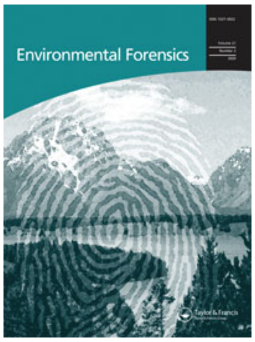

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Water chemistry and estimation of background levels of elements in surface water bodies from a protected area in the vicinity of Fe deposits, Southeastern Amazon

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ABSTRACT

This paper aimed to provide the knowledge of water chemistry and quality and background values of the elements in surface waters around the Fe-ore deposits of N3 and N4WSul of Serra dos Carajás, Brazil. Water samples were collected from 17 monitoring points monthly/quarterly between 2013 and 2016 and the elemental analyses were carried out using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The waters are slightly acidic to slightly alkaline in nature and are classified into "good" and "optimum" water quality category. Seasonal variation impacted water quality, with significantly higher content of metals (such as Fe_d, Fe_t, and Al_d) during the rainy period that is due to more intense surface-runoff and leaching. Comparing with CONAMA 357/05/WHO limits, nonconformities were mainly observed for pH, Fe and Mn, and in some cases for Al_d, Zn_t, Cu_d, Cd_t and Zn_t, and were significantly higher in the N4WSul area than in the N3. Although, Fe and Mn mostly enter the water bodies from catchment weathering, the poor correlation between Fe and Mn indicated that their source and transport processes are different. In fact, elevated Mn_d concentrations associated with low DO content in the dry period are explained by a reductive dissolution of manganese oxides via bacterial decomposition of OM. The background threshold values (BTVs) of elements were estimated by the upper 95% simultaneous limit (USL95; using ProUCL software) and the median ± 2 Median Absolute Deviation (mMAD) method, while the former was considered as the most suitable method for defining BTVs. The BTVs for Al(d), Fe (d), Mn and Zn are mostly exceeding the maximum limits stipulated by the legislation. However, since these areas are located in a protected region, these values are seen as representative of the natural conditions of the study area and reflect geogenic influence.

KEYWORDS

Water quality; baseline threshold values; iron mines; Serra dos Carajás; Carajás National Forest

Introduction

Surface water quality is a matter of serious environmental concerns today as it is directly related to quality of life (Oliveira-Filho and Parron 2007; Muniz et al. 2011). The contamination of river/stream water resources is a direct consequence of population growth and increase of mining, industrial, and agricultural activities (Sahoo et al. 2012, 2013). This has become a major problem in densely urbanized areas (Tiburtius, Peralta-Zamora, and Leal 2004; Demirak et al. 2006) and during the last decades, there has been increasing demand for water quality monitoring. This is also true for mineralized areas where multiple natural anomalous concentrations of different metals in water and soil may derive from weathering and erosion of local rocks and dispersion of metals as well as of mining activities (Salomão et al. 2018; Sahoo et al., 2019a).

In mineralized areas, the local/regional background concentrations of metals can be higher than national background/guidelines. This is not fully considered in the regulations of environmental agencies which in general do not take in account in their definition of maximum metal contents with the strong local influence of geology and mineralogy (Reimann and Garrett 2005; Rodrigues et al. 2013; Sahoo et al., 2019a).

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Situated in the southeastern Amazonia, the Carajás province is a major mining province which contains some of the largest (world-class) iron ore deposits, located in Serra Norte, Serra Sul, Serra Leste and Serra São Félix (DOCEGEO 1988). In Serra Norte, the iron ore deposits of N3 and N4WSul occur in the catchment area of the Parauapebas river and were not being mined before the sampling campaigns. The Carajás province has also active Cu (Au), Ni, and Mn mines and its geological characteristics favor the anomalous concentration of some chemical elements in surface water and soil. On the other hand, the N3 and N4WSul areas selected for study are located in the Carajás National Forest, a protected area covered by preserved dense tropical forest and not subjected to other significant anthropogenic effects than mining activities. Therefore, from an environmental perspective, studies on the characteristics of the surface water around the N3 and N4WSul deposits are necessary, since they should serve as a basis tool for making current diagnoses and assess future environmental impacts in order to protect water resources as well as promote sustainable development for this region. In particular, the definition of geochemical background values of the metallic elements in the area of occurrence of the Carajás iron mines is of extreme relevance to establish policies/guidelines related to environmental monitoring and risk (Salminen and Tarvainen 1997).

A number of methods have been used to define background levels in surface waters, including geochemical analogues and statistical approaches (Smith, Alexander, and Schwarz 2003; Galuszka 2007; Osté, Klein, and Zwolsman 2011; Shah et al. 2012; Arpine and Shahnazaryan 2016; Schneider et al. 2017; Salomão et al. 2018; Sahoo et al. 2019a). However, it is crucial to select the most suitable method to define site-specific background limits to avoid any unrealistic assessment (Salomão et al. 2019; Sahoo et al. 2019a,b). The Environmental Protection Agency (EPA 2013) recommends specific upper limits such as upper 95% tolerance limits (UTLs), defined as the upper 95% confidence interval around the 95th percentile be used for calculating the background threshold values (BTV)s using the ProUCL software (EPA 2013; Daniel 2015). This technique has both parametric and non-parametric methods and it has also ability to work with datasets consisting of non-detected (NDs) with multiple detection limits (DLs) (EPA 2013). Therefore, this technique has many advantages over conventional methods. It has been widely employed in many regions of the USA and considered for decision-making. In addition, currently, the median ± 2 Median Absolute Deviation (mMAD) method is also widely used for deriving BTVs (Reimann et al. 2005; Salomão et al. 2018; 2019; Sahoo et al. 2019a,b). Furthermore, the understanding of geochemical processes that are taking place in the water-sediment interface is important because they exert a large influence in the speciation and mobility of several elements (Sahoo et al., 2019a). In the studied area, it is particularly relevant to understand the behavior of Fe and Mn, because these elements are dominant in surface waters of Amazon region (Salomão et al. 2018; Sahoo et al., 2019a).

