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# Composition and Flux of Dissolved and Particulate Carbon and Nitrogen in the Lower Tocantins River

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**Key Points:**

- The Tocantins River adds water and biogeochemical constituents to the Amazon River plume, but these fluxes have not been directly measured to date
- The Tocantins River contributes 2.8% of Dissolved organic carbon, 2.8% of Dissolved inorganic carbon, and 3.7% of Total dissolved nitrogen fluxes to the Amazon River plume
- In the rainy season, organic matter sources are predominantly terrigenous and in the dry season, the source is predominantly algal and bacterial

**Supporting Information:**

Supporting Information may be found in the online version of this article.

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**Abstract** The Tocantins River contributes ~5% of the total flux of water to the Amazon River plume in the Atlantic Ocean. Here, we evaluate monthly variability in the composition and abundance of carbon, nitrogen, and suspended sediment in the lower reaches of the Tocantins River from 2014 to 2016. Dissolved organic carbon concentrations generally increased during periods of high discharge and are ~1.5 times lower than average concentrations at the mouth of the Amazon River. Dissolved inorganic carbon similarly increased during periods of high discharge. Total dissolved nitrogen and individual nitrogen species followed a similar temporal pattern, increasing during high water. $NO_3^-$ predominated the dissolved inorganic nitrogen pool, followed by $NH_4^+$, and $NO_2^-$, characteristic of environments with a relatively low anthropogenic impact. Dissolved fractions represented 92% of the total carbon exported and 78% of the total nitrogen exported. The suspended particulate sediment flux was $2.72 \times 10^6$ t yr$^{-1}$, with fine suspended sediment dominating (71.3%). Concentrations of carbon relative to nitrogen indicate a primarily terrigenous source of organic matter and $CO_2$ derived from in situ respiration of this material during the rainy season and a primarily algal/bacterial source of organic matter during the dry season. Considering past estimates of dissolved carbon and nitrogen fluxes from the Amazon River to the Atlantic Ocean, the Tocantins River contributes 3% and 3.7% to total fluxes to the Amazon River plume region, respectively. While this contribution is relatively small, it may be influenced by future changes to the basin's land use and hydrology.

**Plain Language Summary** Rivers are important environments that connect the continents to the oceans. The Tocantins basin, which drains part of the Amazon and Cerrado biomes is a hydrographic region typically considered separate from the Amazon basin. This important, but often overlooked, region has experienced increasing anthropogenic pressure from agricultural and hydroelectric development, which can directly affect water quality, biogeochemical fluxes to the ocean, and coastal productivity, and nutrient cycling in the Amazon River plume. In this study, the composition and transport of carbon, nitrogen, and suspended sediment from the Tocantins River were quantified. We found that terrestrial ecosystems were the primary source of carbon and nitrogen to the river during the rainy season in contrast to aquatic sources during the dry season. Although carbon, nitrogen, and sediment fluxes were an order of magnitude lower than from the Amazon River, they may nonetheless influence productivity in the plume and changes to these fluxes due to continued anthropogenic perturbation remains uncertain.

## 1. Introduction

The Tocantins River is the easternmost large tributary in the Amazon basin, draining into the Atlantic Ocean south of Marajó Island, mixing with the Pará River and Amazon River water via the Breves channel (Figure 1). The basin has a drainage area of $920 \times 10^3$ km$^2$, the second largest in Brazil, representing 11% of the Brazilian territory with two distinct transition zones. The main tributary and longest (1,670 km) channel is the Araguaia River, with a drainage area of $385 \times 10^3$ km$^2$, and an annual average discharge of 6,500 m³ s$^{-1}$, approximately 60% of the basin's total flow (Coe et al., 2011; Mérona et al., 2010).

This outflow is combined with the discharge from the Amazon River to the north of Marajó Island, and entrained into the Amazon plume (Ward et al., 2015). The Tocantins River, and the neighboring Tapajós and Xingú rivers, have their origin in the cerrado region of the Central Brazilian archaic shield, and together represent 25% of the

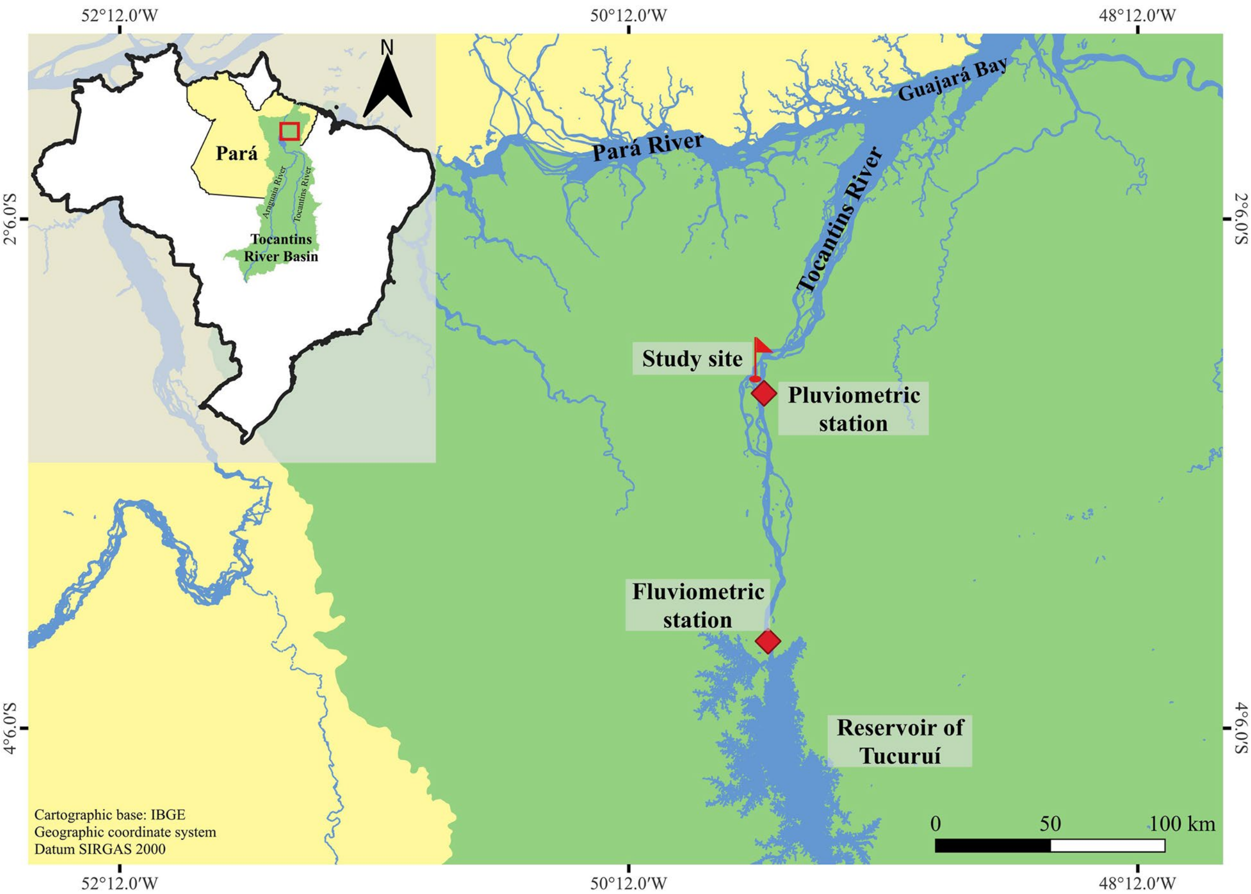


**Figure 1.** Lower Tocantins River, showing the sampling station.

overall land area of the Amazon basin. By the original classification of Sioli (1951), they are considered clearwater rivers, with low concentrations of sediments and solutes. Their lower courses all have extensive mouth-bays, or drowned valleys, formed during the Pleistocene.

The Tocantins basin is one of the most anthropogenically impacted in the Amazon biome, with 58% of its area occupied by agricultural activity (Coe et al., 2009). The conversion of native vegetation to other uses impacts the region's hydrology and alters the basin's water production (Costa et al., 2003). When the loss in native vegetation cover is less than 50% of the basin's coverage, the amount of rainfall over the region generally remains stable. However, when vegetation cover changes exceed 50% of the native cover, models indicate a reduction in rainfall and discharge rates of rivers (Costa et al., 2003). Under optimistic scenarios with intense government control over deforestation rates, estimates indicate that the Tocantins-Araguaia basin may lose about 80% of its native vegetation cover. But under scenarios of low government control, the region could experience a loss of up to 93% of the native vegetation cover (Coe et al., 2009). These changes will result in significant modifications to the region's hydrological regime, with reduced precipitation and outflow from the Tocantins-Araguaia basin (Coe et al., 2009; Costa et al., 2003).

