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# Impact of rapid urbanization on stream water quality in the Brazilian Amazon

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#### Abstract

The most populous city of the world's largest watershed (Manaus, Amazon Basin, Brazil) is experiencing an extensive urban expansion since the early 1970s, with an attendant cost in environmental degradation. The upland area of the Manaus municipality is characterized by several streams. In this work, we aim to gradually measure the anthropogenic effect on water quality: we monitored three streams flowing over three zones: a preserved (where the streams take source), a peri-urban (where rural and leisure activities occur), and an urban area. From June 2013 to May 2015, we characterized the water gual-ity of these streams. Statistical analyses reveal peri-urban activity does not significantly impact the water quality. Indeed, when the disturbance remains space-, time- and intensity-limited, the streams have the capacity to assimilate the anthropo-genic pollution. However, looking at a seasonal finer scale, peri-urban activity slightly affects the natural pattern of water quality, but these changes remain moderated when compared to the original pattern of water quality. Over urban area, the water quality presents significant higher alkalinity, mineralization, turbidity, suspended material, biochemical and chemi-cal oxygen demands, and lower acidity and dissolved oxygen. These alterations originate with sewage deficiency, presence of landfill sites, enhanced leaching of upturned soil and domestic waste. The natural seasonal patterns of water quality are totally disturbed (inversion, intensification) in the urban area. During the wet season, enhanced rainfall in conjunction with human activity generates local seasonal processes of dilution (e.g. negative anomalies for most of the dissolved elements) and concentration (positive Mg and Fe anomalies). The latter can be linked with enhanced leaching during the rainy period (positive Mg and Fe anomalies) and nitrification activity in the urban area (positive NO<sub>3</sub> and negative NH<sub>4</sub> anomalies).

#### Introduction

In the last decades, the Amazon Basin faced an important augmentation of the population, with the population pass- ing from about 2.5 million in 1960 to 28 million in 2015 (FAO 2015; Tritsch and Le Tourneau 2016). This region has undergone an intense process of urbanization responsible for changes in the already observed land use and land cover patterns (Tritsch and Le Tourneau 2016; Feng et al. 2017).

The city of Manaus (Amazonas state, Brazil), almost on the equator (3.101 W, 60.025 S), at the confluence between two major rivers where the Amazon River originates and sur- rounded by forests, is the most populous city in the Amazon Basin.

Due to the implementation of an industrial district in the 70s, the last 40 years have seen huge population growth in Manaus, from about 300,000 residents in 1970 to more than 2 million in 2019 (IBGE 2019). Conjointly, the estimated urban area is 427 km<sup>2</sup> and represents 3.75% of the total municipality area. However, it shows growing rates superior to 100% in less than 20 years (Farias et al. 2017). In addi- tion, 15% of Manaus residents lived in "subnormal agglom- erations"—the Brazilian government's official definition of slums—(IBGE 2019). Inevitably, intense urbanization

induces local impacts, such as changes in atmospheric com- position (e.g. Souza et al. 2016) and the local

ecosystems, such as aquatic ones (e.g. Monteiro Júnior et al. 2015). The high population density, when is not followed by an adequate and minimum sanitation infrastructure, leads to the degrada- tion of water resources and their associated local biodiver- sity (Martins et al. 2017).

Therefore, anthropogenic pressures on the environment are high, especially on aquatic ecosystems. The expansion of the urban limits causes deforestation and alters the water quality, such as decreases in pH-value, dissolved oxygen, electrical conductivity, and total suspended solids (Ríos- Villamizar et al. 2017). The Manaus urban areas and its advancing show a visible degradation at the water resources (Ferreira et al. 2012). In peri-urban zones, they are used as family agricultural production and other gainful activities as housing and recreation. Ferreira et al. (2012) pointed them out as inappropriate for such purposes. Most of the local waterways (> 80%) flows into the Negro River (Fonseca et al. 1982). Studies conducted in the mainstream (*Negro* River) near Manaus have shown that part of the water from the basins has a compromised quality, and that provokes changes in the water quality of some stretches of the main- stream left bank (Pinto et al. 2009).

The Manaus urban and peri-urban areas have several hydrographic basins. These are characterized by extensive and complex streams network. The presence of a 10,000- ha natural reserve (the Adolpho Ducke Forest Reserve) on the outskirts of Manaus offers the opportunity to monitor streams from their original to urban environment. Here, we aimed to evaluate the anthropogenic impacts on stream water. The fieldwork required logistical efforts and human resources to organize high-frequency sample collection and associated laboratory analyses. It consisted in the joint 2-years monitoring of 13 distant places of 20 geochemical water parameters (pH, alkalinity, electrical conductivity, silica, dissolved cations: iron, sodium, potassium, calcium, magnesium and ammonium, and dissolved anions: chlo- ride, nitrate and phosphate, material in suspension, turbid- ity, watercolor, dissolved oxygen, biochemical and chemi- cal oxygen demands, and total iron). Hence, we intended to evaluate 3 streams (Barro Branco, Acará and Bolívia) over different urbanization levels: (i) preserved in the Adolpho Ducke Forest Reserve where the stream have their springs, (ii) peri-urban and (iii) urban.

#### Evaluation of the land-cover evolution for the Municipality of Manaus

For evaluating the land-cover evolution, we used the data provided by the MapBiomas project collection v4.1 (Pro- ject MapBiomas 2020). These data are freely available at https://mapbiomas.org/. This project aims the mapping and quantifying of land use of the Brazilian territory in an auto- mated way. MapBiomas maps are based on images from Landsat series of satellites (5-TM, 7-ETM + , and 8-OLI), providing data from 1985 to the present year (2020). The land use classification procedure used in collection 4.1 includes random forest algorithm and deep learning. Spa- tial resolution of the MapBiomas maps is 30 m. Accu- racy assessment was based on digital imagery products at 1:100,000, with a minimal overall accuracy of 85% (Project MapBiomas 2020).

Initially, the detailed MapBiomas classification includes 27 classes of land-cover (Project MapBiomas 2020). For present research purposes, we aggregated the original classes into three ones: natural, peri-urban and urban areas (Fig. 1), covering in average 95%, 3% and 2% of the Manaus municipality area for the 1985–2015 period, respectively. If the part of forested area remains larger than both other zones, the variations of these latter zones are greater than the forest zone. Indeed, between 1985 and 2015, the urban area has increased of 83%, while forested and peri-urban areas have decreased of – 7% and – 4%, respectively. The decadal analysis evidences the recent processes of urban expansion: forest was first converted into pasture between 1985 and 2005 (considered as peri-urban area) and then into urban during 2005–2015. In this direction, Tritsch and Le Tourneau (2016) studied the importance of the Amazon urbanization process and reported the 'discrete urbaniza- tion' of rural areas, and highlighted the need to better rec- ognize the distinct social and environmental problems of urban areas.

# Materials and methods

#### Study area

The monitored sites (Fig. 2) are part of the Tarumã-Açu Basin which have a size of 1,353,271 km<sup>2</sup> (Costa et al. 2013). Following the Köppen classification (Alvares et al. 2013), the climate is tropical monsoonal, with an annual average temperature of 26 °C, high relative humidity (84%) and yearly precipitation above 2000 mm. The geological domain of the watershed is represented by sediments of the Tertiary *Alter do Chão* Formation.

