters exhibited individual KMO values greater than .5 (Table 3). The overall 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. 2). For the Amazonian catchments, the first component of the S_b PCA (Fig

2a) 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. 2b) 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. 2c) 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. 2d) 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.

Based on the results of the PCAs, we compared TOC, DOC, TIC, DIC, TN and DN (Fig. 3), and NO_3, Ca and K (Fig. 4). With the exception of higher TOC in the APAS catchment, 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. 3a–b). For DIC, the differences in concentration between the Amazonian catchments in S_b and between the Cerrado catchments in S_s (Fig. 3c–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. 4a). Differences in Ca concentrations (Fig. 4b) 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. There were significantly higher K concentrations in both S_b and S_s for the pasture catchments (Fig. 4c).

4.3. Hydrological and CAN output fluxes

The Amazonian catchments exhibited the greater annual average stream discharge with 23.2 L s^{-1} for the AFOR catchment and 18.3 L s^{-1} for the APAS catchment, whereas the stream discharge for the Cerrado catchments were 11.6 L s^{-1} for the CCER catchment and 13.4 L s^{-1} for the CPAS catchment. The average stream discharge during stormflow events were 94.2 L s^{-1} for the AFOR catchment, 89.5 for the APAS catchment, 11.6 L s^{-1} for the CCER catchment and 30.9 L s^{-1} for the CPAS catchment.

In the Amazonian catchments, TOC 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} (Fig. 5). 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 in all catchments. Furthermore, the fluxes in the

pasture catchments were generally higher compared to those of the native vegetation catchments.

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. 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). 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). For some nutrients, i.e. F and Fe, we attributed this to the absence of fertilizer application in the pasture catchments during our study period 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). Indeed, the soils from all catchments exhibited a high content of Al and Fe and, a characteristic often found in Amazon (dos Santos and Alleoni, 2013; Quesada et al., 2011) and Cerrado soils (Buol, 2009).

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 pasture catchments exhibited significantly higher stream Ca concentrations, which reported in 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 significantly higher S_s Ca 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. 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). 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

Except for DIC in the Cerrado catchments, the CAN fluxes were greater in the pasture catchments (Table 4). The Amazonian catchments exhibited the greatest differences in CAN fluxes. In these catchments, S_s showed a greater difference between the APAS and AFOR catchments, with an average APAS:AFOR ratio 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. This is consistent with that fact that nutrients, especially K and Ca, have 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).

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). In this region, the sandy soils, such as the Arenosols, are commonly found and the decrease of their organic matter content owing to their increasingly use for agricultural practices (Speratti et al., 2017) is likely to increase the leaching of nutrients (Hunke et al., 2015a).

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). 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 show 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 5. 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 higher CAN concentrations (Johnson et al., 2006).

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, S_s DIC fluxes represented only 6% of the total output fluxes in the CCER catchment and 10% in the CPAS catchment.

While many recent studies showed insights of high-temporal monitoring schemes in areas with fairly easy access (e.g., close to urban centers accessed via paved roads) in Europe (e.g., Blaen et al., 2016; Cuomo and Guida, 2016) and North America (e.g., Jollymore et al., 2012; Sherson et al., 2015) as a valid and new approach to ensure appropriate management of the natural resources (Skeffington et al., 2015), our study uses this method to assess the impacts of LULC change in catchments located in data-scarce active zones of deforestation of the two largest biomes of South America.

Despite the contribution of our study contributes to the understanding of the hydrochemical fluxes on the AFF, the magnitude and duration of these impacts depend on several catchments characteristics (e.g., soils, morphology and geology) that should also be addressed in further studies (Birkinshaw et al., 2010). Long-term measurements (over 10 years) of stormflow events including quantifying changes in groundwater quality are required to analyze trends in water quality. Biggs et al. (2006) found evidence of long-term increases in solute fluxes following the conversion of forest to pasture in the Amazon. Hence, empirical studies that contemplate the comparison of pastures with different ages are fundamental to quantify the effect pasture age in CAN fluxes.

The degree to which the chemical changes of the streamwater in the Amazon and Cerrado biomes are affecting the CAN delivery to the ocean is poorly understood and

difficult to assess (Bouchez et al., 2014). Notwithstanding, the changes in stream hydrochemistry are likely to unfold greater impacts due to several large dams under construction in this region (Pavanato et al., 2016; Tollefson, 2015), which will receive and store the increased loads of CAN and negatively affect their suitability as aquatic habitats. To that end, we recommend studies that take into account the long-term effects of LULC change on stream hydrochemistry in nested scales and their impacts in large watershed systems in this region.