Anthropogenic activities influence both the hydrology and biogeochemistry of the region. The high concentration of suspended sediment (i.e., above 300 mg $L^{-1}$), observed in parts of the Araguaia River, is linked to these disturbances (Lima et al., 2005). Most of the deposition of these sediments is taking place in the confluence region of the Tocantins and Araguaia rivers, with average daily deposition of ~40,000 t $day^{-1}$ of sediment. This has led to the formation of sandbanks in the backwater region of the Tucuruí Hydroelectric Power Plant reservoir (Lima et al., 2005), the largest Brazilian hydropower dam (E. D. Miranda & Meireles Filho, 2016), with a flooded area of 2,850 $km^2$ (ANA, 2009). The Tocantins basin naturally has clear waters, with a low concentration of suspended sediment, low turbidity, visibility limits greater than 4 m deep (Sioli, 1985) and high rates of primary production. This contrasts with Amazonian tributaries that drain the Andean region such as the Solimões River, which have high sediment loads. However, anthropogenic activities in the Tocantins basin may impact suspended sediment loads and influence the productivity and biogeochemistry of the river network. The Tocantins basin generates ~16% of the total Brazilian hydroelectric power, with a cascade of seven dams (Akama, 2017). The first and largest dam is the Tucuruí hydroelectric dam, which started in 1976 and closed in September 1984 (Barrow, 1988). The total flooded reservoir area varies from 1,500 to 2,500 $km^2$ throughout the year. Following this dam, the region has seen an expansion of a series of medium to large hydroelectric dams between 1996 and 2012. Tucuruí and Serra da Mesa are storage (impoundment) dams, while the rest are run-of-the-river reservoirs. In addition to the dams already installed, another 13 are planned to be built in the coming years. As would be expected, this sequence of dams produces pronounced changes in overall floodplain hydrology (Swanson & Bohlman, 2021), water footprint (Coelho et al., 2017), and flow regime (Timpe & Kaplan, 2017). Upstream of the Tucuruí hydroelectric dam, the formation of sandbanks is indicative of the changes underway (Lima et al., 2004).

At the confluence of the Tocantins and Araguaia rivers, there is daily sediment deposition of around 40,000 t $day^{-1}$, which has led to the formation of sandbanks upstream of the Tucuruí hydroelectric dam (Lima et al., 2004).

The contribution of the Tocantins to carbon and nitrogen fluxes to the ocean is not known, representing a gap in biogeochemical observations on both regional and global scales. Further, there are implications for offshore responses. Recent observations of new blooms of Sargassum in the tropical Atlantic south of the Sargasso Sea (Lapointe et al., 2021; Oviatt et al., 2019) have been attributed in part to nutrient enrichment due to deforestation and fertilizer use in agriculture in the Amazon (Y. Wang et al., 2020).

Here we provide the first detailed examination of carbon and nitrogen cycling and fluxes in the lower Tocantins River. We hypothesize that the lower Tocantins River still maintains the biogeochemical features of clearwater rivers but with interference in nitrogen concentrations and sediment transport. In the function of predicted changes in the basin, resulting from anthropogenic activities, it is essential to quantify the flux of carbon and nitrogen which have never been estimated.

We carried out a study with interannual monitoring of nitrogen and carbon in the lower Tocantins River with the aim of characterizing the biogeochemistry of this system and enabling future evaluation of changes in river biogeochemistry due to increasing anthropogenic impacts. Understanding the ecology, structure, and biogeochemical functioning of this basin is important for evaluating the impact of future development and planning for mitigation and remediation where necessary.

## 2. Materials and Methods

### 2.1. Study Site

The study was conducted in the lower Tocantins basin, Mocajuba municipalities, Pará state—Brazil (49°40′44.7″W, 02°39′09.6″S). The lower Tocantins River is characterized by a complex series of channels and islands (Mérona et al., 2010). For this reason, we collected samples at a location that maintains one well-constrained channel, which is 130 km downstream of the Tucuruí hydroelectric dam (Figure 1). This river reach has a semi-diurnal tidal effect that alters river hydrodynamics while maintaining purely freshwater (Mérona et al., 2010). These tidal effects increase the water's residence time and provide enhanced connection between the riparian zone, floodplains, and the main river channel (Gagne-Maynard et al., 2017).

The Tocantins watershed is covered by savanna (65%) and evergreen tropical forest (35%). This basin is the second largest in Brazil, representing 11% of the Brazilian territory with two distinct transition zones. The cerrado (i.e., savanna) of the central Amazon rainforest transition zone, is in the most critical situation due to continuing deforestation. The other area is the transition from the Amazon rainforest to the caatinga (i.e., arid shrublands and forest) (ANA, 2009).

The climate is tropical with strong seasonality. The dry season is normally from August to November and the rainy season from December to July. Annual average rainfall is 2,533 mm and annual average air temperature is 26°C. The topography of the region consists of broad, gently sloping upland plateaus distant from the rivers and gentle slopes to the waterways. The predominant soils consist of Oxisols (24%), Ultissol (17%), Entisols (23%), and Entisol Plinthic (14%) (ANA, 2009).

### 2.2. Sample Collection and Analysis

Water was collected for analysis using a Shurflo submersible pump with a 297 μm mesh at 60% river depth and from the surface. This depth was determined based on nautical charts (Centro de Hidrografia da Marinha, 2022). Average values from the two depths are presented considering there were not significant differences between the two depths. River depth varied from 1.1 to 9.3 m during our sampling period. Dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), total dissolved nitrogen (TDN), dissolved organic nitrogen (DON), and dissolved inorganic nitrogen (DIN) species ($NO_3^-$, $NO_2^-$, $NH_4^+$) were measured monthly from September 2014 to November 2016 in the Tocantins River. DOC samples were collected in triplicate, filtered through pre-combusted (500°C, 5 hr) GF/F glass fiber filters (Whatman 0.7 μm nominal pore size) and stored into 25 mL pre-combusted glass vials washed with acid, closed with Teflon lids and preserved in the field with 25 μL of 50% HCl. DIC, TDN, nitrate, nitrite, and ammonium were determined from a single sample, filtered through a 0.45 μm cellulose acetate filter, into acid-washed 60 mL HDPE bottles with no headspace to avoid degassing and preserved with thymol (100 mg/1,000 ml of solution). Samples were kept in the dark during transport to the lab. DOC, TDN, and DIC were determined separately using a Shimadzu total carbon analyzer (Model TOCVCPH). Nitrate, nitrite and ammonium were analyzed by flow injection analysis and DON was calculated by the difference between DIN and TDN. Dissolved $O_2$ concentrations were measured in the field, using a YSI 55 probe submerged in an overflowing graduated cylinder. pH was similarly measured using a Thermo Orion 4-star meter. Specific conductivity was determined with Amber Science (model 2052) probes.

Concentrations of coarse particulate organic carbon (CPOC) and coarse particulate organic nitrogen (CPON) were measured by passing water through a 63 μm mesh. The retained material was weighed and analyzed for total carbon and nitrogen content. Fine particulate organic carbon (FPOC) was measured by filtering the sieved water through pre-weighed and combusted 0.7 μm GF/F filters. For determination of total carbon, nitrogen and carbon isotopic composition, coarse and fine samples were dried and acid fumigated prior to analysis. The analyses were conducted on a Fisons EA 1110 CHNS connected to a Finnigan DeltaPlus mass spectrometer. The $^{13}C/^{12}C$ ratio was defined through the equation: $\delta^{13}C = \{R_{sample} - R_{standart}\}*1000/R_{standard}$, expressed in δ (‰). This value indicates the deviation of the isotopic ratio of a given material in relation to its standard. The international standards compared was, from the Pee Dee Formation of the Grand Canyon region of the United States. Particulate organic carbon (POC) and particulate organic nitrogen are the sum of the fine and coarse fractions, which were sampled monthly. The C:N ratio is related to the species' ratio, for example, when about dissolved, is about DOC:DIN and etc.

Due to the sensitive connection between hydrologic and biogeochemical flows, we divided years into four hydrological periods for the sake of data interpretation: low, rising, high, and falling water. Low water represents the dry season from July to October (with monthly precipitation lower than 100 mm), and high water corresponds to January to April. The two transitional periods are rising water, from November to December, and falling water, from May to June. Discharge data were obtained from the fluviometric ANA station (Agência Nacional das Águas) localized in Tucuruí about 130 km upstream from the sampling station and rainfall data from the nearest ANA (Agência Nacional de Águas) pluviometric station, situated in Baião about 14.3 km upstream of the sampling station.