The dominant soils are yellow ferralsols rich in clay, acidic, with high aluminum content and low cation exchange capacity (Chauvel et al. 1987). Quantitative information on the local weathering has not been reported in the literature, but it is noteworthy to mention that tropical climatic conditions favor weathering activities. This studied watershed is located in the western part of Manaus. It is partially urbanized (18%), but the main land-cover remains the forest (69%) (Vasconcelos 2015). Spreading up to the urban part of Manaus, the process of

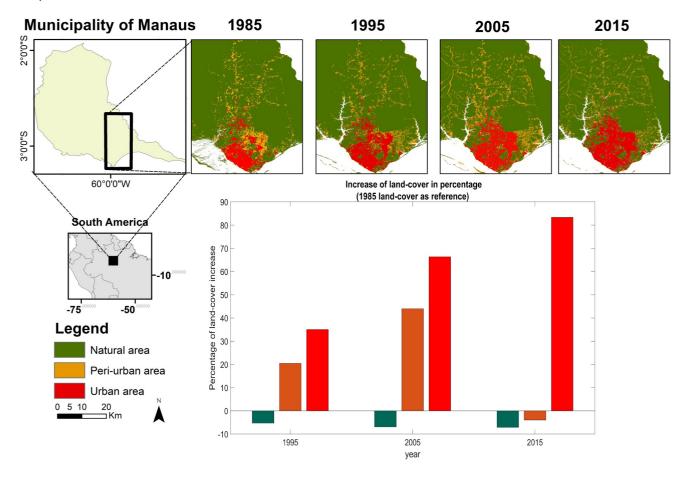


Fig. 1 Spatial analysis of land-cover evolution of Manaus between 1985 and 2015

urban expansion highly affects the Tarumã-Açu Basin. The studied sites were distributed through three distinct areas: *terra firme* forest (preserved, zone 1), rural properties (peri- urban, zone 2) and urban area (zone 3).

The forest area is part of the Adolpho Ducke For- est Reserve. Created in 1963, it is located at 26 km from Manaus in the Northern direction (3.102 S, 60.025 W). It contains the springs and their streams in natural conditions (no human impact). The studied streams are named Barro Branco, Acará and Bolivia streams. The Barro Branco and Acará are, respectively, Bolivia's sub-affluent and afflu- ent. The elevation range of sample sites from this zone is 55–69 m a.s.l.. The terra firme forest constitutes the main land-cover (Hopkins 2005). Litter and humic material cover the yellow ferralsols soil.

In the transition area between the forest and urban area, the occupation is practically restricted to rural proper- ties. Anthropogenic interference is limited to small con- structions and vegetation still covers a considerable area with natural and secondary forest, and plantations. Some owners raise small animals (chickens and ducks) around the streams for family consumption. They also alter the stream margins removing part of the riparian vegetation and change a part of their shore for local watering. Some places are also used for aquatic leisure. Other disturbances of the riverbeds occur when public authority opens parallel accesses and try to trespass streams by building galleries (concrete or metal tubes). This downtake pipe system has a block effect over the watercourses. Consequently, such installation creates at the upstream part an artificial lake with lentic characteristics, whereas the streams initially present predominant lotic characteristics. The elevation range of sample sites from zone 2 is 37–60 m a.s.l.

The urban area comprises several properties including illegal occupations with no basic sanitation works.

Veg- etation has been removed. The waste produced in illegal occupation is directly flushed into the streams. The poor service of the waste collection also contributes to the population exhaust their domestic waste (plastic, organic matter, glass...) in inappropriate places. These result in an additional source of water contamination due to the residential waste, which is carried via precipitation. The elevation range of sample sites is 30–33 m a.s.l.

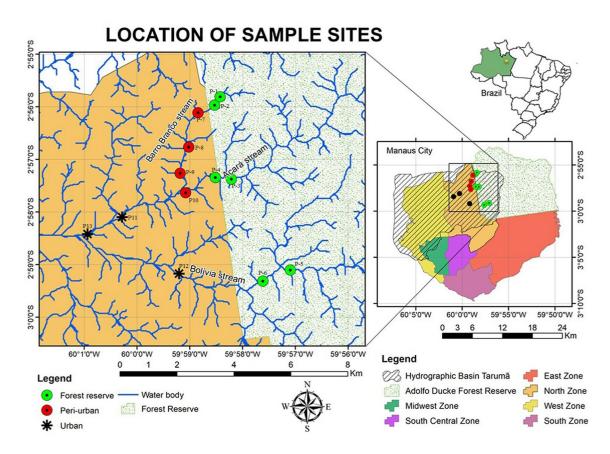


Fig. 2 Study area with the location of the sample collection sites

# Sample collection sites

A total of 13 samples sites are distributed along the streams that flow over the three zones (Fig. 2). The Bolivia Basin is a sub-basin of Tarumã-Açu Basin. The confluence of its tributaries (Acará) and subaffluent (Barro Branco) occurs outside the limits of the Ducke Reserve. We used the D8 algorithm (Jenson and Domingue 1988) to extract the three watersheds. The areas of the basins of Bolivia, Acara and Barro Branco in the Ducke Reserve are 11.23 km<sup>2</sup>, 17.73 km<sup>2</sup> and 2.70 km<sup>2</sup>, respectively. The discharges of the Barro Branco and Acara streams have a 2015–2016 averaged value of 0.38 ± 0.55 m<sup>3</sup> s<sup>-1</sup> and 0.16 ± 0.22 m<sup>3</sup>. s<sup>-1</sup>, respectively. They vary between 0.07 m<sup>3</sup> s<sup>-1</sup> and

17.34  $m^3 s^{-1}$ . The width at sample sites ranges from 1 to

15 m. We have 6 points over the preserved area (P1, P2, P3, P4, P5 and P6), 4 over the peri-urban area (P7, P8, P9 and P10) and 3 points in the urban area (P11, P12, and P13). The Barro Branco stream flows over the natural (P1 and P2) and peri-urban areas (P7, P8 and P9). The points collected along the Acará stream (P3, P4, P10 and P11) cover the three types of environments. The Bolivia stream covers natural (P5 and P6) and urban (P12 and P13) areas.

Also noteworthy is that P11 point (Acara stream) is not as much urbanized as P12 and P13 point (Bolivia stream).

# Physicochemical and chemical analyses

Twenty water quality parameters are considered in this study (Table 1). From June 2013 to May 2015, we collected water samples every 2 weeks from superficial waters. Hence, the original dataset covers two dry and wet seasons. We stored the collected water in polyethylene bottles-capacity 1000 mL and measured all variables in the laboratory located near col- lection sites. Table 1 presents the measurement methods and the used devices. We add here information about the used methods. Alkalinity was determined by titration using a digi- tal potentiometer with 0.02 N sulfuric acid solution ( $H_2SO_4$ ) for samples with pH higher than 4.3. The cations and ani- ons concentration and total solids in suspension have been determined by sample filtering of a specific water volume (500 ml). We used pre-weighed filters and Whatman GF/F glass microfiber filters (0.7 µm pore). Regarding oxygen analysis, we collected water samples in Winkler flasks. The samples for the dissolved