In the present work, chemical analyses of surface waters from the N3 and N4WSul areas in Serra Norte were carried out to: (i) evaluate water quality and its seasonal variability; (ii) understand the fate and mobility of Fe and Mn; (iii) and estimate the baseline threshold values of metals in surface water bodies of these areas. This evaluation will provide support for the establishment of baseline values of critical metals in preserved areas of southeastern Amazon and contribute for the definition of water quality standards and management of water resources.

Description of the study area

Hydrography and physiography

The N3 and N4WSul areas are situated in the catchment of the Itacaiúnas river and are drained by the left margin tributaries of the Parauapebas river (Figure 1). The Carajás National Forest is a protected area that cover a large part of the Serra dos Carajás, a plateau of ca. 700 to 800 m height that stands out in the regionally dominant lowlands. The Parauapebas river source is located near the Serra Arqueada to the south of Serra dos Carajás. It is one of the main tributaries of the Itacaiúnas river and flows from south to north. In the studied area, its main left margin tributaries are the Taboca, Jacaré and Gelado streams. The main active mines of iron, copper, nickel, and manganese are located in the Itacaiúnas catchment and mostly in the Serra dos Carajás or in its vicinity. The Carajás National Forest is covered mostly by dense and primitive tropical rain forest with occurrences of savanna vegetation (canga) over the areas of ferruginous lateritic crusts. There is a strong seasonal variation in the local pluviometry. Historical data (1982 to 2015) of rainfall obtained from a meteorological monitoring station located near N4 iron mine at Carajás demonstrate that there is a raining season from November to April and a comparatively dry

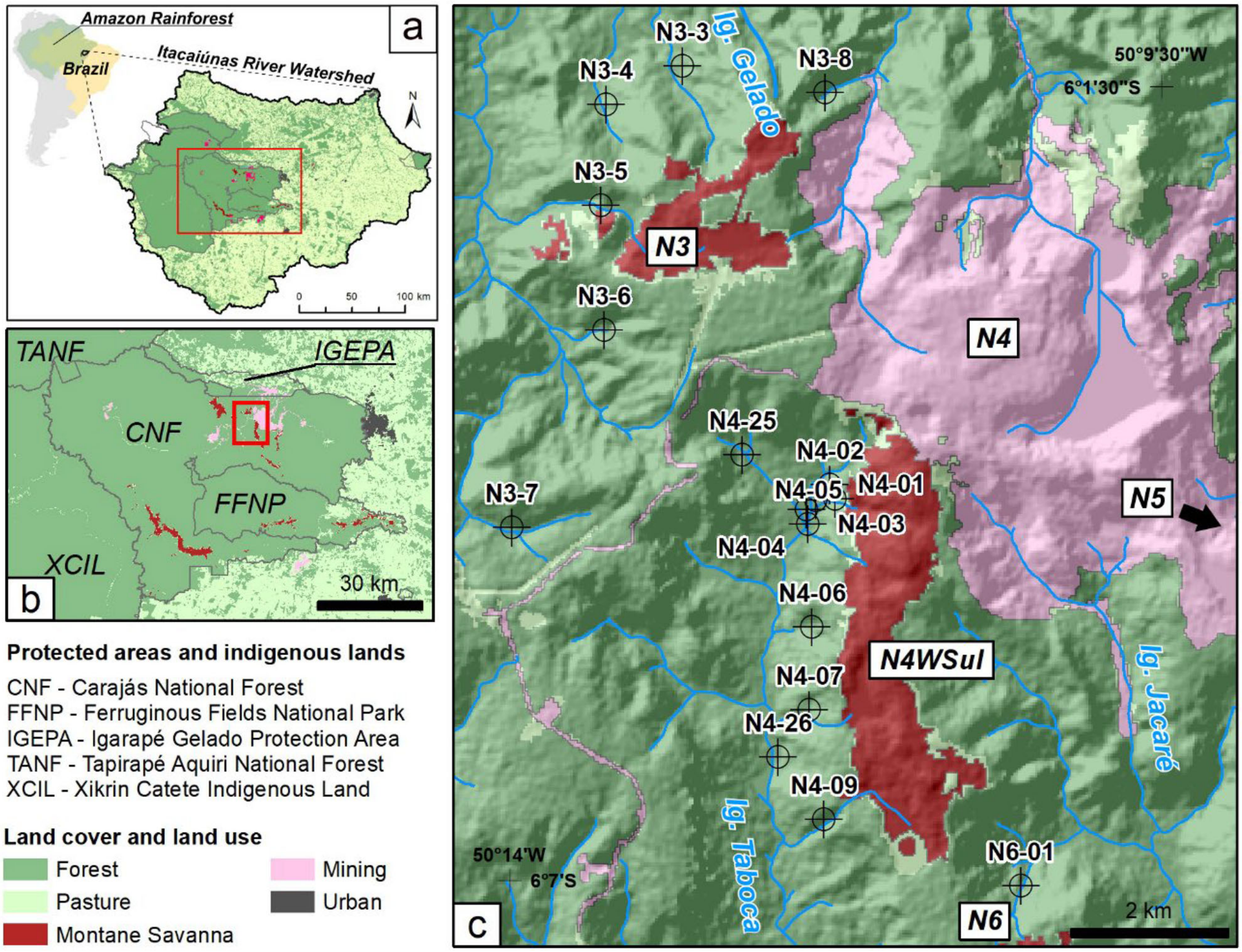

Figure 1. Study area map showing the land use and land cover patterns and the sampling locations of surface water collected around N3 and N4WSul areas, which are located in the Itacaiúnas River Watershed in the southeastern Brazilian Amazon. *Source*: (Souza-Filho et al. 2016; Vasquez et al. 2008).

season from May to October. The contrast between the rainfall average during December to April and June to September is remarkable and the water flow in the Itacaiúnas basin shows extreme variations in between these two periods of the year (Silva Júnior et al. 2017). The rainy period concentrates ca. 80% of the annual rainfall. As a consequence, most of the right margin tributaries of the high course of the Parauapebas river are intermittent during most years along the dry season. This behavior is also observed in other first order tributaries of the Itacaiúnas catchment.