### 2.3. Statistical Analysis

Shapiro-Wilk normality hypothesis tests were performed with significance levels (*p*-value) higher than 0.05. Due to the non-normality of some variables, we used the non-parametric statistical Kruskal Wallis test to evaluate differences between depths and seasons. This test was complemented with the Nemenyi post hoc test to verify which seasons differed significantly from each other. Considering the statistical similarity between the studied sampling depths, we considered data from all depths for the seasonal variability test, using the mean concentration between the sampled depths. Significance levels (*p*-value) of 0.05 were considered in both tests (Table S1 in Supporting Information S1). Non-parametric Spearman correlation was used, at significance levels below 0.05, to study the correlation between parameters (Supporting Information S1). All statistical tests, analyses and construction of graphs were performed in the software RStudio, version 1.1.453.

### 2.4. Flux Estimates

For dissolved organic, inorganic carbon and nitrogen (DOC, DIC, DON, DIN, $NO_2^-$, $NH_4^+$, $NO_3^-$), coarse and fine particulate organic C and N (CPOC, FPOC, CPON, Fine Particulate Organic Nitrogen (FPON)) fine and Coarse

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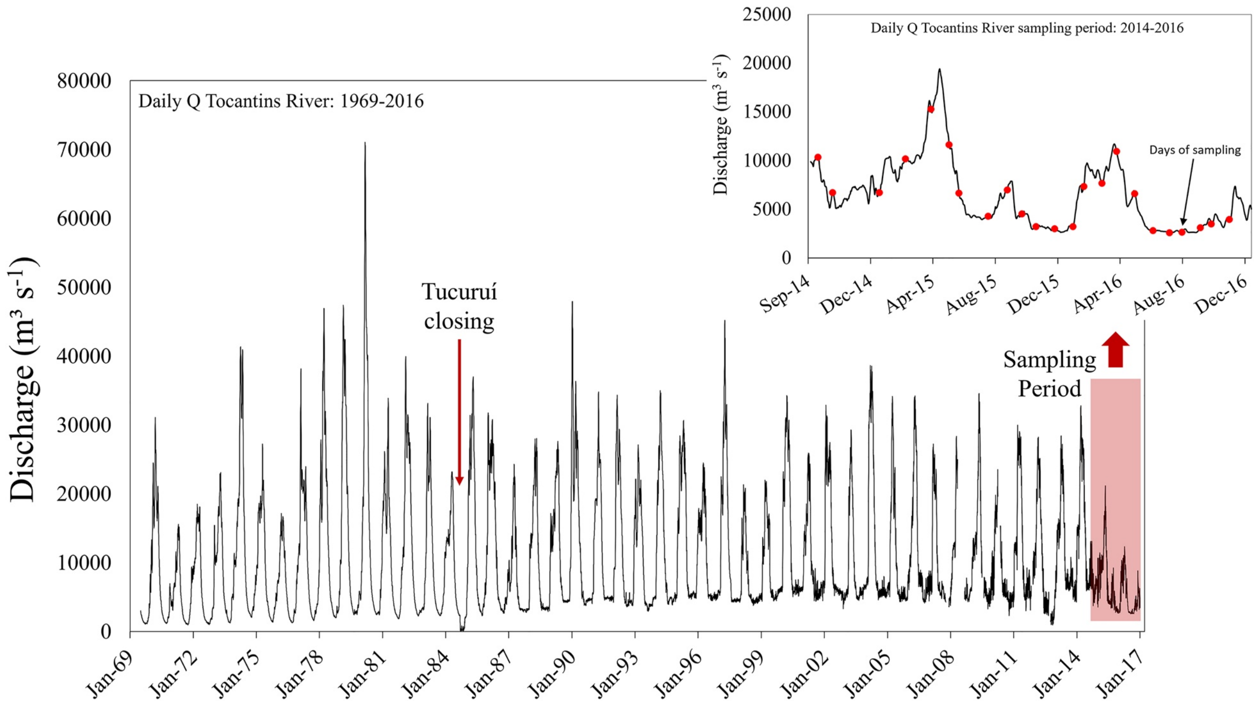


**Figure 2.** Daily discharge between 1969 and 2016 from Tucuruí station (29700000). Data source: ANA (2017).

Suspended Sediment (CSS) (fine suspended sediment (FSS), CSS) the flux were modeled using daily discharge measurements from 2014 to 2016, and monthly concentration data input into the FORTRAN Load Estimator (LOADEST) program (Runkel et al., 2004). The annual flux was obtained by sum of daily flux and, finally, an average was obtained for the period under study.

## 3. Results and Discussion

### 3.1. Climatic and Hydrological Variability

The annual average precipitation over the period of record (1985–2020) at the gauging station nearest to the sampling site (Baião) station was 2,743 mm yr$^{-1}$, or 229 mm mo$^{-1}$, with average peak of 623 mm mo$^{-1}$. The mean monthly from 1985 to 2008 was 238 mm mo$^{-1}$, with a peak of 682 mm mo$^{-1}$, and a periodicity of ~4 years. Following a high in 2008 of 411 mm mo$^{-1}$ with a peak of 1,243 mm mo$^{-1}$, the average 2009–2016, including the period of sampling, was 196 mm mo$^{-1}$, a reduction of 18% from the 1985–2008. The peak precipitation for 2009–2016 was reduced by 34%, relative to 1985–2008. Precipitation rose back to 1985–2008 levels in 2017–2020.

The annual average discharge (historical series 1970–2016) at the Tucuruí guaging station was 10,800 m$^3$ s$^{-1}$ (ANA, 2017), with systematic trends. The main tributary and longest channel is the Araguaia River, with a drainage area of 385 × 10$^3$ km$^2$, and an annual average discharge of 6,500 m$^3$ s$^{-1}$ (Coe et al., 2011; Mérona et al., 2010). Prior to the closure of the Tucuruí dam (1970–1983), the annual average was 10,600 m$^3$ s$^{-1}$, with minimum and maximum flows of 1,700 and 34,600 m$^3$ s$^{-1}$, respectively. When the dam closed in 1984, the flow was substantially reduced to an annual of 8,000 m$^3$ s$^{-1}$, with a maximum of 23,200 m$^3$ s$^{-1}$ and minimum of 40 m$^3$ s$^{-1}$. From 1985 to 2016, the annual average of 11,000 was comparable to prior, but the hydrograph became more dampened, with minimum discharge increasing to 3,600 m$^3$ s$^{-1}$ while the maximum decreased to 30,500 m$^3$ s$^{-1}$. However, during the period of sampling, September 2014–November 2016, discharge was 6,520 m$^3$ s$^{-1}$, or about 60% of the long-term average. The overall timing of the minimum flows was in late September with little variance between 1970 and 1986. The timing of minimum flows had greater fluctuation from 1987 to 2016, ranging from early July to late December. The period from 1986 to 1990 had anomalously early maxima in the respective water years (Figure 2). The period of the sampling reported here had substantially reduced precipitation and reduced discharge. Relative to the long-term mean, the reduction in precipitation was more slight than the discharge, which that one besides being more accentuated there was a progressive reduction.

**Table 1**
*Overall and Seasonal Average of Specific Conductivity (μS cm$^{-1}$), Dissolved Oxygen (mg L$^{-1}$), pH, and Temperature (°C) of Tocantins River Water*

| | | | | Sampling season | | | |
|---|---|---|---|---|---|---|---|
| Parameters | Average | Minimum | Maximum | High | Falling | Low | Rising |
| Conductivity | 42.7 ± 2.8 | 38.7 | 49.1 | 45.5 ± 2.7[a] | 40.5 ± 2.0[b] | 41.5 ± 1.7[b] | 42.2 ± 2.3[ab] |
| Dissolved oxygen | 6.5 ± 0.7 | 5.1 | 8.0 | 6.1 ± 0.5[ab] | 5.9 ± 0.4[b] | 6.9 ± 0.6[a] | 6.7 ± 0.6[ab] |
| pH | 7.18 ± 0.47 | 6.21 | 7.87 | 6.99 ± 0.57[a] | 6.98 ± 0.17[a] | 7.30 ± 0.41[a] | 7.52 ± 0.49[a] |
| Temperature | 30.2 ± 0.6 | 28.9 | 31.1 | 29.6 ± 0.7[a] | 30.6 ± 0.1[a] | 30.4 ± 0.5[ac] | 30.4 ± 0.4[bc] |

*Note*. Values with the same letters were not significantly different ($p > 0.05$) based on upon a Nemenyi post hoc test. The test was performed contrasting the mean season value within each parameters.