oxygen analysis were fixed at the time of collection with 1 mL of sodium azide (7.	5 g L <sup>-1</sup>	) and
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Table 1 List of assessed variables	Variable	Unit	Ab.**	Measurement methods, device
	Hydrogenionic potential	pН	pН	Direct measurement, S230 Seven Compact™
	Alkalinity	Mg L <sup>-1</sup>	Alk	Titration, digital potentiometer
	Electrical conductivity	$\mu$ S cm <sup>-1</sup>	EC	Direct measurement, Mettler Toledo™
	Total suspended solids	mg L <sup>-1</sup>	TSS	Gravimetric method
	Turbidity	NTU	Turb	Direct measurement, Alfakit turbidimeter
	Watercolor	HU	Color	Spectrophotometry of filtered water samples
	Dissolved oxygen	mg L <sup>-1</sup>	DO	Winkler's method with azide modification (APHA 2012)
	Biochemical oxygen demand	mg L <sup>-1</sup>	BOD	Winkler's method (APHA 2012)
	Chemical oxygen demand	mg L <sup>-1</sup>	COD	Standard water analysis method (APHA 2012)
	Total iron	mg $L^{-1}$	Fe-T	Spectrophotometry (APHA 2012), Shimadzu UV-1800
	Dissolved silica conc.*	mg L -1	SiO <sub>2</sub>	Molybdosilicate method (APHA 2012)
	Dissolved iron conc.*	mg L <sup>-1</sup>	Fe	Spectrophotometry (APHA 2012), Shimadzu UV-1800
	Dissolved calcium conc.*	mg L <sup>-1</sup>	Ca	Atomic absorption-Perkin-Elmer Model 1100B
	Dissolved magnesium conc.*	mg L <sup>-1</sup>	Mg	Atomic absorption-Perkin-Elmer Model 1100B
	Dissolved sodium conc.*	mg L -1	Na	Atomic absorption-Perkin-Elmer Model 1100B
	Dissolved potassium conc.*	mg L <sup>-1</sup>	Κ	Atomic absorption-Perkin-Elmer Model 1100B
	Dissolved ammonium conc.*	mg L <sup>-1</sup>	$NH_4$	Spectrophotometry (APHA 2012), Shimadzu UV-1800
	Dissolved chloride conc.*	mg L <sup>-1</sup>	Cl	Spectrophotometry (APHA 2012), Shimadzu UV-1800
	Dissolved nitrate conc.*	mg L <sup>-1</sup>	$NO_3$	Spectrophotometry (APHA 2012), Shimadzu UV-1800
	Dissolved phosphate conc.*	mg L -1	PO4	Spectrophotometry (APHA 2012), Shimadzu UV-1800

Conc.\*=concentration, Ab.\*\*=abbreviation

1 mL of manganese sulfate (118.3 g  $L^{-1}$ ). To estimate the biochemical oxygen demand, we covered the samples vials with aluminum foil immediately after collection to prevent light from entering, and incubated for five days. Chemical oxygen demand was determined using potassium perman- ganate as an oxidizing agent (APHA 2012).

# **Statistics**

The data were analysed with standard statistical descriptors such as mean and standard deviation. Regarding the assess- ment of the data homogeneity, we used the one-way analysis of variance (ANOVA) to consider whether data from the dif- ferent areas have a common mean for each studied variable. For each parameter, we examined the differences between the means over each zone through the Tukey's range test at  $p \le 0.01$  (Lark 2008).

We also perform multivariate statistics through a princi- pal component analysis (PCA). The advantages of the PCA are that it is a non-parametric method of dimension reduc- tion (Wunderlin et al. 2001). We perform two preliminary analyses to examine the suitability of the observed data for PCA analysis: the computation of the Kaiser–Meyer–Olkin (KMO) criterion and the Bartlett test. The KMO criterion is a measure of sampling adequacy that indicates the pro- portion of variance that is common variance, i.e. caused by underlying factors. A high score (close to 1) indicates that the PCA should be useful. If the KMO test score is less than 0.5, the PCA will not be useful. The Bartlett test of spheric- ity indicates whether correlation matrix is an identity matrix. This indicates that variables are unrelated. A significance level close to 0 indicates that there are significance relation-ships among variables. To perform the PCA, we normalize the data. Hence, the correlation and covariance matrices coincide.

# Results

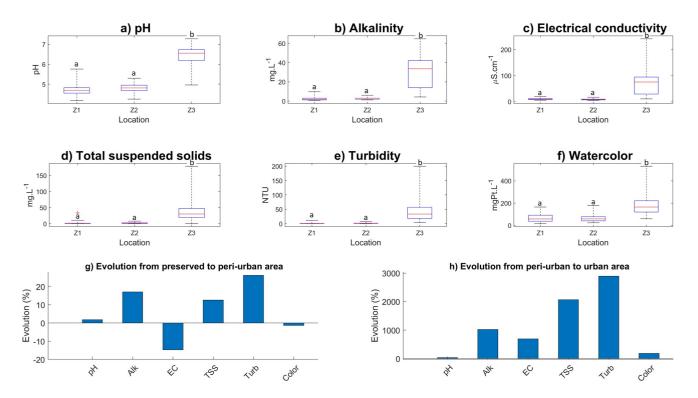
# Descriptive analysis of observed variables

Table 2 regroups descriptive statistics of all the studied variables and the recommended concentrations for Class 2 waters according to resolution No. 357/2005 of the National Environmental Council (MMA 2005). All the computed and displayed values have been rounded to one decimal place.

Among the environmental variables, the pH values measured in the preserved and peri-urban areas are simi- lar and acidic with mean values of  $4.7 \pm 0.2$  and  $4.8 \pm 0.2$ , respectively (Fig. 3a). However, in the urban area, pH values increase ( $6.4 \pm 0.4$ ). Similarly, the alkalinity pre- sents low values in the primary and peri-urban area with averaged values of  $2.3 \pm 1.2$  mg L<sup>-1</sup> and  $2.7 \pm 0.9$  mg L<sup>-1</sup>, whereas the urban area has the highest alkalinity records ( $30.6 \pm 16.4$  mg L<sup>-1</sup>) (Fig. 3b). The EC observed in the pre- served and peri-urban areas remains low and similar with