Local geological setting

The Carajás province is composed of Archean and subordinate Proterozoic units (Machado et al. 1991), partially covered by Tertiary lateritic formations and Quaternary alluvial deposits. In the Serra dos Carajás, the main exposed Neoarchean unit is the Grão Pará Group (Beisiegel 1982), divided in a metavolcanic sequence (Parauapebas and Cigarra formations) and banded iron formations (BIFs; Carajás Formation). The metavolcanic rocks are mostly mafic to intermediate in composition. The Carajás Formation is covered by ferruginous laterites which are at the origin of the huge iron deposits. Mafic dikes and sills cut or were emplaced in the mentioned Neoarchean units. The Paleoproterozoic siliciclastic sequence of the Águas Claras Formation overlap discordantly the Grão-Pará Group (Nogueira, Truckenbrodt, and Pinheiro 1995). The Serra dos Carajás Granite crosscuts the previously mentioned units (DOCEGEO 1988; Machado et al. 1991).

The occurrences of the Carajás Formation are covered by lateritic ferruginous crust devoid of forest vegetation. The main iron mines of that area are the N4 and N5 mines. The N4WSul deposit was an extension of the N4 mine elongated in the north-south direction, with a length of 8 km and 200 meters thick. In the period of water sampling for the present study, the N4WSul deposit was not being mined but recently the mining activities in the area were initiated and are in progress nowadays. The N3 iron deposit is located to northwest of N4WSul deposit (Figure 1). It is 2.7 km long and has an area of 3.5 km^2.

In terms of hydrogeology, the study area is characterized by the presence of rocks that generally have low permeability except in areas of intense shearing (VALE/AMPLO, 2010). The chemical composition of the water is strongly dependent of the dominant lithology. During the raining season, the run-off is prominent and the water composition reflects the situation of the catchment area in terms of erosion, generation of suspended sediments and metal availability.

Materials and methods

Sampling and analytical techniques

Surface water samples were collected at 17 monitoring points (Figure 1) in the vicinity of N4WSul (11 points, including one point from N6) and N3 (6 points) Fe-ore deposits, which were supposedly free of significant anthropic effects and seen as representative of pristine or 'natural' areas. The monitoring points were placed in the proximity of the N4WSul and N3 clearings in areas considered as pristine. The sampled areas are situated in the watersheds of the Gelado, Taboca and Jacaré streams (Figure 1). For N4WSul, the monitoring was carried out in a monthly basis in the period from December 2013 to January 2015, while for N3 it was undertaken in quarterly campaigns during the period from May 2014 to May 2016. This was done in order to obtain enough data to carry out the statistical treatments to evaluate the effects of the seasonal variations in surface waters. The differences in the sampling periods of the two studied areas were due to logistical difficulties of access to N3 and to the beginning of mining activities in N4WSul. The chemical analyses and physico-chemical parameters measurements were performed by SGS-Geosol Laboratórios Ltda. The water samples were collected from the surface of the streams with a stainless steel bucket and then transferred to polypropylene and dark glass bottles using a mug. The samples to determine total concentration of metals were acidified using 0.5 M nitric acid ($pH < 2$) (ultra-pure, Merck) immediately after collection, while the samples to determine dissolved concentration of metals were filtered through Whatman^{TM} GD/X Nylon Syringe Filters with pore size 0.45 µm and then acidified with HNO_3. All sample bottles were sealed and stored at 4 °C after collection until dispatched for analysis (APHA 2005; USEPA 2013). Physicochemical parameters such as temperature, pH, dissolved oxygen (DO), electrical conductivity, turbidity, and total dissolved solid (TDS) were determined in situ with a Water Quality Monitoring System (HANNA, Model No. 98194). The methods used to determine the inorganic and organic parameters are in accordance with the following standards and guidelines (NBR 9897/87; NBR 9898/87; CETESB 1988; APHA 2005; ISO/IEC 17025: 2005; SMEWW). The total (t) and dissolved (d) concentrations of metals (Ag, Al, As, B, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, U, V and Zn) were determined by inductively coupled plasma mass spectrometry (ICP-MS). Anions (fluoride, chloride, nitrate, and sulfate) were measured by ion chromatography. For total phosphorous (TP), samples were digested using sulfuric acid at $pH < 2$ and then analyzed colorimetrically. Turbidity was determined by a nephelometer and total dissolved solids (TDS) by the gravimetric method. BOD was measured after 5 days incubation period at 20 °C using Titration method (SMEWW 5210 B) and Thermotolerant Coliforms estimated by membrane filter method (SMEWW 9222 B-D). In order to validate the analysis of ICP-MS, the limit of detection (LOD) and limit of quantification (LOQ) were evaluated. The LOD was defined as 3 times the standard deviation (SD) of the 5 blank (de-ionized water) measurements and LOQ was similarly defined as 10 times the SD of the 5 blank measurements (Choi et al. 2019 and reference therein). This shows that most of the metals analyzed had detection limits close to 1 ppb. For method calibration, working standard solutions were prepared from multi-element stock standard solution (10 ppm) of CertiPUR using 1% ultrapure grade of HNO_3 and Milli-Q water (18 MΩ). Ultrapure HNO_3 (20%) was used to clean all glassware and containers and, finally rinsed with Milli-Q ultrapure water for several times and oven-dried prior to use. The calibration method was checked by running a 100 µg/L of standard solution (CertiPUR) after every 10 samples. The results indicated a good agreement between the referred and observed values (between ±2 to ±10%) for all metals. The precision was also checked by several duplicate analyses, which standard deviation ranged from ±0.5 to ±10%.