### 3.2. Terrestrial and In Situ Sources and Sinks of Carbon and Nitrogen

The specific conductivity of river water is a basic indicator of the extent to which groundwater interacts with soil and rocks while draining a watershed. The average specific conductivity during our study was 42.7 ± 2.8 μS cm$^{-1}$ and was significantly higher during rising and high water compared to falling and low water ($p < 0.05$; Table 1; Table S2 in Supporting Information S1). Though the seasonal differences observed here are fairly small, this trend contrasts observations in the Amazon River, where the highest conductivity values are observed during low water as a result of longer contact time of groundwater with soil and rocks during low water (Ker, 1997; Moline & Coutinho, 2015) and dilution during high water (Drake et al., 2021). This basic data demonstrates a fundamental difference in seasonal subsurface hydrological dynamics between the Amazon and Tocantins basins. pH, which is related to both in situ process (e.g., respiration and primary production) and soil/groundwater inputs, ranged from close to neutral (6.99 ± 0.57) during high water to slightly basic (7.52 ± 0.49) during rising water, with an average of 7.18 ± 0.47. Seasonal differences in pH were not significant ($p > 0.05$; Table 1) and there was a significant negative correlation between pH and discharge ($r = -0.64$; $p < 0.05$; Figure S2 in Supporting Information S1). The slightly more basic pH values observed during lower discharge conditions is likely due to enhanced algal productivity, which is discussed in more detail below. In contrast, microbial decomposition of organic matter and release of organic acid and $CO_2$, along with acidic groundwater inputs to the stream may be responsible for the more acidic conditions during higher discharge periods (Oliveira et al., 2006; Sawakuchi et al., 2017). pH values in the Tocantins River were similar to those observed in the Tapajós River (7.44), a highly productive clearwater tributary of the Amazon River (R. G. Miranda et al., 2009).

Dissolved $O_2$, which similarly reflects the balance between respiration and photosynthesis, was near atmospheric saturation (6.5 ± 0.7 mg L$^{-1}$; Table 1) with similar values as observed in the Tapajós and Xingu clearwater Amazonian rivers, with average values of 6.9 ± 0.8 and 6.1 ± 0.5 mg L$^{-1}$, respectively (Gagne-Maynard et al., 2017). Other studies in the Tocantins River, which did not have as high of temporal resolution as this present study, observed $O_2$ concentrations between 6.6 and 7.7 mg L$^{-1}$ for the lower river (Mérona et al., 2010), and 7.9 mg L$^{-1}$ for the upper Tocantins River (savanna biome) (J. J. L. S. D. Silva et al., 2010). Dissolved oxygen varied significantly ($p < 0.05$) between falling and low water periods, where the lowest and highest mean values were observed, respectively. Generally, clearwater rivers have higher concentrations of dissolved oxygen relative to other water types (Gagne-Maynard et al., 2017; R. G. Miranda et al., 2009; J. J. L. S. D. Silva et al., 2010). The low suspended sediment levels permit light to penetrate further into the water column, stimulating photosynthetic activity, which results in oxygenated waters.

The inorganic fraction of DIC represents inorganic carbon both delivered to the river from the watershed and produced via respiration in the river. DIC concentrations showed a significant correlation with river discharge, explaining about 16% of the variation in DIC concentrations ($r = 0.4$; $p < 0.05$; Figure S1 in Supporting Information S1), which has also been observed by Richey et al. (1990) in the Amazon River mainstem. However, seasonal averages did not show statistical differences ($p > 0.05$) and the average concentration was 3.6 ± 0.5 mg L$^{-1}$. In a first order clearwater stream with clear waters, in Tanguro Ranch—Mato Grosso state (Transitional Biome Savanna-Amazon), Neu et al. (2011) observed DIC concentrations between 6 and 20 mg L$^{-1}$ Johnson et al. (2006, 2008) measured concentrations between 9 and 27 mg L$^{-1}$ in Juruena—Mato Grosso. Our observed DIC concentrations are likely lower due to the river hierarchy, that is, lower order streams generally

**Table 2**
*Average ± Standard Deviation, Minimum, and Maximum Concentrations (mg L$^{-1}$) of Fine and Coarse Suspended Sediment (CSS) (Fine Suspended Sediment and CSS), Fine Particulate Organic Nitrogen (FPON) Content (% FPON), Coarse Particulate Organic Nitrogen (CPON) Content (% CPON), Fine Particulate Organic Carbon (FPOC) Content (% FPOC), Coarse Particulate Organic Carbon (CPOC) Content (% CPOC), Stable Isotopic Composition (‰) of Fine and Coarse Sediment of Tocantins River Water, and Carbon and Nitrogen Ratio (C:N) of Fine and CSS of Tocantins River Water*

| | | | | Sampling season | | | |
|---|---|---|---|---|---|---|---|
| Parameters | Average | Minimum | Maximum | High | Falling | Low | Rising |
| FSS | 3.9 ± 2.9 | 1 | 10.2 | 6.8 ± 2.5$^{a}$ | 4.8 ± 2.1$^{a}$ | 1.8 ± 0.7$^{b}$ | 1.6 ± 0.04$^{bc}$ |
| CSS | 0.3 ± 0.5 | 0.04 | 2.38 | 0.6 ± 0.9$^{a}$ | 0.2 ± 0.1$^{a}$ | 0.2 ± 0.1$^{a}$ | 0.1 ± 0.1$^{a}$ |
| %FPON | 2.5 ± 1.2 | 1 | 6 | 1.5 ± 0.7$^{bc}$ | 2.3 ± 0.9$^{ac}$ | 3.2 ± 1.3$^{a}$ | 3.1 ± 0.8$^{a}$ |
| %CPON | 1.0 ± 0.7 | 0.1 | 2.6 | 0.7 ± 0.6$^{a}$ | 1.4 ± 0.8$^{a}$ | 1.0 ± 0.7$^{a}$ | 1.2 ± 0.7$^{a}$ |
| %FPOC | 19.8 ± 8.6 | 7.7 | 42.5 | 11.4 ± 4.7$^{bc}$ | 17.9 ± 6.9$^{ac}$ | 24.9 ± 8.1$^{a}$ | 24.5 ± 6.7$^{a}$ |
| %CPOC | 7.8 ± 4.7 | 0.7 | 17.8 | 4.9 ± 3.5$^{a}$ | 10.4 ± 5.9$^{a}$ | 8.3 ± 4.3$^{a}$ | 9.9 ± 5.5$^{a}$ |
| FPO$^{13}$C | −29.3 ± 1.5 | −32.4 | −26.4 | −27.6 ± 1.3$^{bc}$ | −29.3 ± 0.5$^{ac}$ | −30.2 ± 1.2$^{a}$ | −30.2 ± 0.3$^{a}$ |
| CPO$^{13}$C | −28.1 ± 1.8 | −31.6 | −25.8 | −27.3 ± 0.7$^{a}$ | −29.1 ± 0.9$^{a}$ | −28.7 ± 1.6$^{a}$ | −27.1 ± 1.9$^{a}$ |
| FSS (C:N) | 7.9 ± 0.7 | 6.9 | 10 | 7.9 ± 1.2$^{a}$ | 7.9 ± 0.3$^{a}$ | 7.9 ± 0.8$^{a}$ | 7.9 ± 0.2$^{a}$ |
| CSS (C:N) | 8.7 ± 1.8 | 5.6 | 12.3 | 8.7 ± 2.2$^{a}$ | 7.7 ± 0.5$^{a}$ | 9.4 ± 2.0$^{a}$ | 8.5 ± 1.3$^{a}$ |

have higher DIC concentrations (Johnson et al., 2008). The abundance of DIC is largely influenced by subsurface water contributions, biological processes in the river, and lithology/weathering in the drainage basin (Richey et al., 1990; Stallard & Edmond, 1983; Tundisi & Tundisi, 2008). About 60%–90% of DIC exists in bicarbonate form ($HCO_3^-$) depending on pH (Richey et al., 1990), and is influenced by autochthonous processes in the river. High algal photosynthetic rates remove $CO_2$ from the water and shift the pH to basic, favoring DIC in the form of bicarbonate (Melo et al., 2013).

Stable isotopic values observed during low and rising waters are one indicator for enhanced algal productivity during these time periods. δ$^{13}$C-FPOC had an average value of −29.3 ± 1.5‰, and the most negative values (−32.4‰) were observed during low water (Table 2) similar to other studies in Amazonian clearwater rivers with high productivity by phytoplankton such as the Tapajós River (Martinelli et al., 2009; Ward et al., 2015). DOC:-DON ratios also indicate a predominance of algal productivity during the fall and low tide (22.7) and flood (21.3).