<pre>Furthan an Sd** Range an Sd** Range 0.2 4.3-5.3 0.9 1.2-6.1 2.5 4.7-17.4 1.4 0.2-8.0 1.0 0.3-7.8 3 3.3-7.5 0.8 0.3-7.8 0.8 0.0-5.4 0.1 0.1-0.4 0.1 0.1-0.4 0.1 0.1-0.4 0.1 0.0-0.2 0.3 0.1-1.9 0.3 0.1-1.9 0.3 0.1-1.9 0.3 0.1-1.9 0.3 0.1-1.9 0.3 0.1-1.9 0.3 0.1-1.9 0.3 0.1-2.3 0.0 0.0-0.7 0.0 0.0-0.7 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.0-0.1 0.0 0.00011 0.0 0.00011 0.0 0.00011 0.0 0.00011 0.0 0.00011 0.0 0.00011 0.0 0.00011 0.0 0.0 0.00011 0.0 0.00011 0.0 0.0 0.00011 0.0 0.00011 0.0 0.</pre>													
Mean         Sd**         Range         Wet M.***         Dry M.****         Mean         Sd**         Range           4.7         0.2         4.2–5.8         4.7         4.7         4.8         0.2         4.3–5.3           2.3         1.2         0.6–9.8         2.3         2.3         2.3         2.7         0.9         1.2–6.1           1.6         3.5         0.2–337         1.7         1.4         1.4         0.2         4.3–5.3           1.1         1.4         0.2         1.7         1.4         1.8         1.4         0.2–8.0           1.1         1.4         0.2–11.7         1.0         1.4         1.4         0.2–8.0           1.1         1.4         0.3–11.7         1.0         1.4         1.8         1.4         0.2–8.0           1.1         1.4         0.3–11.7         1.0         1.4         1.0         0.3–7.8           65.1         34.7         15.8–164.8         65.8         64.0         64.3         31         23.6–178.8           0.6         0.6         0.6         0.7         0.6         0.8         0.3–5.4         0.7           1.4         1.2         0.5         0.6			Peri-ur	pan				Urban					Brazilian Stand-
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$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	-33.7 1.7	1.4	1.8	4	0.2 - 8.0	1.9	1.6	38.9	29.7	0.5-178.7	41.2	35.2	< 500
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	-11.7 1.0	1.4	4.1	1.0	0.3-7.8	1.4	1.5	42.7	34.5	3.9-199.7	47.6	35.1	< 100
		64.0	64.3		23.6-178.8		66.1	181.5	85	59.1-531.1	191.2	165.3	<75
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		6.1	5.7		3.3-7.5		5.6	2.9	1.4	0.3-7.9	29	2.8	<5
31.6 $16.2$ $5.0-727$ $32.5$ $30.0$ $29.9$ $15.3$ $4.3-72.5$ $0.2$ $0.1$ $0.1-1.8$ $0.2$ $0.2$ $0.1$ $0.1-0.4$ $2.4$ $0.5$ $1.4-5.2$ $2.4$ $2.5$ $0.1$ $0.1-0.4$ $2.4$ $0.5$ $1.4-5.2$ $2.4$ $2.5$ $2.6$ $0.4$ $1.6-3.5$ $0.2$ $0.0$ $0.0-0.3$ $0.2$ $0.1$ $0.1-0.4$ $1.6-3.5$ $                                                -$		9'0	0.8		0.0-5.4		0.6	25	1.0	05-4.5	2.5	2.6	5
		30.0	29.9		4.3-72.5		29.0	41.4	3.0	5.6-72.7	426	39.4	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		0.2	0.2		0.1-0.4		0.2	15	0.6	0.2-4.0	1.4	1.5	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		2.5	2.6		1.6-3.5		2.7	3.5	0.9	1.5-5.9	34	3.7	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.1	02		0.0-0.2		0.2	03	0.1	0.0-1.1	0.3	0.3	<03
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	I	ı					I	4.6	2.3	0.2-9.3	4.3	4.9	
0.4         0.3         0.0-2.4         0.4         0.4         0.4         0.3         0.1-1.9           0.1         0.1         0.1         0.0-0.4         0.1         0.1         0.0         0.5         0.0-0.5           0.3         0.1         0.1-0.7         0.3         0.3         0.0         0.7         0.0-0.7           0.8         0.2         0.3-1.8         0.8         0.8         0.1         2.3         0.1-2.3           0.0         0.0         0.0         0.3         0.0         0.7         0.0-0.7           0.8         0.2         0.3-1.8         0.8         0.8         0.1         2.3         0.1-2.3           0.0         0.0         0.0         0.0         0.0         0.0         0.0-0.1	ī	ı	0.2		0.0-1.0		0.4	0.6	0.5	0.1 - 2.7	0.6	0.5	
0.1         0.1         0.1         0.0         0.4         0.1         0.1         0.1         0.0         0.5         0.0         0.5         0.0         0.5         0.0         0.5         0.0         0.5         0.0         0.5         0.0         0.5         0.0         0.5         0.0         0.5         0.0         0.5         0.0         0.7         0.0         0.7         0.0         0.7         0.0         0.7         0.0         0.7         0.0         0.7         0.0         0.7         0.0         0.7         0.0         0.7         0.0         0.7         0.0         0.7         0.0         0.7         0.0         0.7         0.0         0.7         0.0         0.7         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0         0.0 <th>-2.4 0.4</th> <td>0.4</td> <td>0.4</td> <td></td> <td>0.1-1.9</td> <td></td> <td>0.4</td> <td>62</td> <td>3.6</td> <td>1.0-18.1</td> <td>6.0</td> <td>6.5</td> <td></td>	-2.4 0.4	0.4	0.4		0.1-1.9		0.4	62	3.6	1.0-18.1	6.0	6.5	
0.3         0.1         0.1-0.7         0.3         0.3         0.0         0.7         0.0-0.7           0.8         0.2         0.3-1.8         0.8         0.8         0.1         2.3         0.1-2.3           0.0         0.0         0.0         0.0         0.0         0.0         0.0-0.1		0.1	0.0		0.0-0.5		0.1	2.2	1.5	0.2 - 5.4	20	2.4	
0.8 0.2 0.3-1.8 0.8 0.8 0.1 2.3 0.1-2.3 0.0 0.0 0.0-0.1 0.0 0.0 0.0 0.0-0.1		0.3	0.0		0.0-0.7		0.3	3.5	2.9	0.2 - 10.6	28	4.6	< 3.7
0.0 0.0 0.0-0.1 0.0 0.0 0.0 0.0 0.0-0.1		0.8	0.1		0.1-2.3		0.8	7.4	4.7	1.5-27.2	67	8.6	< 250
		0.0	0.0		0.0-0.1		0.0	2.0	2.6	0.0-13.0	2.1	1.7	<10
0.0 0.0-0.3		0.0	0.0	0.0	0.0-0.3	0.0	0.0	0.1	0.1	0.0-0.0	0.1	0.1	

Var\*= variable; \*\*Sd=standard deviation, Wet M.\*\*\*=average during the wet season, Dry M.\*\*\*\*=average during the dry season



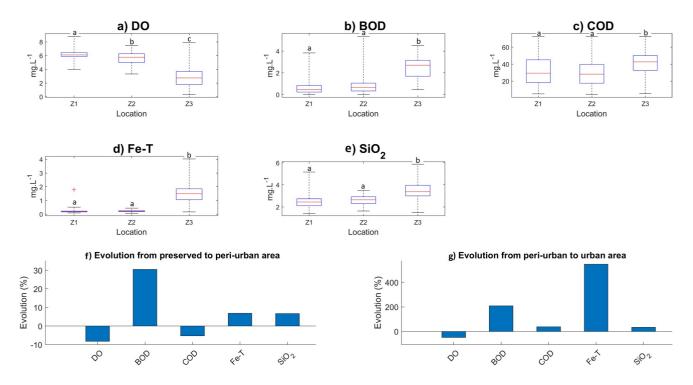
**Fig. 3** Boxplot diagrams of **a** pH, **b** alkalinity, **c** electrical conductiv- ity, **d** total suspended material, **e** turbidity, **f** watercolor according the three zones. Boxplots with the same letter are not significantly dif-ferent by Tukey's test at  $p \le 0.01$ , **g** evolution from preserved to peri- urban area, **h** evolution from peri-urban to urban area

mean values of  $10.2 \pm 3.0 \ \mu\text{S cm}^{-1}$  and  $8.7 \pm 2.5 \ \mu\text{S cm}^{-1}$ , respectively. In the urban area, we observe higher values ( $68.7 \pm 37.5 \ \mu\text{S cm}^{-1}$ ) (Fig. 3c). Regarding the TSS (Fig. 3d), the preserved and peri-urban areas show low values with an average of  $1.6 \pm 3.5 \ \text{mg L}^{-1}$  and  $1.8 \pm 1.4 \ \text{mg L}^{-1}$ , respec- tively, while TSS presents the highest concentrations in the urban zone ( $38.9 \pm 29.7 \ \text{mg L}^{-1}$ ). Conjointly, the turbidity (Fig. 3e) remains low in the preserved area ( $1.1 \pm 1.4 \ \text{NTU}$ ) and in the peri-urban zone ( $1.4 \pm 1.0 \ \text{NTU}$ ). It remains in the urban zones superior to 40 NTU ( $42.7 \pm 34.5 \ \text{NTU}$ ). Regarding the watercolor, the preserved and peri-urban areas present the lowest values (<  $65.1 \ \text{HU}$ ), whereas urban area shows the higher records ( $181.5 \pm 85.0 \ \text{HU}$ ) (Fig. 3f). The 6 previous studied variables (Figs. 3a–f) statistically conclude to differentiate natural and peri-urban areas from urban area.