6. Conclusions

Our research demonstrates how the conversion of natural vegetated landscapes (forest and cerrado) to pasture changes stream hydrochemistry, which can disturb the natural carbon and nutrient balance in the Amazon and Cerrado biomes. 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. This indicates that the unaccounted stream carbon and nutrient fluxes derived from sampling approaches on a daily or weekly basis are substantially great. Our study confirms the need for detailed temporal data on stream hydrochemistry that include

the sampling of short-lived stormflow events to not only to understand natural tropical ecosystems, but also to unveil impacts of anthropogenic changes in these environments.

Although the acquisition of high-temporal resolution 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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FIGURE CAPTIONS

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

Figure 2. Biplots of the PCAs after varimax rotation for the first (C1) and second (C2) components of the: a) Amazon catchments base streamflow (S_b); b) Amazon catchments storm streamflow (S_s); c) Cerrado catchments base streamflow (S_b); and d) Cerrado storm streamflow (S_s).

Figure 3. 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 4. 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.

Figure 5. Annual carbon and nutrient output fluxes of base streamflow (S_b) and storm streamflow (S_s).

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, above mean sea level)	292.4	223.0	811.1	817.8

Table 2. Mean, one standard deviation and sample size (*n)* of soil physical and chemical properties.

	Amazonian catchments		**Cerrado catchments**	
Soil properties	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)[a]	6.4 ± 0.7 (3)[a]	3.6 ± 0.3 (6)[c]	4.4 ± 0.5 (8)[d]
C (%)	3.19 ± 2.54 (5)[a]	1.47 ± 0.45 (6)[a]	3.41 ± 3.88 (6)[c]	1.33 ± 1.01 (8)[c]
N (%)	0.27 ± 0.22 (5)[a]	0.12 ± 0.04 (6)[a]	0.18 ± 0.20 (6)[c]	0.07 ± 0.05 (8)[c]
C:N ratio	11.9 ± 1.8	11.8 ± 0.5	17.9 ± 2.4	18.3 ± 3.3
Al (g kg^{-1})	57.8 ± 16.3 (8)[a]	43.1 ± 19.2 (8)[a]	26.5 ± 23.4 (6)[c]	16.1 ± 3.4 (8)[c]
Ca (g kg^{-1})	1.0 ± 0.6 (8)[a]	0.5 ± 0.2 (8)[a]	<0.1 ± <0.1 (6)[c]	0.2 ± 0.1 (8)[d]
Fe (g kg^{-1})	15.5 ± 6.1 (8)[a]	11.5 ± 6.8 (8)[a]	10.8 ± 4.6 (6)[c]	13.2 ± 6.8 (8)[c]
K (g kg^{-1})	3.0 ± 2.2 (8)[a]	5.6 ± 3.4 (8)[b]	1.0 ± 1.4 (6)[c]	0.1 ± <0.1 (8)[c]
Mg (g kg^{-1})	0.4 ± 0.2 (8)[a]	0.8 ± 0.5 (8)[b]	0.1 ± 0.2 (6)[c]	0.1 ± 0.1 (8)[c]
Mn (g kg^{-1})	0.8 ± 1.0 (8)[a]	0.2 ± 0.2 (8)[b]	<0.1 ± <0.1 (6)[c]	<0.1 ± <0.1 (8)[c]
P (g kg^{-1})	0.2 ± 0.1 (8)[a]	0.2 ± 0.1 (8)[a]	0.2 ± 0.2 (6)[c]	0.1 ± <0.1 (8)[c]
S (g kg^{-1})	0.2 ± 0.1 (8)[a]	0.2 ± 0.1 (8)[a]	0.2 ± 0.2 (6)[c]	0.1 ± <0.1 (8)[c]

Significant differences ($p < .05$) are indicated by different letters. Comparisons were performed between catchments within the same biome.

Table 3. Correlations between variables and components 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
Variability (%)	48.2	31.7	36.6	28.8	20.9	57.7	25.4	34.0	28.4	25.4

Correlations between variables and components greater than .5 are bolded.

Table 4. 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

Table 5. Percentage ratio of the storm streamflow duration, volume and fluxes to the total streamflow.

			S_s:S_t (CAN fluxes)								
Catchment	S_s:S_t (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%

Table A.1. Descriptive statistics of the base streamflow hydrochemistry[a].