As with all parameters discussed so far, DOC is also related to both in situ production and terrestrial inputs. The average DOC concentration was 2.8 ± 0.9 mg L$^{-1}$, similar to other clear waters rivers such as the Tapajós River (1.8 ± 0.1 mg L$^{-1}$) and lower than the mouth of the Amazon River (4.2 ± 0.9 mg L$^{-1}$; (white water) (Ward et al., 2015, 2016), and Amazonian black water rivers, where that ranging range from 7 to 10 mg L$^{-1}$ (Richey et al., 1990). DOC concentrations did not correlate with river discharge ($p > 0.05$); the lowest DOC concentrations were observed during low and rising water (Table 3). During the high and falling water periods, the river has a dominant input from the terrestrial environment. During low water, the pH was basic likely because of the high productivity of algae and aquatic macrophytes (Esteves, 1998), though it is also possible that increased organic acid inputs played a role similar to in the Congo River (Z. A. Wang et al., 2013). Algal blooms were apparent by the green coloration of the water during this period, this is an important flowpath for removing $CO_2$ from water and reducing acidity. But it is also an important source of autochthonous algal material, which is a labile carbon and nitrogen source (Groffman & Rosi-Marshall, 2015). During low water, relatively higher rates of respiration compared to high water are balanced by intense photosynthesis, which consumes $CO_2$ (Richey et al., 2009; Ward et al., 2013).

DOC and DON were the dominant carbon and nitrogen fractions when compared to POC and nitrogen matter, FPOC, CPOC, FPON, and CPON (Figure 3), similar to observations in the Amazon River by Ward et al. (2015), Hedges et al. (1994), and Lewis et al. (1999). DOC was positively correlated with DON ($p < 0.05$; $r = 0.7$; Table 3). DOC, DON, and $pCO_2$ decreased during low water (September to October) (Figure 4). The higher DOC and DON levels during high water indicates mobilization of carbon and nitrogen from the terrestrial landscape similar to the Amazon River (Drake et al., 2021).

**Table 3**

*Concentrations of Dissolved Inorganic Carbon (mg L$^{-1}$), Dissolved Nitrogen (mg N L$^{-1}$), and Nitrogen Species (mg N L$^{-1}$) in Tocantins and Other Amazon Rivers* $NO_2^-$

| | DOC | DIC | TDN | DON | DIN | $NO_2^-$ | $NO_3^-$ | $NH_4$ | DOC:DON |
|---|---|---|---|---|---|---|---|---|---|
| This study | | | | | | | | | |
| Mean | 2.8 ± 0.9 | 3.6 ± 0.5 | 0.27 ± 0.08 | 0.12 ± 0.07 | 0.15 ± 0.02 | 0.01 ± 0.00 | 0.11 ± 0.03 | 0.03 ± 0.01 | 40.0 ± 37.2 |
| High water | 3.2 ± 1.2[a] | 3.9 ± 0.5[a] | 0.30 ± 0.06[a] | 0.15 ± 0.07[a] | 0.15 ± 0.03[a] | 0.009 ± 0.002[ac] | 0.12 ± 0.03[a] | 0.02 ± 0.01[a] | 30.3 ± 26.7[a] |
| Falling water | 3.4 ± 0.5[a] | 3.7 ± 0.6[a] | 0.29 ± 0.09[a] | 0.15 ± 0.10[a] | 0.15 ± 0.02[ac] | 0.008 ± 0.002[ac] | 0.12 ± 0.02[a] | 0.02 ± 0.01[a] | 51.3 ± 60.2[a] |
| Low water | 2.5 ± 0.6[a] | 3.3 ± 0.4[a] | 0.27 ± 0.06[a] | 0.11 ± 0.06[a] | 0.16 ± 0.02[ac] | 0.006 ± 0.003[bc] | 0.12 ± 0.02[a] | 0.03 ± 0.02[a] | 29.5 ± 16.7[a] |
| Rising water | 2.2 ± 0.2[a] | 3.5 ± 0.6[a] | 0.15 ± 0.03[b] | 0.04 ± 0.03[a] | 0.11 ± 0.00[bc] | 0.012 ± 0.005[a] | 0.08 ± 0.01[a] | 0.03 ± 0.01[a] | 79.0 ± 56.3[a] |
| Other rivers | | | | | | | | | |
| Xingu river[1] | 2.4 ± 0.3 | | | | | | | | |
| Tapajós river[1] | 1.8 ± 0.1 | | | | | | | | |
| Pará River[2] | 4.3 ± 1.5 | | | | | | | | |
| Amazon river (mouth)[2] | 4.2 ± 0.9 | | | | | | | | |
| Amazon river (Óbidos)[3] | 3.9 ± 0.6 | | | | | | | | |
| Black waters systems (Amazon basin)[3] | 7–10 | | | | | | | | |
| Araguaia (GO)[4] | | | | | | | 0.03–0.12 | | |
| Araguari (AP)[5] | | | | | | | 0.02–0.25 | | |
| Madeira (RO)[6] | | | | | | 0.001 | 0.04 | 0.042 | |
| Urubuí (AM)[7] | | | | | | | 0.05–0.07 | 0.081–0.258 | |
| Negro (AM)[8] | | | | | | 0.003–2.505 | | 0.904–7.464 | |
| Amazon river (Óbidos)[9] | 4.19 | | | 0.2 | | | | 8.29 | |

*Note*. Values with the same letters were not significantly different ($p < 0.05$) based upon a Nemenyi post hoc test. The test was performed contrasting the mean season value within each parameter.
[1]Ward et al. (2016). [2]Ward et al. (2015). [3]Richey et al. (1990). [4]R. L. D. Silva (2009). [5]Bárbara et al. (2010). [6]Arantes Junior (2011). [7]Aprile and Mera (2007). [8]Pinto et al. (2009). [9]Drake et al. (2021).

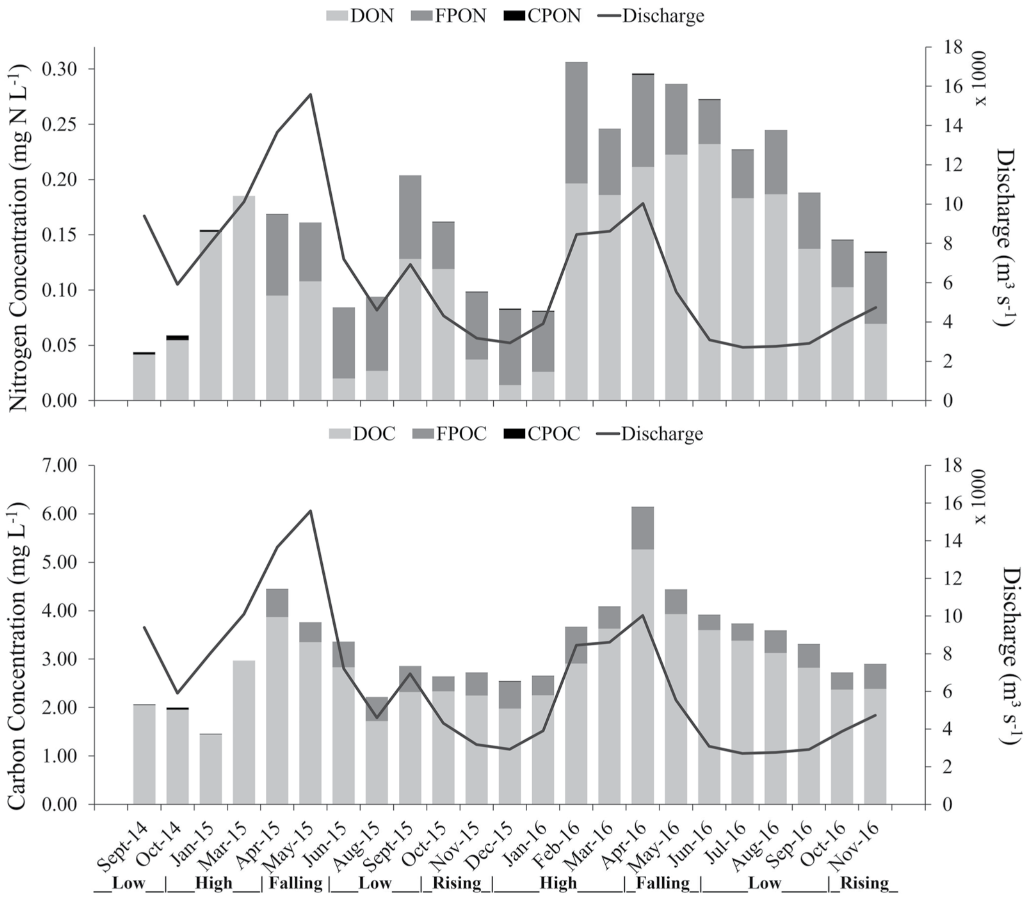


**Figure 3.** Organic fractions concentrations of nitrogen and carbon: dissolved organic nitrogen, Fine Particulate Organic Nitrogen, coarse particulate organic nitrogen, Dissolved organic carbon, Fine particulate organic carbon, and coarse particulate organic carbon.