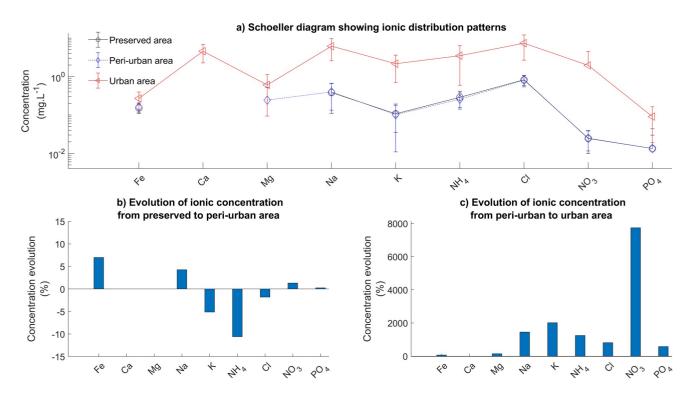
The DO concentration (Fig. 4a) remains higher in the preserved  $(6.2 \pm 0.6 \text{ mg L}^{-1})$  and in the peri-urban  $(5.7 \pm 0.8 \text{ mg L}^{-1})$  than in the urban  $(2.9 \pm 1.4 \text{ mg L}^{-1})$  zone. The averaged BOD values at natural and peri-urban areas are  $0.6 \pm 0.6 \text{ mg L}^{-1}$  and  $0.8 \pm 0.8 \text{ mg L}^{-1}$ , respectively. The highest BOD (Fig. 4b) value is observed in the urban zone  $(2.5 \pm 1.0 \text{ mg L}^{-1})$ . Regarding COD (Fig. 4c), preserved and peri-urban zones present similar concentrations with aver- aged values of  $31.6 \pm 16.2 \text{ mg L}^{-1}$  and  $29.9 \pm 15.3 \text{ mg L}^{-1}$ , respectively. The highest concentrations are observed in the urban area  $(41.4 \pm 13.0 \text{ mg L}^{-1})$ . The Fe-T concentration (Fig. 4d) varies in average from  $0.2 \pm 0.1 \text{ mg L}^{-1}$  in the pre- served area to  $1.5 \pm 0.6 \text{ mg L}^{-1}$  in the urban area. The mean values of SiO<sub>2</sub> concentrations (Fig. 4e) in the protected and peri-urban areas are  $2.4 \pm 0.5 \text{ mg L}^{-1}$  and  $2.6 \pm 0.4 \text{ mg L}^{-1}$ , respectively. The urban area presents the highest averaged SiO<sub>2</sub> concentration ( $3.5 \pm 0.9 \text{ mg L}^{-1}$ ). Statistical analysis shows that each previous parameter allows differentiating natural and peri-urban areas from urban area, except for the DO parameter whose Tukey test concludes that each zone has a DO mean significantly different from the others.

The Schoeller diagram designed for the cations (Fe, Ca, Mg, Na, K, NH<sub>4</sub>) and anions (Cl, NO<sub>3</sub>, PO<sub>4</sub>) (Fig. 5) gives the ionic signature of the three zones. From a general point of view, the ionic concentrations remain stable between the preserved and the peri-urban area (variations lower than

- 11%), but highly augment in the urban area (averaged vari- ation between preserved and peri-urban area above 1700%). Among the cations, in most of the collection points in the reserve (> 90%), the Ca and Mg concentrations are below the detection limit (20  $\mu$ g L<sup>-1</sup>). In the peri-urban area, the Ca remains on low levels below the detection limit. The cations concentrations have the following order in the pre- served and the peri-urban area: Na > NH<sub>4</sub> > Fe > K, Mg and Ca, while on the urban zone, the cations order was Na > Ca > NH<sub>4</sub> > Mg > K > Fe. Considering the concentra- tion in the preserved area as a reference, between natural



**Fig. 4** Boxplot diagrams of **a** DO, **b** BOD, **c** COD, **d** Fe-T, **e** SiO<sub>2</sub> according to the three zones. Boxplots with the same letter are not signifi- cantly different by Tukey's test at  $p \le 0.01$ , **e** evolution from preserved to peri-urban area, **f** evolution from peri-urban to urban area



**Fig. 5 a** Schoeller diagram: distribution of the cations (Fe, Ca, Mg, Na, K, NH<sub>4</sub>) and anions (Cl, NO<sub>3</sub>, PO<sub>4</sub>) according to the three zones, **b** Evo- lution of ionic concentration from preserved to peri-urban area, **c** Evolution of ionic concentration from peri-urban to urban area

and urban area, sodium, ammonium, potassium concentra- tions increases by more than 1000%. Unlike the Ca, the Mg is slightly detected in the peri-urban area. In the urban area, these cations concentrations have distinct behaviours: the Mg stays at low stages ( $0.6 \pm 0.5 \text{ mg L}^{-1}$ ), whereas the Ca concentration increases ( $4.6 \pm 2.3 \text{ mg}$  L<sup>-1</sup>). Over natural and peri-urban area, the dissolved Fe is stable ( $0.2 \pm 0.0 \text{ mg L}^{-1}$ ), while its concentration augments to  $0.3 \pm 0.1 \text{ mg L}^{-1}$  over urban area. Regarding the anions, independently from the area, the anions order remains Cl > NO<sub>3</sub> > PO<sub>4</sub>. In the urban area, the chloride concentration reaches an average 7.4 ± 4.7 mg L<sup>-1</sup>. Considering the concentration in the pre-

served area as reference between the natural and urban area, chloride, and phosphate concentrations increase of more than 500%. Nitrate augments in higher proportion (above 7800%). Noteworthy is that even if the augmentation per- centages are elevated, ionic concentrations are still not extreme compared to industrial contaminations for example.

# Principal components analysis

For reasons of high lacunas presence or low variations of some variables, we only compute the PCA on the follow- ing variables: pH, EC, Color, Alk, Turb, DO, BOD, COD, Fe-T, Fe, Na, NH<sub>4</sub> and Cl. The KMO measure of sampling adequacy for PCA was 0.90. The Bartlett test of spheric- ity indicates that with a given significance level of 0.05, the assumption of sphericity is tenable. Hence, it makes sense to apply the PCA. The PCA results show that most of the variation (77%) in the explanatory parameters can be reduced to the first two principal components. First andsecond principal components respectively represents 66% and 11% of the observations.

Figure 6a highlights that DO is negatively correlated with all other variables through the first component of the PCA. It is the only parameter that decreases with the increase of degree of urbanization. Regarding the second component, turbidity, Fe, Color, BOD and COD are negatively correlated with the pH, alkalinity, EC and ions used in the PCA (NH<sub>4</sub>, Cl and Na). Water samples from preserved and peri-urban areas clustered in close proximity to each other and were distributed on the negative side of PC1 in Fig. 6b, and urban waters clustered on the positive side of PC1 (with the excep- tion of one point) and presented a diffuse cloud.

# Seasonal analysis

Based on the PCA, regrouping the score of observations by zone and then studying the score of the averaged values during wet and dry season (Fig. 6c), stresses the signifi- cant impact of climate seasonality on urban water quality. Indeed, for both other zones, we observe that these average values are slightly sensitive to the climatic seasons. How- ever, focusing on urban water quality, we observe shifts fol- lowing both axes PC1 and PC2, between averaged value in the dry and the wet season.