	Amazonian catchments																											
Parameter	**AFOR**								**APAS**							**CCER**							**CPAS**					
(mg L^{-1})	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[b]	1.33	0.50	0.51	0.30	0.59	96	< LOD[b]	2.21	0.86	0.92	0.51	0.56	126	< LOD[b]	3.37	0.03	0.38	0.66	1.75	86	< LOD[b]	3.23	< LOD[b]	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[b]	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[b]	1.44	0.23	0.29	0.34	1.16	95	< LOD[b]	2.08	0.25	0.47	0.49	1.06	101	< LOD[b]	3.19	0.00	0.20	0.59	2.93	73	< LOD[b]	1.40	< LOD[b]	0.05	0.23	4.53
DOC	73	< LOD[b]	9.76	3.29	3.54	1.95	0.55	95	< LOD[b]	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[b]	0.28	< LOD[b]	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[b]	0.64	0.01	0.05	0.11	2.03	88	< LOD[b]	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	70	< LOD[b]	0.63	0.04	0.08	0.10	1.29	87	< LOD[b]	0.34	0.04	0.06	0.05	0.93	119	< LOD[b]	0.50	0.06	0.08	0.08	0.95	88	< LOD[b]	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[b]	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[b]	0.11	< 0.01	0.01	0.02	1.54	95	< LOD[b]	0.06	< 0.01	0.01	0.01	1.73	126	< LOD[b]	0.05	< 0.01	< 0.01	0.01	3.18	87	< LOD[b]	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[b]	0.73	0.10	0.16	0.13	0.86	87	< LOD[b]	1.40	0.23	0.27	0.16	0.59
P	75	< LOD[b]	0.11	0.04	0.04	0.03	0.78	95	< LOD[b]	0.15	0.03	0.03	0.04	1.03	126	< LOD[b]	0.09	< 0.01	0.01	0.02	1.92	87	< LOD[b]	0.20	< 0.01	0.02	0.04	1.92
S	75	< LOD[b]	0.27	0.03	0.05	0.05	1.07	95	< LOD[b]	0.19	0.04	0.05	0.03	0.66	126	< LOD[b]	0.06	< 0.01	0.01	0.01	1.63	87	< LOD[b]	0.21	< 0.01	0.01	0.04	2.51

[a] The results of the base streamflow chemistry are related to sampling routines performed from 04/2013 to 07/2014 in the Amazonian catchments and from 12/2012 to 07/2014 in the Cerrado catchments.
[b] LOD stands for limit of detection.

Table A.2. Descriptive statistics of the storm streamflow hydrochemistry[a].

Parameter	Amazonian catchments															Cerrado catchments												
	AFOR							APAS								CCER							CPAS					
(mg L^{-1})	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[b]	2.70	0.52	0.64	0.49	0.76	119	< LOD[b]	3.79	< LOD[b]	0.17	0.58	3.44	43	< LOD[b]	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[b]	2.10	0.34	0.52	0.56	1.06	125	< LOD[b]	2.60	0.30	0.45	0.51	1.14	115	< LOD[b]	2.25	< LOD[b]	0.12	0.40	3.43	41	< LOD[b]	3.90	< LOD[b]	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[b]	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[b]	0.33	0.01	0.01	0.03	2.93	36	< LOD[b]	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[b]	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	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[b]	0.06	0.01	0.01	0.02	1.04	160	< LOD[b]	0.23	0.03	0.03	0.03	1.02	119	< LOD[b]	0.11	0.01	0.02	0.02	1.09	42	< LOD[b]	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[b]	0.11	< LOD[b]	0.02	0.03	1.45	160	< LOD[b]	0.14	0.01	0.04	0.04	1.13	119	< LOD[b]	0.11	< 0.01	0.02	0.03	1.39	42	< LOD[b]	0.09	< 0.01	0.02	0.03	1.82
S	109	< LOD[b]	0.52	0.05	0.07	0.08	1.18	160	< LOD[b]	0.21	0.07	0.07	0.05	0.78	119	< LOD[b]	0.26	0.02	0.03	0.03	1.18	42	< LOD[b]	0.09	< 0.01	0.01	0.03	1.76

[a] The results of the storm streamflow chemistry are related to sampling obtained from 02/2013 to 02/2014 in the Amazon and Cerrado catchments.
[b] LOD stands for limit of detection.