TDN concentrations varied between 0.12 and 0.43 mg N $L^{-1}$ with an average of 0.27 ± 0.08 mg N $L^{-1}$. TDN varied significantly between seasons ($p < 0.05$) and was positively correlated with river discharge ($p < 0.05$, $r = 0.492$). DIN was not correlated with discharge ($p > 0.05$; Figure S1 in Supporting Information S1) but had statistically significant differences between low and rising waters ($p < 0.05$) (Table 3). Nitrate ($NO_3^-$) had significant seasonal variability ($p < 0.05$; Figure S4 in Supporting Information S1) with the lowest concentrations observed during rising water (Table 3 and Figure 5), indicating dilution during this period, similar to that observed by Drake et al. (2021). In the Tocantins River, the average nitrate concentration was 0.11 ± 0.03 mg N $L^{-1}$, which is higher than other tropical rivers such as the Araguaia River (0.03 ± 0.12 mg N $L^{-1}$; R. L. D. Silva, 2009), Araguari River (0.02 ± 0.25 mg N $L^{-1}$; Bárbara et al., 2010), and the Madeira River (0.04 mg N $L^{-1}$; Arantes Junior, 2011).

Ammonium concentrations were 0.03 ± 0.01 mg N $L^{-1}$, lower than white water rivers such as the Madeira River (0.04 mg N $L^{-1}$) and black water rivers such as the Negro River (0.90–7.46 mg N $L^{-1}$; Pinto et al., 2009). This is potentially indicative of low anthropogenic impact to the river (Neill et al., 1995). The $NO_2^-$ concentrations were also very low, with an average 0.01 ± 0.00 mg N $L^{-1}$ (and often below the detection limit 0.003 mg N $L^{-1}$). High levels of oxygen generally result in a low nitrite concentration, because it is highly reactive and is only present for a very short time in aquatic ecosystems (Esteves, 1998; Groffman & Rosi-Marshall, 2015; Tundisi & Tundisi, 2008). Arantes Junior (2011) observed even lower concentrations of nitrite in the Madeira River (0.001 mg N $L^{-1}$).

Although nitrate is the predominant form of inorganic nitrogen, $NH_4^+$ is the form preferably assimilated by phytoplankton because it is the optimal oxidation state for the protein-forming process (Braga et al., 2017). High nitrate and low ammonium concentrations (Figure 5) are characteristic of aerobic systems and low anthropogenic impact. The predominance of nitrate shows that nitrification is not limited throughout the year, likely due to the high

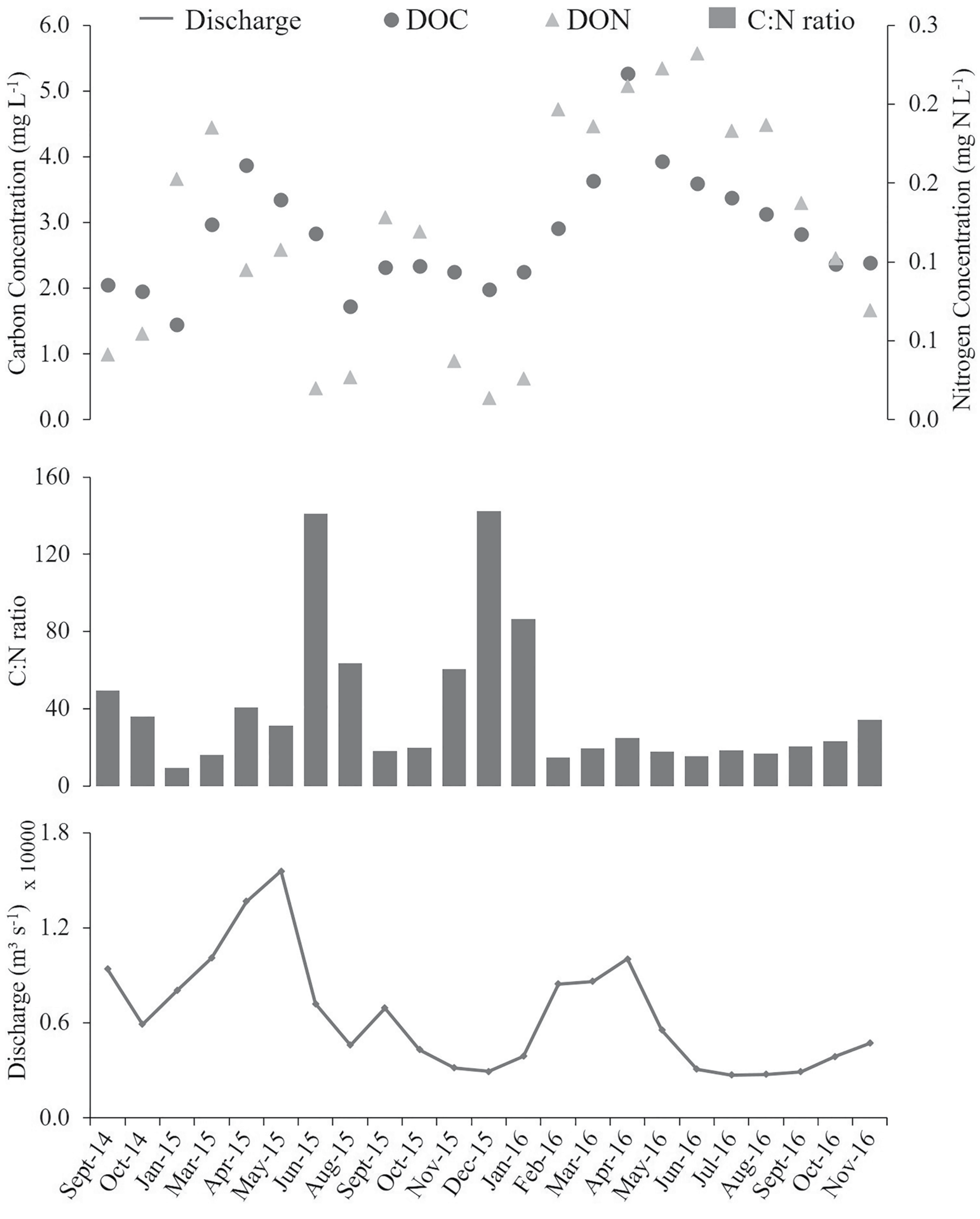


**Figure 4.** Monthly concentration of Dissolved organic carbon (mg $L^{-1}$), dissolved organic nitrogen (mg N $L^{-1}$), C:N ratio and river discharge ($m^3\ s^{-1}$) in the low Tocantins River, from September 2014 to November 2016.

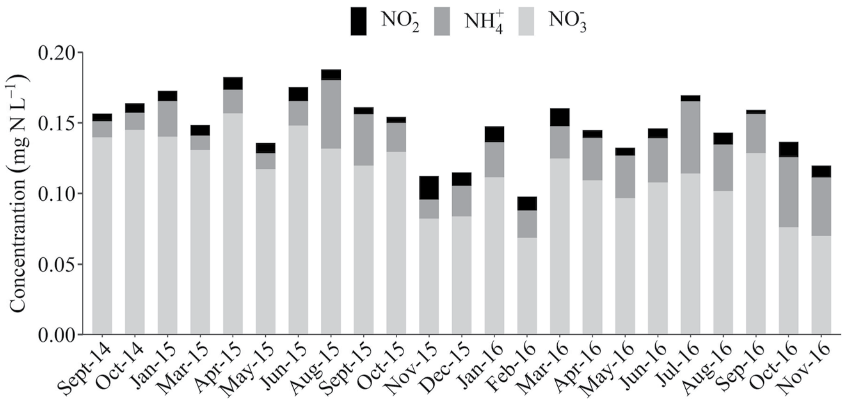


**Figure 5.** Concentrations (mg N L$^{-1}$) of $NO_3^-$, $NO_2^-$, and $NH_4^+$ in the lower Tocantins River.

dissolved oxygen concentrations in the water column throughout the hydrological cycle. Nitrate is easily transported from soils via subsurface water flow (Chapin et al., 2002; Follett & Delgado, 2002; Neill et al., 1997, 1999; Piccolo et al., 1994) and is an important source of nutrients for both river and coastal ecosystems, being the main fraction of DIN (Groffman & Rosi-Marshall, 2015). Generally, clearwater rivers with low anthropogenic impact are well oxygenated, favoring nitrification. Large rivers generally have high turbulence, resulting in greater circulation of oxygen and consequently oxidation processes (Van Bennekon & Salomons, 1981).