Going further, for each variable, we compute anomalies for each zone, and present the seasonal averages of nor-malized values (Fig. 7a–c). Apparent discrepancies can be noted between Table 2 and Fig. 7a–c, but these are due to the display with one decimal place in Table 2. The same Y-axis scale has been conserved along the three graphics to

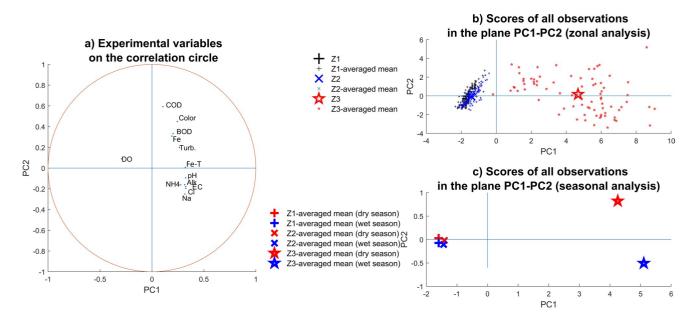


Fig. 6 PCA results: a Experimental variables on the correlation circle, b Score of all observation in the plane PC1–PC2 (zonal analysis), c Score of all observation in the plane PC1–PC2 (seasonal analysis)

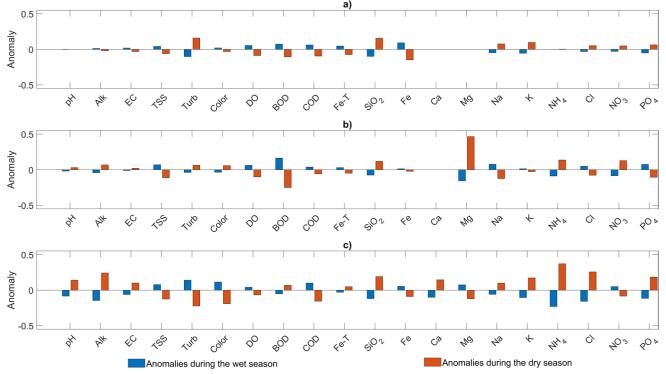


Fig. 7 Seasonal anomalies of normalized values, for each studied parameter over the three zones: a preserved area, b peri-urban area, c urban area

facilitate the comparison between the areas. From a general point of view, seasonal variations of water quality are much important in the urban zone. Although we have observed that peri-urban activity does not affect the water quality for the studied variables, the comparison between Fig. 7a and b shows that seasonal patterns for Mg and BOD are modi- fied. For the former, no natural pattern could be defined over natural environment (undetectable concentration), whereas, over peri-urban area, Mg shows distinct negative and posi- tive anomalies during wet and dry seasons, respectively. For the latter, we observe an intensification of the natural sea- sonal pattern. Other variables present slight seasonal varia- tion for both areas. The comparison of Fig. 7a, c highlights disturbances in the seasonal pattern: inversion (e.g. BOD, Turb, NO<sub>3</sub>) and intensification (e.g. pH, TSS, Color, COD, K, NH<sub>4</sub>, Cl, PO<sub>4</sub> and SiO<sub>2</sub>).

# Discussion

The analysis of each variable reflects the homogeneity of water quality between preserved and peri-urban zones. The PCA (Fig. 6b) confirmed the water quality from preserved and peri-urban areas are similar, homogeneous and different from urban water quality that is heterogeneous. All the vari- ables submitted to the Tuckey test (Fig. 3a–f and Fig. 4a–e) showed significant differences in the mean between urban zone and both other zones. Consequently, urban area heavily and distinctly affects the water quality, whereas peri-urban activities slightly impact on water quality.

#### Water quality in the preserved and peri-urban area

Typical values of pH, EC, and alkalinity of surface water from *terra firme* forest of Central Amazon are pH values between 4 and 5 (Pascoaloto 2001; Horbe et al. 2005; Fer- reira et al. 2012), low EC values below 10  $\mu$ S cm<sup>-1</sup> (Horbe et al. 2005; Nascimento and Silva 2010; Franken and Vital 2016), and low alkalinity below 5.0 mg L<sup>-1</sup> (Melo et al. 2006). Soil geochemistry, bedrock, vegetation and organism activities, and atmosphere influence the chemical composi- tion, and consequently the pH, EC, and alkalinity of surface water (Walker 1995; Tundisi and Tundisi 2000). Observed acidity is due to the presence of dissolved humic acids (Leenheer and Santos 1980). These humic substances origi- nate with forest litter decomposition. The low conductivity and alkalinity are associated with the dominant dystrophic soil in Central Amazon. Here, characteristics of superficial waters from the preserved and peri-urban areas originate local soil quality (high acidity, low concentration of major ions, and low alkalinity) (Fig. 3a–c).

Turbidity, TSS, and watercolor are linked variables. Local studies conducted about *terra firme* forest streams in Central Amazon reported low values of turbidity ranging between 4 and 19 NTU, and TSS varying from 1 to 43 mg  $L^{-1}$  (Pas- coaloto 2001; Melo et al. 2006; Nascimento and Silva 2010; Ferreira et al. 2012). Watercolor values ranging between

28.5 and 627 HU were already recorded in the literature for Amazonian blackwater rivers and streams (Ríos-Villamizar et al. 2020a). Our measurements of these variables are in agreement with literature values.

Oxygen parameters (DO, COD, and BOD) were conclu- sive to statistically discriminate preserved and periurban areas from urban area. The DO, COD, and BOD measured values in two former areas were similar to values observed in forest streams from the Western and Central Brazilian Ama- zon (Pascoaloto 2001; Melo et al. 2006; Ríos-Villamizar et al. 2011, 2013, 2020b). With a temperature close to 25 °C, the oxygen saturation point was 8.3 mg L<sup>-1</sup> (Wetzel and Likens 1991). Hence, although streams are aerated, the measured DO remained below the saturation point. Oxygen sources are likely due to diffusion caused by natural or windinduced flow turbulence. Nutrient shortage and forest foli- age that reduces the light entrance, minimize photosynthetic autotrophic activity in forest streams. The COD remains ele- vated because of the high content in organic matter where the humic substances are the most representative. Unlike DO and COD values, the BOD averages remained low in the preserved and peri-urban areas because of pristine forest and low human intervention.

All ionic concentrations remain very low in the reserve area. These are not linked to an important dilution, but they are characteristic from the streams waters in upland forest area in Central Amazon (Santos et al. 1984; Horbe et al. 2005). Among the cation, in the forest, the Mg and Ca were not in sufficient quantity to be detected. Santos et al. (1984) reported that both components are almost inexistent in the Negro River Basin (Central Amazon). In the same direction, Furch (1984) reported low concentration for both cations (< 0.038 mg L<sup>-1</sup>) for forest streams from Central Amazon. Low ionic concentration reflects soil characteristics (Sioli 1985). This low K, NH<sub>4</sub>, NO<sub>3</sub> and PO<sub>4</sub> concentrations are also linked with plants assimilation that uptake the associ- ated nutrient (Ferreira et al. 2006).

Regional characteristics also explain the spatial vari- ability of dissolved chemical species. The rocks weathering of the *Alter Do Chão* Formation contributes to high SiO<sub>2</sub> concentrations (Walker 1995). The measured SiO<sub>2</sub> concent rations are similar to ones reported in other central Ama- zonian streams (Horbe et al. 2005). Chloride is attributed to dissolved marine aerosols in the rainwater and evaporative rocks (Gaillardet et al. 1997). However, the values observed in these areas are at minimum 65% lower than concentra- tions reported by Furch (1984).

Besides, local specificities (natural streams flowing near an urban pole) can also explicate differences in some dis- solved element concentrations. For instance, sodium col- lected in a natural environment presents almost twice the concentrations of values reported by Furch (1984). This positive anomaly could be associated with the addition of anthropogenic sodium. The Ducke Reserve is presently under pressure from the urbanization that has now been set- tling around it. Cecchini et al. (2016) showed that Manaus has a polluting atmospheric plume with a 100 km radius and this impacts local rain physical quality. Hence, urban aerosol could also cause changes in the water quality in the preserved area. Further studies should consider joint moni- toring of the geochemistry from rain and natural streams to investigate the impacts of urban aerosol on water quality streams.