Water quality evaluation

Evaluation of the surface water quality was made following Brazilian surface water guidelines presented in the CONAMA Resolution No. 357/2005, Class II (BRASIL 2005) and the Water Quality Index (WQI). The WQI was calculated using 9 parameters: DO (weight = 0.17), BOD (w = 0.10), E. coli (w = 0.15), temperature (w = 0.10), total N (w = 0.10), pH (w = 0.12), total P (w = 0.10), total solid (w = 0.08) and turbidity (w = 0.08), following the Eq. (1) presented in CETESB (2016).

$$WQI = \prod_{i=1}^{n} q_i^{W_i} \tag{1}$$

The WQI values are then converted into rankings by using the categorization scheme of CETESB (2003) as follows: 0–25 (very bad); 26–50 (bad); 51–70 (reasonable); 71–90 (good); 91–100 (excellent).

Statistical treatment and estimation of background threshold values

The basic statistical analyses include descriptive statistics (minimum, maximum, and mean), normality test and a non-parametric version of the ANOVA (Kruskal-Wallis test). They were carried out on water quality parameters using Statistical Package for the Social Sciences (SPSS) software package 16. The latter was performed to test significant difference ($p > 0.05$) of water quality parameters between the rainy and dry periods and between the N3 and N4WSul areas. Box-and-whisker plots were generated in R (R Core Team, 2018) to better visualize the distribution of water quality parameters.

Background threshold values (BTVs) of metals (Ag, Al, As, B, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, U, V and Zn) were computed using the ProUCL software version 5 developed by the United States Environmental Protection Agency (EPA 2013). The schematic diagram of this method is presented in Figure 1 (Supplementary material). Following this method of ProUCL (EPA 2013), the distribution of the dataset has been determined and then the outliers identified. Once the outliers were removed, BTVs were calculated using parametric statistical methods if their appropriate distribution fits to normal, lognormal or gamma distributions. If none of these distributions appeared to be appropriate, a nonparametric method was employed. Depending upon the sample size, data distribution and data variability, one of the following upper limits was used to estimate BTVs: upper 95% simultaneous limits (USL95), upper 95% tolerance limits of the 95th percentile (UTL95-95), upper 95% prediction limit (UPL95) (EPA 2013). This was made for each point individually and for the set of points of each study area. In these calculations, the outliers were first examined. In this estimation, some parameters presented more than one limit of quantification—LQ, in which case the non-parametric method of estimation of the BTV was applied. For those that presented a single limit, the normal or gamma distribution method was used, preferably the first one, when applicable. Additionally, the median ± 2*median absolute deviation (mMAD) method was applied to derive baseline/background threshold values following recommendations in the literature (Reimann et al. 2005, Reimann et al. 2018; Reimann and Garrett 2005; Salomão et al. 2018, 2019; Sahoo et al. 2019b). A requirement for using mMAD technique is that for a given dataset, the element should follow a normal distribution (Reimann et al. 2018), unusually seen in geochemical dataset. Hence, to use this method, the data were transformed to common logarithm ($\log_{10}$) scale (Eq. (2)), where $x_{(i,j)}$ is the raw dataset (usually in mg L^{-1}) and $y_{(i,j)}$ is the $\log_{10}$ transformed data. Then the results were back-transformed by raising 10 to the power of the obtained result.

$$y_{(i,j)} = \log_{10}\left[x_{(i,j)}\right] \tag{2}$$

The median absolute deviation (MAD_j, Eq. (3)), calculated with a constant of 1.48, leads to a consistent estimation of the underlying standard deviation (Reimann et al. 2018).

$$MAD_{(y)} = 1.48 \cdot median_i \left| y_i - median_j(y_j) \right| \tag{3}$$

Then, finally the results were back-transformed according to the Eq. (4) in order to derive the upper baseline limit.

$$mMAD = 10^{(median_{(y)} + \ 2 \ \cdot [MAD_y])} \tag{4}$$

Results

General characteristics of surface water

The water quality parameters obtained from N3 and N4WSul areas during the rainy and dry season in 2013–2016 along with their respective guidelines or legislation limits are tabulated in Table 1 (full chemical data are provided in Table 1, Supplementary material) and selected parameters are visually presented in Figure 2. The Kruskal-Wallis test shows that there are significant differences (p-value $>$ 0.05) of water quality parameters between the dry and rainy seasons and between the N4WSul and N3 areas (Table 2). The water temperature was significantly higher in the dry period (23.2 to 32.3 °C) than in the rainy period (23.1 to 27.7 °C). The temperature variation in the surficial water is quite similar to that registered in the air. The pH values varied widely among sampling points ranging from 4.12 to 9.72 in N4WSul

Table 1. Descriptive statistics of water quality parameters in the dry and rainy seasons from N3 and N4WSul areas.