The Tocantins River has a relatively low content of suspended material, similar to other clear and black water systems such as the Tapajós and Negro rivers (Hedges et al., 1994; Meade et al., 1985). The high concentrations of suspended sediments of anthropogenic origin in the middle Tocantins region (Lima et al., 2004) are not observed in the Lower Tocantins. A fraction of the suspended material generated in the upper and middle Tocantins are either deposited or degraded at the confluence between the Tocantins and Araguaia rivers, upstream of the Tucuruí reservoir, before arriving in the lower Tocantins (Lima et al., 2004; Tundisi & Tundisi, 2008).

Similar to other studies, the coarse fraction has the lowest concentrations, ranging from 0.04 to 2.38 mg L$^{-1}$, and did not vary significantly throughout the year (Table 2). Fine suspended sediment concentrations ranged from 1.0 to 10.2 mg L$^{-1}$and varied significantly by season ($p < 0.05$) with the highest concentrations (6.8 ± 2.5 mg L$^{-1}$) associated with maximum discharge (Figure S3 in Supporting Information S1). In parts of the Araguaia River, suspended sediment concentrations are very high, with values above 300 mg L$^{-1}$, which is higher than white water rivers in the Amazon basin (Lima et al., 2004). At the confluence of the Tocantins and Araguaia rivers, there is daily sediment deposition of around 40,000 t day$^{-1}$, which has led to the formation of sandbanks upstream of the Tucuruí hydroelectric dam (Lima et al., 2004). The lowest FSS concentrations occurred during low water (1.6 ± 0.04 mg L$^{-1}$). Ward et al. (2015) observed similar seasonal variation near the mouth of the Amazon River, but overall higher concentrations (14.4 ± 4.4 during low water and 40.5 ± 4.8 mg L$^{-1}$ during high water).

The stable carbon isotope composition ($\delta^{13}C$) of organic matter reflects the dynamics of isotopic assimilation of the inorganic carbon source (Garcette-Lepecq et al., 2000). In the Tocantins River, we observed that the percentage of organic carbon and nitrogen of FSS (%FPOC and %FPON) varied significantly ($p < 0.05$) between seasons, with the lowest values for both parameters observed during high water (Table 2). $FPO^{13}C$ values ranged from −32.4‰ during low water to −26.4‰ during high water, similar to previous measurements in the Tocantins River (−26.5‰ ± 1.7‰; Ward et al., 2015). Low and rising water compositional signatures are indicative of a more degraded biogenic and soil source of FSS from primarily algal production (Martinelli et al., 2009; Ward et al., 2015).

FPOC and FPON had distinct C:N ratios and isotopic signatures compared to CPOC and CPON. The fine fraction had 2.6 and 2.8 times more carbon and nitrogen, respectively, than the coarse fraction, similar to studies conducted by Hedges et al. (1994), and the carbon was more $^{13}C$ depleted in the fine fraction. The coarse fraction had higher C:N ratios than the fine fraction, similar to observations by Hedges et al. (1986) and Hedges and Stem (1984), indicative of a higher contribution of wood and leaf-derived material from the terrestrial biosphere.

In these waters, FSS has a predominantly autochthonous origin (C:N values ranging between 6 and 8) with no seasonal variation, which is typical of clear water rivers and Amazonian lakes with high primary productivity.

This results in a lighter isotopic value especially during falling and low water, periods in which phytoplankton abundance is maximal and stable isotopic values are the most negative. Amazonian rivers have an average isotopic value of −27‰, and can be as low as −33.8‰, while clear water tributaries have isotopic values around −32‰. The observed changes in stable isotopic composition and low variability of C:N ratios may be related to the genesis of particulate matter. The fine fraction is characterized by the composition of soils and more degraded humic material, while the coarse fraction has a predominance of plant material (Amorim et al., 2009; Martinelli et al., 2009).

### 3.3. Anthropogenic Impacts

Nitrate as the predominant fraction is characteristic of a well-oxygenated environment, where nitrification processes are favored. The concentration and distribution of nitrogen in aquatic systems is significantly influenced by anthropogenic inputs, associated with land use and land cover (Castillo et al., 2000). Low ammonium concentrations (Figure 5) are characteristic of aerobic systems and low anthropogenic impact, due to the biological degradation process of organic matter. Higher concentrations can be found in sewage and industrial effluents (Parron & Pereira, 2011). Unlike temperate regions, studies carried out in areas of agricultural cultivation in Mato Grosso, indicated that Nitrate can accumulate in deep soils of tropical agricultural areas, influencing its concentration in surface waters (Jankowski et al., 2018). Therefore, the impacts of intense cultivation in this region still need to be studied in more detail.

Ammonium concentrations were $0.03 \pm 0.01$ mg N $L^{-1}$, which is lower than white water rivers such as the Madeira River (0.04 mg N $L^{-1}$) and black water rivers such as the Negro River (0.90–7.46 mg N $L^{-1}$; Pinto et al., 2009). This is potentially indicative of low anthropogenic impact to the river (Neill et al., 1995). As weel, in deep soils whit crop agriculture, low solute concentrations in strems, can be controlled by high soil hydraulic conductivity, groundwater-dominated hydrologic flowpaths, and the absence of nitrogen fertilization. These factors have buffered streams from the large increases solute concentrations in intensive croplands (Riskin et al., 2017). The $NO_2^-$ concentrations were also very low, with an average $0.01 \pm 0.00$ mg N $L^{-1}$ (and often below the detection limit 0.003 mg N $L^{-1}$). High levels of oxygen generally result in a low nitrite concentration, because it is highly reactive and is only present for a very short time in aquatic ecosystems (Esteves, 1998; Groffman & Rosi-Marshall, 2015; Tundisi & Tundisi, 2008). Arantes Junior (2011) observed even lower concentrations of nitrite in the Madeira River (0.001 mg N $L^{-1}$). Although nitrate is the predominant form of inorganic nitrogen, $NH_4^+$ is the form preferably assimilated by phytoplankton because it is the optimal oxidation state for the protein-forming process (Braga et al., 2017).

Based on DIN fractions and suspended sediment, the lower Tocantins region is characterized as an environment with relatively low anthropogenic influence. The structural pattern of anastomosed drainage, its large dimension, and the presence of many islands influence the resistance and resilience of the channel to natural and anthropic disturbances through greater retention of nutrients, organic matter, and transported sediment. The multiple channels and islands, which are of great importance in increasing housing heterogeneity, create nutrient and organic matter retention zones that contribute to increasing the river's resilience to natural and anthropogenic disturbances (Petts, 2000).

A significant portion of the suspended material generated in the upper and middle Tocantins region is deposited and/or degraded before reaching the lower Tocantins (Lima et al., 2004; Tundisi & Tundisi, 2008). The relatively low content of suspended material is similar to other clear and black water systems, such as the Tapajós and Negro rivers (Hedges et al., 1994; Meade et al., 1985). In the middle and final course, a region where the water residence time increases due to the physical effect of the tide, the river widens and the current is not so strong, which also favors the reabsorption zones, deposition of sand, and fine materials.

### 3.4. Fluxes to the Amazon River Plume

The total flux of suspended particulate sediments from the Tocantins basin to the ocean was $2.72 \times 10^6$ t $yr^{-1}$; of this total, 71.3% were fine sediments and only 28.6% were coarse sediments (Table 4). The CSS yield was 1.04 and FSS was 2.59 g $m^{-2}$ $yr^{-1}$. The low fluxes are likely the result of the Tucuruí dam; according to Lima et al. (2004) a considerable deposition of sediment occurs at the confluence of the Araguaia and Tocantins rivers and in the Tucuruí reservoir.

The annual flux of POC from the Tocantins basin was $0.17 \times 10^6$ t C yr$^{-1}$, 99% of which was FPOC. This flow represents ~1.4% of the total POC exported by the Amazon River (Richey et al., 1990). The CPOC yield was 0.004 and FPOC yield was 0.22 g m$^{-2}$ yr$^{-1}$. Particulate organic nitrogen had a flux of $0.021 \times 10^6$ t N y$^{-1}$, 98% of which was in the fine fraction. The CPON yield was 0.0006 and FPON was 0.03 g m$^{-2}$ yr$^{-1}$. The predominance of the fine fraction is expected in medium to large river systems (Hedges et al., 1994; Tundisi & Tundisi, 2008).

DOC represented 46% of the total DIC flux (Table 4), with a flux from the basin of $0.85 \times 10^6$ t DOC yr$^{-1}$; this represents ~2.8% of DOC exported by the Amazon River to the plume and 0.34% of the DOC exported from rivers to the ocean, globally (Hedges et al., 1997). These estimates were slightly smaller than the 0.4% estimated previously, with a flow of $1.12 \times 10^6$ t DOC yr$^{-1}$ (apud Raymond & Spencer, 2015). The difference can be associated with the methodology applied. Previous estimates used only an annual average concentration of DOC. With these databases available, the export of DOC through the Amazon delta was estimated to be ~$26 \times 10^6$ t C yr$^{-1}$, similar to estimates by Raymond and Spencer (2015). This represents ~10.4% of total DOC exported to the world's oceans.