Finally, regarding physico-chemical characteristics, the similar values observed in the peri-urban and preserved areas indicates, that, when the disturbance remains space-, time- and intensity-limited, the forest streams have the capacity to assimilate the anthropogenic pollution. This absorption is achieved through dilution or removal through biological or physico-chemical processes. In the same lines, Pinto et al. (2009) investigated the water quality of the mainstream that flows in front of Manaus (*Negro* River) and concluded that in spite of the human contribution from its urban tributar- ies, the *Negro* River still maintains its ability for diluting pollutants.

#### Urban impact on water quality

From a global point of view, our results stresses that urban environment significantly alters water geochemistry. In this study, studied streams flow into the residential part of Manaus and investigated pollution is mainly linked with domestic pollution. Cisneros (2011) describes the main polluting agents linked with such a pollution type: acids, disinfection by-products (residual chlorine), emerging pol- lutants (endocrine disrupters, personal care, and pharma- ceutical products), fecal pathogens, heavy metals, hydro- carbons, nutrients, nonmetal and anions, biodegradable and non-biodegradable organic matter and pesticides. Several local studies relate the causes of such degradation sewage deficiency (Cleto Filho and Walker 2001; Dos Santos et al. 2006; Melo et al. 2006; Nascimento et al. 2007; Ferreira et al. 2012), presence of managed and non-managed landfill site (Dos Santos et al. 2006; Santana and Barroncas 2007; Miyagawa et al. 2019), enhanced leaching of upturned soil or domestic waste (Melo et al. 2006), intensified weathering in the urban area (Craul 1985). The sewage deficiency is linked with a poor quality of domestic sewage and the irregular occupation of the streams banks without sewage connection. Several alterations of monitored variables render sewage deficiency. Indeed, regarding the Brazilian law, the sewage watercolor cannot exceed 75 HU (MMA 2005). With such norm and the natural elevated watercolor (average of 65.1 HU), when entering the urban area, watercolor should have decreased or remained stable. Going further, Fig. 5a-c shows that urbanisation strongly alters the ionic distribution. Indeed, between pre- served and urban areas, the concentration significantly aug- ments, except for the SiO<sub>2</sub> that remains stable (+ 34%). The NO<sub>3</sub> and Ca performed the greatest increases since the Ca was undetectable in preserved area. Such augmentation of ionic concentration has been related in various local stud- ies such as Dos Santos et al. (2006), Melo et al. (2006) or Nascimento and Silva (2010). Observations from the latter study reported a high heterogeneity over the urban area (e.g. EC varying from 6.5 to 267.0  $\mu$ S cm<sup>-1</sup>) with higher values encountered in the most urbanized locations. This observed increase of dissolved elements, as well as that of the other chemical parameters (EC, pH and alkalinity), corroborates that untreated sewage is discharged into watercourses. Domestic wastewater includes dissolved and suspended organic and inorganic solids, nutrients (nitrogen, phospho- rus), chloride and grease (Pescod 1992). Untreated sewage also provides comfortable conditions for bacteria prolif- eration. (Couceiro et al. 2006) reported that DO, BOD and COD reflect the modifications resulting from anthropogenic eutrophication induced by untreated effluent. Hence, domes- tic sewage explains the increase of BOD between peri-urban and urban areas (> 200%). In the same direction, the COD augmented from peri-urban to urban area (+ 38%), display- ing higher concentrations variations of oxidizable organic matter in the urban area. The DO concentrations decreased in half, locally reaching situations close to anoxia, favour- ing the development of other bacteria, highlighting spatial heterogeneity of the urban water pollution as also reported by Melo et al. (2006). For instance, the DO recorded at P12 (Fig. 2) presented an averaged value of 1.6 ± 0.7 mg L<sup>-1</sup>. Such observed low DO is due to the local specific configu- ration: (i) two sewage stations at upstream and (ii) at the sample location, two hydraulics structures (weir and cul- vert) that turn a lotic into lentic environment. Hydraulics structures modify flow characteristics, and therefore affect the water quality. Most research focuses on oxygen trans- fer at hydraulic structures (see the review by Baylar et al. (2010). Hydraulic structures, such as dams, can limit natural reaeration processes and concentrating pollutants, whereas others, such as weirs, can be used as aeration devices by cre- ating turbulent conditions Gulliver et al. (1998). Moreover, Pagotto et al. (2000) reported that the material used for the structure can reduce the amount of hydrocarbons and metals through the retention of particulate pollution.

Besides, the augmentation of TSS (+ 2000%), SiO<sub>2</sub> and Fe-T concentrations (+ 34% and + 500%, respectively) reflects intensified processes of soil leaching and erosion over the urban area. Domestic sewage usually presents low contents of SiO<sub>2</sub> and Fe-T in and SiO<sub>2</sub> is a geogenic com- ponent. Hence, the increase in both ionic concentrations is probably an indication of the rocks weathering of the *Alter Do Chão* Formation and the leaching of ferralsols soils. Indeed, on-going urban development includes modifications of the land cover and soil properties. In this direction, the large TSS increase can be associated with leaching. The run- off of tropical rainfall favors the dragging into the streams of the upturned soil resulting from urban development and the abandoned waste.

The study of water quality in the urban area highlights that the stream water flows are not sufficient to cover the disturbances caused by urban activity. Unlike the peri-urban streams, the capacity of maintaining natural water quality is altered. Ferreira et al. (2012) reported this phenomenon persists when the urban streams return in the natural envi- ronment. Besides, Santana and Barroncas (2007) studied the water and sediments quality of streams located around a landfill site located in the peri-urban area of Manaus. They highlighted that the aquatic environment has the capacity to dilute the landfill leachate and hence reduce the impacts caused by the landfill. Dos Santos et al. (2006), who also monitored the watercourses around this landfill, stressed the difficulty of chemically differentiating pollution from waste- water or from the landfill. Further studies need to be concentrated on emerging pollutants, i.e. complex organic chemi- cal compounds such as endocrine disrupter compounds and personal care and pharmaceutical products. For reasons of complex and costly equipment, these are not usually moni- tored. Research efforts should also be concentrated towards studying biological risks for human and aquatic ecosystem.

#### Seasonal variations of water quality

The tropical monsoonal climate of Central Amazon is char- acterized by two distinct seasons: rainy (November–May) and dry (June–October). Important heavy rainfall (81% of the total rain) and high relative humidity (86%) character- ize the former, whereas the latter shows little rainfall (19% of the total rain) and less relative humidity (78%). Tem- peratures remain almost constant along the year. Figure 6c highlights that seasonal effects over natural and peri-urban areas remain small when compared to ones over urban area. This is partly due to the statistic processing: the PC1 and PC2 are built to maximize the dataset variance, which is higher in the urban zone. The detailed representation of the normalized seasonal patterns (Fig. 7a–c) confirms seasonal patterns of water quality are more pronounced over urban area. It also points out (i) within a zone, each parameter has a specific seasonal pattern; (ii) unlike urban activity, peri-urban activity slightly affects the seasonal pattern of water quality (Fig. 7a, b).