			N4WSul								N3							
		CONAMA 357/2005 Class II	Rainy				Dry				Rainy				Dry			
Parameters	Unit		Min	Avg	Max	>%*	Min	Avg	Max	>%*	Min	Avg	Max	>%*	Min	Avg	Max	>%*
Alkalinity	mg·L^{-1}		<1.5	6.942	45.00		<2	9.69	98.70		6.00	7.269	13.30		<2	6.923	38.70	
ColiTh	UFC.100ml^{-1}	1000	<1	197.46	5650.0	0	<1	44.56	176.0	0	<1	162.7	780.00	0	<1	57.207	250.00	0
EC	µS.cm^{-1}		5.70	33.71	152.00		5.77	28.37	174.0		3.80	37.58	196.00	0	5.65	14.264	56.00	0
BOD	mg·L^{-1}	5	<2	2.43	3.00	0	<2	2.18	3.00	0	3.00	3.00	3.00		<2	2.655	3.00	
DO	mg·L^{-1}	5	4.67	7.72	8.68		4.26	7.74	9.41		5.49	7.79	8.87		5.75	7.971	9.25	
pH		6 to 9	4.80	6.66	9.72	30	4.12	6.17	7.70	37.7	5.77	6.92	7.53	5.5	5.01	6.542	7.80	27.5
TDS	mg·L^{-1}	500	5.00	22.29	77.00	0	5.00	29.05	126.0	0	5.00	22.83	117.00	0	4.00	15.448	30.50	0
TSS	mg·L^{-1}		2.00	9.63	50.80		2.00	9.679	38.00		11.00	11.80	21.50		2.00	9.121	14.00	
Temp (air)	°C		22.9	27.52	31.0		25.76	28.32	32.0		28.0	29.24	31.00		23.8	29.56	34.3	
Temp (water)	°C		22.7	25.47	29.7		23.20	26.13	30.0		23.10	25.0	26.70		23.7	26.09	32.3	
Turbidity	NTU	100	0.37	4.892	33.40	0	0.34	4.282	28.6	0	0.30	2.271	5.53	0	0.30	2.537	5.76	0
TP	mg·L^{-1}	0.1	<0.01	0.019	0.060	0	<0.01	0.016	0.14	0	0.020	0.023	0.080	0	<0.01	0.020	0.040	0
NO_3	mg·L^{-1}	10	<0.1	0.696	4.550	0	<0.1	1.237	11.30	0	<0.1	0.464	1.810	0	<0.1	0.810	4.000	0
NO_2	mg·L^{-1}	1	0.020	0.043	0.270	0	0.020	0.030	0.17	0	0.050	0.054	0.066	0	0.020	0.043	0.120	0
NH_3-N	mg·L^{-1}		<0.02	0.081	0.370		<0.02	0.056	0.23		0.060	0.078	0.220		<0.02	0.074	0.270	
SO_4^{2-}	mg·L^{-1}	250	<1	1.614	14.60	0	<1	1.758	7.16	0	<1	1.490	5.62	0	<1	1.284	8.80	0
F^-	mg·L^{-1}	1.4	<0.05	0.109	0.530	0	<0.05	0.091	0.100	0	<0.05	0.058	0.170	0	<0.05	0.222	1.270	0
Cl^-	mg·L^{-1}	250	<1	2.750	73.60	0	<1	2.182	7.57	0	<1	1.473	4.18	0	<1	4.576	85.50	0
Al_d	mg·L^{-1}	0.1	<0.005	0.109	3.520	12.6	<0.005	0.040	0.210	11.7	0.050	0.100	0.840	5.5	<0.005	0.052	0.130	6.8
Ba_t	mg·L^{-1}	0.7	<0.006	0.021	0.130	0	<0.006	0.017	0.121		<0.01	0.012	0.020		<0.006	0.011	0.040	0
B_t	mg·L^{-1}	0.5	<0.02	0.100	0.200	0	<0.02	0.054	0.200		<0.02	0.200	0.200		<0.02	0.139	0.200	0
Cd_t	mg·L^{-1}	0.001	<0.001	0.001	0.011	7.5	<0.001		<0.001	0	<0.001		<0.001		<0.001		<0.001	0
Pb_t	mg·L^{-1}	0.01	<0.01	0.012	0.100	6.3	<0.01	0.011	0.030	3.7	<0.01	0.010	0.010	0	<0.01	0.010	0.020	3.4
Co_t	mg·L^{-1}	0.05	<0.009	0.009	0.010	0	<0.009	0.009	0.010		<0.01		<0.01		<0.009	0.010	0.010	0
Cu_d	mg·L^{-1}	0.009	<0.003	0.009	0.051	27.8	<0.003	0.008	0.087	13.2	<0.009		<0.009	0	<0.003	0.008	0.020	6.8
Cr_t	mg·L^{-1}	0.05	<0.01		<0.01	0	<0.01		0.020		<0.01	0	<0.01		<0.01	0	<0.01	0
Fe_d	mg·L^{-1}	0.3	<0.05	0.238	3.380	11.3	<0.05	0.156	2.330	9.4	0.100	0.140	0.540	0	<0.05	0.090	0.240	0
Fe_t	mg·L^{-1}	0.3#	<0.05	0.678	13.700	27.8	<0.05	0.421	7.580	17	0.100	0.139	0.340	11	<0.05	0.135	0.480	6.9
Mn_d	mg·L^{-1}		<0.025	0.084	0.840		<0.025	0.091	0.830		<0.025	0.107	0.790		<0.025	0.032	0.090	
Mn_t	mg·L^{-1}	0.1	<0.025	0.101	1.020	22.7	<0.025	0.304	5.370	18.8	<0.025	0.107	0.790	11	<0.025	0.033	0.090	0
Ni_t	mg·L^{-1}	0.025	<0.01	0.011	0.030	3.7	<0.01		<0.01	0	<0.01		<0.01		<0.01	0.010	0.020	0
Zn_t	mg·L^{-1}	0.18	<0.005	0.060	0.450	1	<0.005	0.078	1.280	3	<0.1		<0.1		<0.005	0.072	0.100	0

Max, maximum; Min, minimum; Avg, average; Data not available was left blank. For average calculation, below detection limit (DL) values were substituted by DL values, $_{(t)}$: total, $_{(d)}$: dissolved, ColiTh: coliform thermotolerant, Temp: temperature, TDS: total dissolved solid, TSS: total suspended solid; >%*: percentage of samples exceeded the respective CONAMA Class II limit (# WHO drinking water limit).