The Tocantins DOC yield (i.e., fluxes normalized to basin area) was significantly less (1.13 g C m$^{-2}$ yr$^{-1}$) compared to the largest tropical rivers such as the Amazon (5.45 g C m$^{-2}$ yr$^{-1}$; Drake et al., 2021), Congo, Orinoco and average of global rivers (2.15 g C m$^{-2}$ yr$^{-1}$; Raymond & Spencer, 2015). However, they were slightly smaller than previous estimates for the Tocantins basin (1.5 g C m$^{-2}$ yr$^{-1}$; Raymond & Spencer, 2015) and other smaller tropical watersheds, such as the Darro (0.17 g C m$^{-2}$ yr$^{-1}$; Neu et al., 2016) and Paragominas (0.41 g C m$^{-2}$ yr$^{-1}$; Markewitz et al., 2004). Floodplain interactions in rivers such as the Amazon River, which are covered with vegetation during the dry season, are likely a significant source of carbon and organic nitrogen for these systems with relatively high DOC yields.

DIC was the predominant form of carbon exported from the Tocantins River ($0.99 \times 10^6$ t y$^{-1}$) similar to observations by Richey et al. (1990) in the Amazon River. Considering the Amazon River DIC flux of ~$35.0 \times 10^6$ t C yr$^{-1}$ (Richey et al., 1990), the Tocantins River contributes to 2.8% of the DIC exported by the Amazon River plume, and 2.8% of the total DIC from the Amazon River Plume. DIC yield presented higher values (1.32 g C m$^{-2}$ yr$^{-1}$) than those found in the Darro River (0.17 g C m$^{-2}$ yr$^{-1}$; Neu et al., 2016).

The TDN flux was $0.076 \times 10^6$ t yr$^{-1}$, with a predominance of nitrate and DON fractions, which represented 93% of the total nitrogen flux. The total flux of dissolved nitrogen from the Amazon River to the Atlantic Ocean is $1.96 \times 10^6$ t N yr$^{-1}$ (Drake et al., 2021); thus, the Tocantins basin, represents 3.7% of total nitrogen export to the Amazon plume. The nitrogen yield from the Tocantins basin was 0.04 of DON; 0.06 g N m$^{-2}$ yr$^{-1}$ of DIN; 0.065 of $NO_3$; 0.003 of $NO_2$; and 0.01 N m$^{-2}$ yr$^{-1}$ of $NH_4^+$.

However, it is necessary to highlight that the study period was atypical compared to the historical average discharge. To understand how fluxes, vary as a function of interannual hydrological variability, we performed an estimate for a "normal" year. In general, the flows are lower (Table 4). However, for more accurate estimates, it is necessary to increase the historical series of samplings and include measurements of the Pará River and other tributaries that make up the southern part of the Amazon delta. Recent studies using a discharge model for the Pará-Amazon estuary estimate that the discharge of the Tocantins River represents about 52% of the flow of the Pará River. Another 48%, that is, a discharge of 9,959 m$^3$ s$^{-1}$ is not computed in the export to the ocean (Prestes et al., 2020).

## 4. Conclusions

The chemistry of the lower Tocantins River reflects both inputs from the terrestrial environment and processing, and production in the reservoir of the Tucuruí reservoir. The terrestrial environment is an important source of carbon and nitrogen for the Tocantins River during the rainy season. We clearly identify two distinct periods that align with the flood pulse concept (Junk et al., 1989): during the rainy season there is a predominance of allochthonous organic matter input from the terrestrial environment and respiratory processes prevail, showing that the river network has a tendency to be heterotrophic. During low and rising water, organic carbon and nitrogen are largely derived from the decomposition of autochthonous organic matter, more specifically algal and planktonic material. During this period, primary production interacts with the decomposition of terrestrial vegetation and algae-derived organic matter which influence the river to present conditions that resemble autotrophic environments despite relatively high rates of respiration. The allochthonous contribution of organic matter, associated

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**Table 4**
*Fluxes of: Coarse Suspended Sediment; Fine Suspended Sediment; Coarse Particulate Organic Carbon; Fine Particulate Organic Carbon; Coarse Particulate Organic Nitrogen; Fine Particulate Organic Nitrogen; Dissolved Organic Carbon; Dissolved Inorganic Carbon; Dissolved Organic Nitrogen, Dissolved Inorganic Nitrogen, and Nitrogen Species ($NH_4^+$, $NO_2^-$, $NO_3^-$) for the Study Time and an Estimate of Flows for a Normal Period*

| | CSS $10^6$ | FSS $10^6$ | CPOC $10^3$ | FPOC $10^6$ | DOC $10^6$ | DIC $10^6$ | CPON $10^3$ | FPON $10^3$ | DON $10^3$ | DIN $10^3$ | $NH_4$ $10^3$ | $NO_3$ $10^3$ | $NO_2$ $10^3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Study site | t $y^{-1}$ | | t C $y^{-1}$ | | t $y^{-1}$ | | t N $y^{-1}$ | | | | | | |
| Lower Tocantins (this study) | 0.78 | 1.94 | 3.27 | 0.17 | 0.85 | 0.99 | 0.43 | 20.8 | 32.8 | 43.2 | 4.60 | 37.9 | 2.11 |
| | Hedges et al. (1994) | | | | Richey et al. (1990) | | | | Lewis et al. (1999) | | | | |
| Óbidos | 315.4 | 1,116.4 | 2097.1 | 12.2 | 24.5 | 35.0 | | | 970.0 | 960.0 | 0.12 | 840.0 | |
| Vargem Grande | 167.1 | 479.3 | 687.5 | 5.8 | 6.9 | 20.0 | | | | | | | |
| Rio Içá | 0.0 | 12.6 | 37.8 | 0.3 | 0.7 | 0.7 | | | | | | | |
| Rio Juruá | 0.0 | 9.5 | 50.5 | 0.1 | 0.6 | 1.2 | | | 26.6 | 40.0 | | 40.0 | |
| Rio Japurá | 0.0 | 18.9 | 53.6 | 0.5 | 1.7 | 1.6 | | | 55.2 | 61.2 | | 61.2 | |
| Rio Purús | 6.3 | 53.6 | 154.5 | 0.9 | 4.2 | 2.9 | | | | | | | |
| Manacapurú | 154.5 | 457.3 | 1,293 | 5.6 | 13.2 | | | | | | | | |
| Rio Negro | 0.0 | 0.0 | 0.0 | 0.0 | 10.7 | 1.6 | | | 153.8 | 41.5 | | 41.5 | |
| Rio Madeira | 53.6 | 324.8 | 337.4 | 2.4 | 3.5 | 5.0 | | | 169.0 | 169.0 | | 169.0 | |
| | | | | | Drake et al. (2021) | | | | | | | | |
| Óbidos | | | | | 25.5 | | | | 1,140 | | 16.8 | | |

with the high concentration of dissolved oxygen and relatively low DOC:DON ratios in the river, can promote aerobic decomposition and nitrification.

Collectively, these results represent the first detailed temporal evaluation of carbon and nitrogen abundance and speciation in the lower Tocantins River, a relatively understudied system of global significance. We find that the Tocantins River may contribute an additional 3% and 3.7% of DIC and nitrogen fluxes to the Amazon plume, respectively, when compared to Amazon River fluxes. Based on this study, we did not observe signatures of significant anthropogenic impacts on river biogeochemistry, though in situ production and metabolism may mask such effects. The anthropogenic pressures that the basin currently experiences in its headwaters have not been identified in the lower Tocantins, which is indicative of the system's resilience or may even be influenced by the Tucuruí dam. But there is no evidence that land use practices are contributing to excess nutrient loads promoting Sargassum development, as has been hypothesized (e.g., Y. Wang et al., 2020). Continued and comprehensive analyses using simulations are needed to determine the influence of human perturbations and El Niño phenomenon over the biogeochemical cycling in this rapidly changing basin. While changes in river discharge patterns have been observed over decadal time scales as a result of deforestation, no such time series exists for biogeochemical parameters not only for the Tocantins River, but many aquatic systems worldwide.

## Data Availability Statement

All data supporting the analyses and conclusions of this study are presented in the figures, tables, and Supporting Information S1 of this manuscript. A file containing all data are been uploaded to the repository and are available at https://doi.org/10.5281/zenodo.7749272. For flux estimates we used the Purdue LOADEST online simulator, available at https://engineering.purdue.edu/mapserve/LOADEST/.

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