Climate variations slightly influence the water qual- ity of Amazonian forest stream (Furch 1984; Horbe et al. 2005; Ferreira et al. 2016). Forest activity depends on the season (Luizão et al. 2009): it produces litter during dry period, whereas, during wet season, elevated temperatures and higher precipitations favor organic nutrients cycling and matter decomposition. Therefore, it can explain positive BOD anomaly during wet season. Heavy rainfall enhances erosion and soil leaching, leading to positive anomaly of TSS, Fe-T and dissolved Fe (the predominant soils are yel- low ferralsols) during the rainy period. It also generates seasonal processes of dilution as also observed by Ríos- Villamizar et al. (2020b), explaining negative anomaly of turbidity and all the dissolved elements (except for Fe) dur- ing the wet season.

Although we have shown that peri-urban activity does not affect the water quality, it slightly affects the seasonal pat- tern of water quality. However, these changes remain moder- ated when compared to the original pattern of water qual- ity (Fig. 7a, b). Some dissolved elements are not anymore submitted to dilution phenomenon during the wet season (Na, K, Cl and PO<sub>4</sub>). This can be associated with exter- nal sources linked with anthropic activity (agricultural and leisure practices). Regarding Mg seasonal variations in the peri-urban area, one may note that the observed concentra- tions remain low with (81% of the measures under detection limit and 80% of the detected measures under 0.4 mg L<sup>-1</sup>). The increase in positive BOD anomaly during the wet season suggests that anthropic sources such as local domestic efflu- ents combined with heavy rainfall enhance eutrophication and biological activity (Couceiro et al. 2006). Conversely, the increase in negative BOD anomaly during the dry sea- son over peri-urban shows forested environments have the capacity to maintain a higher biological activity during the dry season.

Besides, seasonal patterns in the urban area are different and more marked when compared with the ones in the pre- served area (Fig. 7a, c). Climatic variations in conjunction with urban activity generate seasonal processes of dilution and concentration that modify (inversion, intensification) locally in time and space the water quality (Dos Santos et al. 2006). The higher magnitude of anomalies can be associated with higher observed values as described in "Descriptive analysis of observed variables". Despite elevated concen- trations of dissolved elements, also reported in other local study (Dos Santos et al. 2006), during the wet season, a dilution effect can be observed for all the dissolved elements (negative anomaly), except for Fe, Mg and NO<sub>3</sub>. The aug- mentation of Fe concentration during wet seasons suggests the importance of soil leaching. Soil impermeabilization favors the leaching and the soil cannot act anymore as a filter (Scalenghe and Ajmone-Marsan 2009). Hence, additional sources of Mg could result from rainfall runoff that takes out the domestic waste from precarious dwellings (Melo et al. 2006). Urban rainfall takes also out upturned soil into the streams, explaining positive TSS, turbidity, and watercolor anomalies during the wet season. The positive NO<sub>3</sub> and negative NH<sub>4</sub> anomalies during the rainy period can be associ- ated with enhanced nitrification process in the urban area. Also, during the rainy season, others localized concentration phenomena could result from a higher sewage discharge and an alteration of the natural hydrologic connectivity (due to artificial modification of riverbeds, some streams and reser- voirs should be only connected during wet season).

#### Water quality management: monitoring network

This study points out that urbanization significantly affects the water quality. Therefore, there is a crucial need into monitoring the water quality all over the municipality ter- ritory (natural, peri-urban and urban areas) for questions of eco-hydrologic (e.g. Martins et al. 2017), public health (e.g. Kulinkina et al. 2016), among others. The recent develop- ment of IoT-based (Internet-of-things-based) allows merging in situ sensors, remote sensing for real-time water quality monitoring solution. Through this technology, several smart cities are experimenting a local and real-time water qual- ity monitoring (e.g. Chen and Han 2018). For management facilities, all here measured parameters (a total of 20) should also be resumed in a clear index such as the Water Pollution Index (WPI, Milijašević et al. 2011). This index should be adapted to local context: since Ca and Mg concentrations in Amazonian forest streams are usually low (< 0.05 mg L<sup>-1</sup>) (Furch 1984; Santos et al. 1984; Walker 1995), higher values may be robust indicators of anthropogenic pressures.

Regarding Brazilian legislation (MMA 2005), our study shows that the urban streams do not success in respecting the official concentration limits in terms of watercolor, Turb, DO Fe, NH<sub>4</sub>, NO<sub>3</sub> and pH (Table 2). Noteworthy is that pH, watercolor and DO from natural waters are outside of Brazilian standards. This suggests the Brazilian legisla- tion for water quality is not adapted for streams of Central Amazon as also reported by Rocha da Silva et al. (2019). The evidenced large spatio-temporal variability for all vari- ables suggests that there is a need in implementing a dense monitoring network over urban area. To comply with the law, local policies should identify the places of the uncon- trolled entrance of sewage, garbage, or upturned soil, and take steps to remedy the problem. Besides these preventive measures, Nascimento and Silva (2010) propose the empty- ing of the streams banks and the restoration of the riparian forest. To institute a sustainable development regime, water management studies (e.g. Qin et al. 2014) suggest: (1) an upgrade of the wastewater infrastructure and facilities in line with the urbanization, to improve their nitrogen and phos- phorus removal efficiencies; (2) an encouragement of both regulation and economic incentives policies to reduce the pollution; (3) several policies to increase the environmental awareness of local population; (4) a better interplay between planners and policymakers to make decisions on integrated planning for socio-economic development and wastewater facilities improvement.

# Conclusions

To assess the impact of rapid urbanization on surface water quality, we monitored for two years, twenty water quality variables, including pH, EC, dissolved elements concentra- tions and oxygen parameters, over three zones around the Amazonian largest urban-pole (Manaus, Brazil): preserved, peri-urban and urban.

Statistical analyses first evidence peri-urban activity does not significantly affect the water quality. Indeed, when the disturbance remains space-, time- and intensity-limited, the streams have the capacity to assimilate the anthropogenic pollution. Hence, the water quality of peri-urban and natu- ral streams presents similar characteristics of high acidity and COD, low mineralization, alkalinity, turbidity, concen- tration in suspended sediment and BOD. There are mainly related to local geology (*Alter do Chão* Formation), humic substances

(originating with litter decomposition) covering yellow ferralsols. Looking at a seasonal finer scale, climate variations induce a discrete seasonal pattern of water quality. Peri-urban activity slightly affects this water quality pattern. However, these changes remain moderated when compared to the original pattern of water quality.

In the urban area, the water quality presents higher alkalinity, mineralization, turbidity, material in suspen- sion, biochemical and chemical oxygen demands, and lower acidity and dissolved oxygen. These alterations originate with sewage deficiency, presence of managed and non-managed landfill site, enhanced leaching of upturned soil or domestic waste and intensified weathering in urban area. The large variability of all parameters in the urban zone, especially of oxygen parameters, highlights a spatial heterogeneity of the urban water pollution. Seasonal pat- terns of water quality are totally disturbed over urban area (inversion, intensification). During wet season, enhanced rainfall in conjunction with urban activity generates pronounced seasonal processes of dilution (e.g. negative anomalies for most of the dissolved elements) and concen- tration (e.g. positive TSS, turbidity and watercolor anoma- lies). The latter can be linked with enhanced leaching during the rainy period (positive Mg and Fe anomalies) and nitrification activity in the urban area (positive NO<sub>3</sub> and negative NH<sub>4</sub> anomalies). Other localized concentration phenomena during the wet period can also be associated with higher sewages discharge and alterations of the natu- ral hydrologic connectivity.

To institute sustainable urban development, sanitation policy measures should be taken to ensure the protection and monitoring of water resources all over the municipality terri- tory (natural, peri-urban, and urban areas). Further research should consider the implementation of a broad-based moni- toring network (combining loT-based technology and in situ sensors, detecting emerging pollutants) and the development of local indicators to detect environmental changes in better and faster ways.

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#### Declarations

Conflict of interest The authors declare no conflict of interest.

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