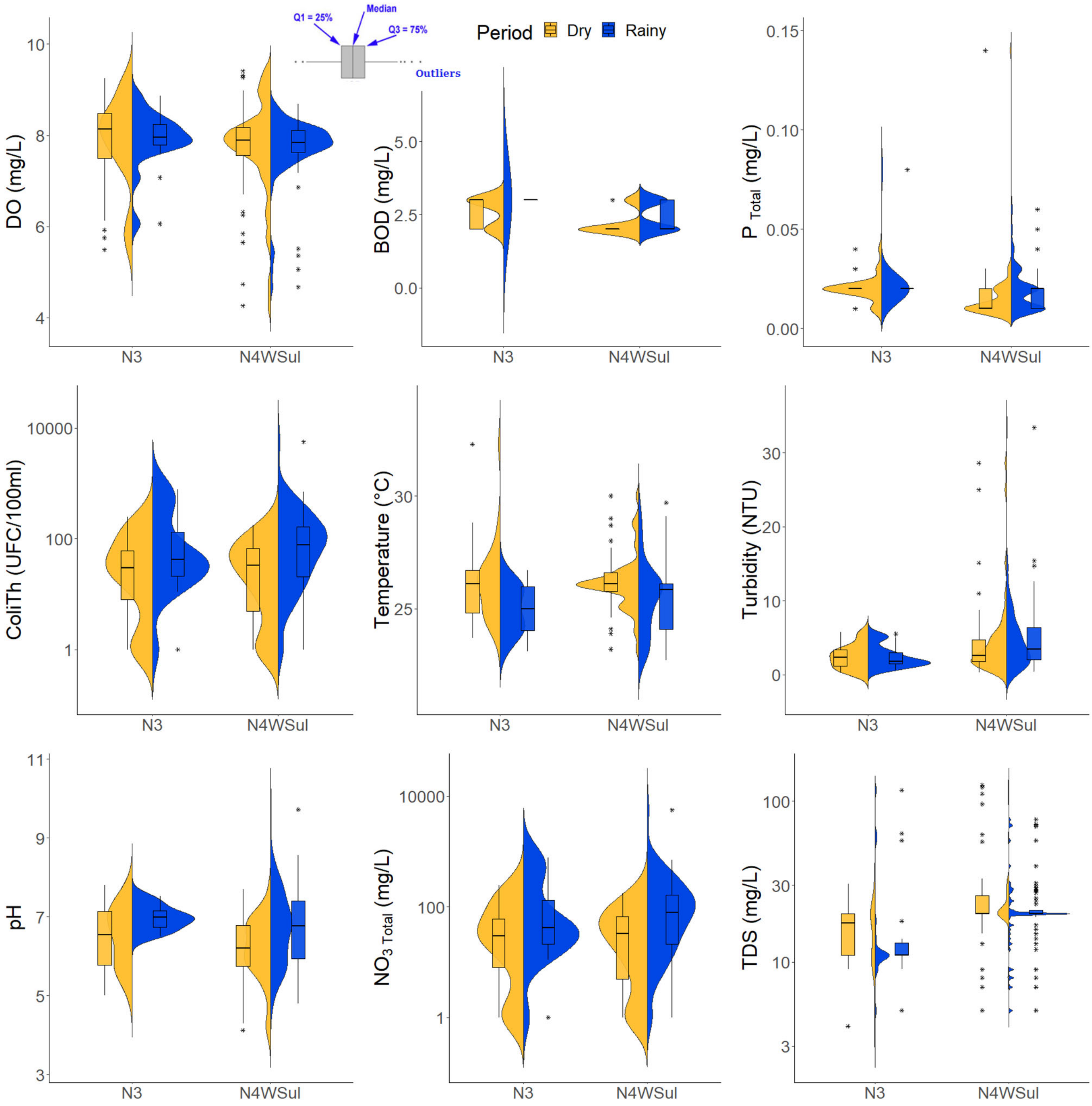

Figure 2. Violin plots showing visual distribution of selected physico-chemical parameters and metals in both dry and rainy periods from N3 and N4WSul areas. The box represents 25th percentile, median, and 75th percentile of the data. The whiskers show 95% confidence interval, the values exceeding the 95th percentile are shown as outliers.

area and from 5.1 to 7.8 in the N3 area, but they are largely concentrated in between 6.0 and 7.5 (Figure 2). Comparing between the seasons, pH values were significantly higher in the rainy season than in the dry season and also a little higher in N3 compared to N4WSul. Some of the values are lower than 6 and in nonconformity with the 6.0–9.0 interval defined in CONAMA Resolution 357/2005. Independent of seasonal variations and except for some outliers, all other analyzed physico-chemical parameters are in good agreement with the values indicated in the CONAMA Resolution 357/2005. The average turbidity ranged from 4.2–4.8 NTU in N4WSul and from 2.27–2.53 NTU in N3 area, but it doesn't show any significant variation between the rainy and dry seasons (Tables 1 and 2). The analyzed waters can be classified as clear water. The EC and TDS values were significantly higher during the rainy period (mainly in the

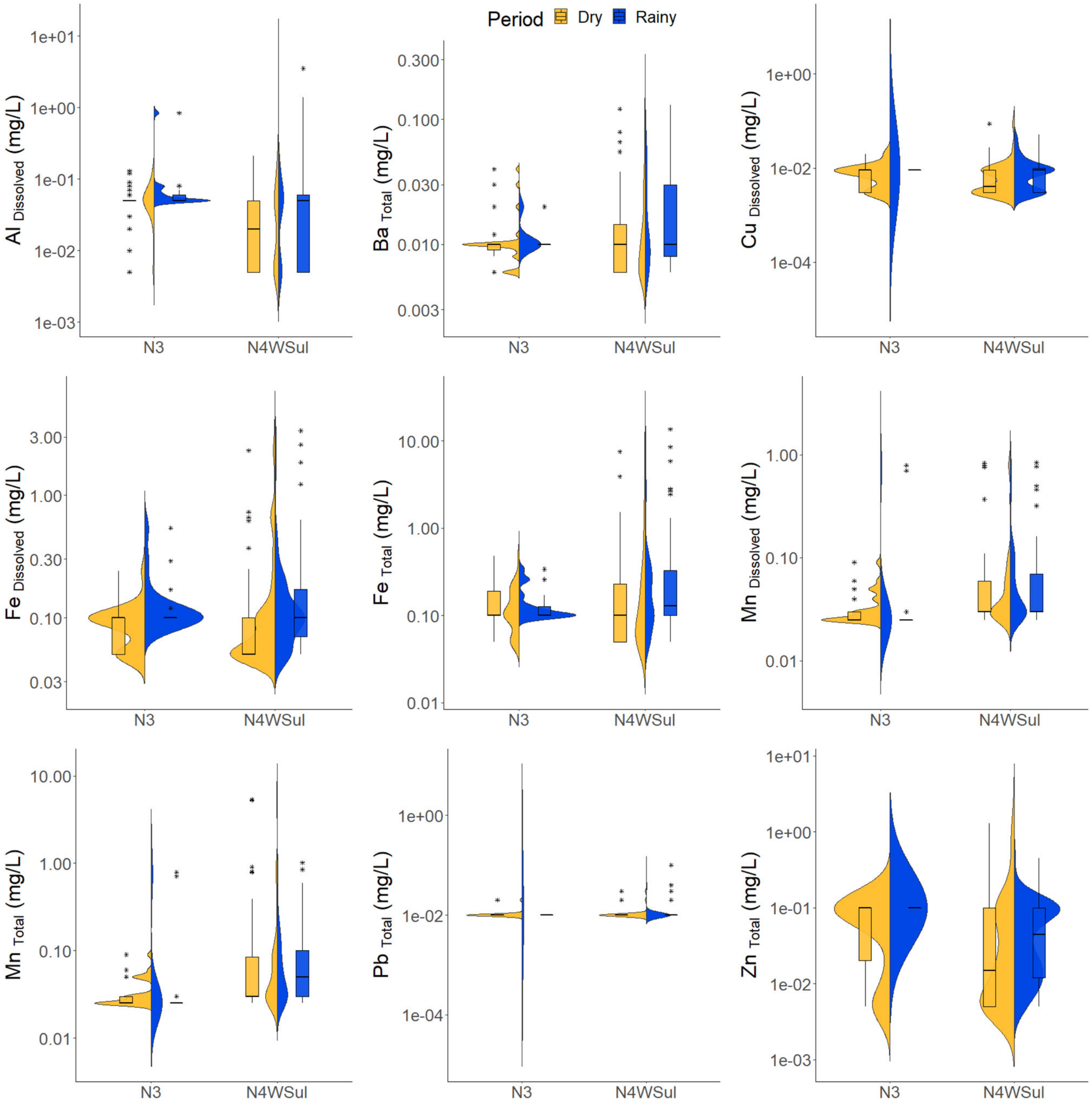

Figure 2. Continued.

N4WSul area) (Tables 1 and 2; Figure 2), but all obtained values were within the permissible limit. Higher TDS during rainy period may be due to a more intense catchment weathering and run-off that leads to the increase of metals in waters. However, in the N3 area, the values obtained in both seasons are mostly superposed and the average is a little higher in the dry season compared to the rainy one (Table 1). The DO values are mostly higher than 5.0 (minimum value admitted for CONAMA) and their average values are similar either in the two seasons and in both studied areas varying from 7.73 to 7.97 (Table 1). Although BOD was significantly different between both periods, in all the investigated samples its values were low (≤3 mg/L; Table 1). This indicates absence of significant organic pollution. The average NO_3 concentration was slightly higher in the dry period (0.81–1.24 mg/L; respectively for N3 and N4; Table 1) than in the rainy period (0.46–0.70 mg/L), and the concentrations were higher in N4 than in N3 area. Total phosphorus concentration was low and do not show significant variations in both periods or areas

Table 2. Non-parametric Kruskal-Wallis test results of the surface water quality parameters from the N4WSul and N3 areas in the dry and rainy periods.

	Test statistics—N4WSul area (Dry vs. Rainy period)																								
	Alk.	Cl	EC	BOD	Colit	TP	NO3	DO	pH	TDS	TSS	SO4	Temp	Turb	Ald	Bat	Cdt	Pbt	Fed	Fet	Cud	Mnd	Mnt	Nit	Znt	WQI
Chi-Sq.	0.32	2.56	5.18	8.28	12.6	8.46	5.78	0.01	6.46	3.70	1.95	0.41	10.01	2.6	5.13	3.56	4.92	0.46	14.9	6.09	3.91	0.31	0.01	2.04	8.30	0.27
Asy. Sig.	0.57	0.11	**0.04**	**0.00**	**0.00**	**0.00**	**0.04**	0.93	**0.01**	**0.04**	0.16	0.52	**0.00**	0.13	**0.03**	0.06	**0.03**	0.50	**0.00**	**0.01**	0.05	0.58	0.93	0.15	**0.00**	0.54
	Test statistics—N3 area (Dry vs. Rainy periods)																								
	Alk.	Cl	EC	BOD	$Coli_t$	TP	NO_3	DO	pH	TDS	TSS	SO_4	Temp	Turb	Al_d	Ba_t	Cd_t	Pb_t	Fe_d	Fe_t	Cu_d	Mn_d	Mn_t	Ni_t	Zn_t	WQI
Chi-Sq.	5.47	2.83	5.64	7.72	2.57	0.59	3.92	0.71	3.26	0.53	11.92	2.28	7.00	0.82	3.28	3.06	0.00	0.62	8.35	0.50	4.26	1.35	1.41	0.62	7.60	0.31
Asy. Sig.	0.05	0.09	0.42	**0.01**	**0.04**	0.44	0.05	0.40	0.07	0.47	**0.00**	0.13	**0.01**	0.36	0.07	0.08	1.00	0.43	**0.00**	0.48	0.05	0.25	0.23	0.43	**0.01**	0.73
	Test statistics (N4WSul vs. N3)																								
	Alk.	Cl	EC	BOD	$Coli_t$	TP	NO_3	DO	pH	TDS	TSS	SO_4	Temp	Turb	Al_d	Ba_t	Cd_t	Pb_t	Fe_d	Fe_t	Cu_d	Mn_d	Mn_t	Ni_t	Zn_t	WQI
Chi-Sq.	5.84	9.42	10.3	28.66	0.57	15.0	2.20	5.64	3.16	21.5	20.82	5.90	0.00	9.87	8.94	0.20	2.58	0.86	4.13	3.90	1.82	30.67	36.22	0.01	13.9	2.2
Asy. Sig.	0.06	**0.00**	**0.00**	**0.00**	0.38	**0.00**	0.14	0.05	0.08	**0.00**	**0.00**	**0.02**	0.95	**0.00**	**0.00**	0.65	0.11	0.36	**0.05**	**0.05**	0.18	**0.00**	**0.00**	0.94	**0.00**	0.12

Alk: alkalinity; $Coli_t$: coliform thermotolerant; Turb: turbidity; significantly different at $p < 0.05$, **bold** values indicate the parameters are significantly different between seasonal periods.

(all average values of 0.02; Table 2). Fecal coliform (thermotolerant) varied significantly between the seasons (Table 2; Figure 2). Higher values in rainy season are possibly due to addition of wild animal waste into the water as a result of more surface runoff. This is possibly also caused significant increase of TP and NO_3 concentration in the rainy period (mainly in the N4WSul area). As for metals, significantly higher concentrations of Fe_d, Fe_t, and Al_d were mostly identified in the rainy season (Tables 1 and 2; Figure 2) and are probably due to the greater rainfall with a more intense catchment weathering and run-off. Although, total Mn didn't show significant seasonal variation, higher average values were noted in the dry season in N4 and in the rainy season in N3 (Table 1). When compared between the N4WSul and N3 areas, turbidity, EC, TDS, TSS, Cl, SO_4 were significantly different (p-value < 0.05). Among metals, the Al_d, Fe_d, Fe_t, Mn, Ba, and Zn concentrations were significantly higher in N4WSul than in the N3 area and, in some points, such as N4-07, the concentration of some of these elements exceeded the legislation limit. The values obtained for Ba, B, total Co, Cr, and Zn are all in conformity with CONAMA rules. Pb, Cd, and Ni show some values in non-conformity but they are in each case less than 5% of the analyzed samples and the average values are all below the maximum values admitted by CONAMA. The metals with highest concentrations in the surficial waters are Al, Cu, Fe, and Mn. They are also those with larger percentages of unconformity values compared to CONAMA rules. The highest proportion of unconformity values occur in the N4WSul area (11.3% for Fe_d, 27.8% for Fe_t, 22.7 for Mn_t, 27.8% for Cu, < 8% for Cd, Ni, and Pb) compared to N3 (< 7% for Fe_t, Cu_d, Al_d, and 3.4% for Pb) (Table 1). In a first approach, these metals look strictly associated to the dominant lithologies in the studied areas. The sampling point N4-07 had an anomalous behavior and of 12 samples collected in it, 11 samples have shown dissolved Fe concentrations higher than the values admitted for Class II fresh waters. In that point, it was also identified the largest turbidity values. Although these turbidity values are still below CONAMA limits, these aspects had evidenced that around that point the environment was disturbed probably by activities of mineral exploration in the area.

WQI results shows that the surface waters in the N4WSul and N3 areas are classified in general as "good" (52 – 79) to "excellent" (80 – 100) categories (Figure 3). Rarely, reasonable (37–51) quality conditions are observed in both areas (Figure 3). While

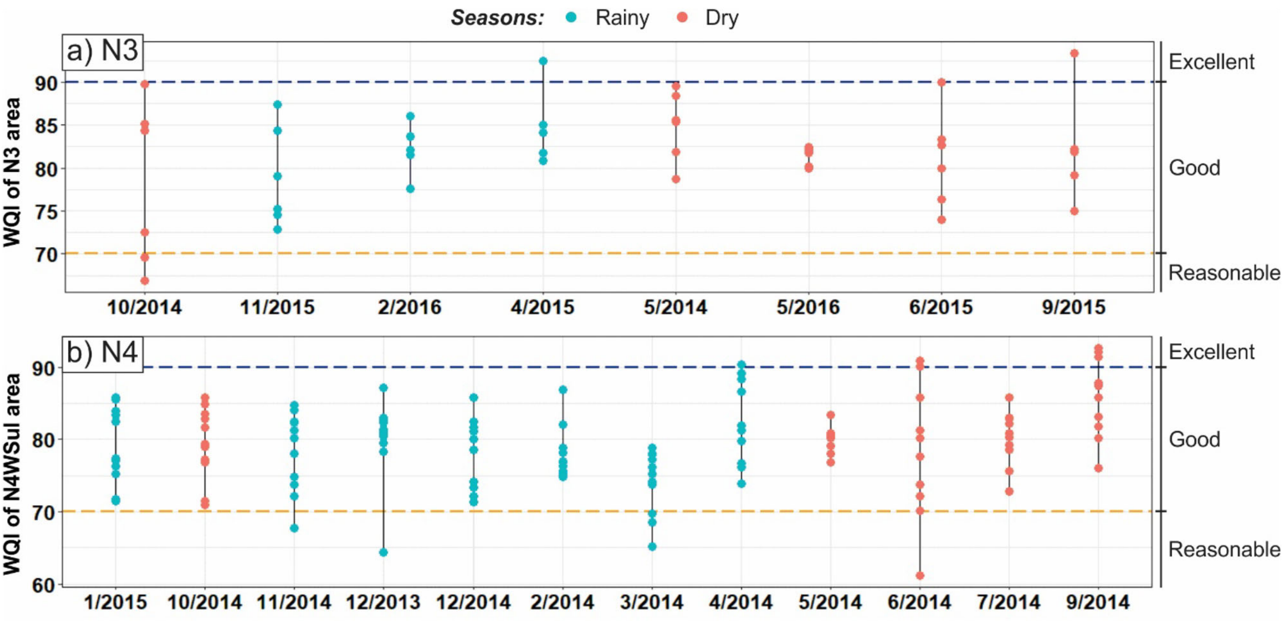

Figure 3. Water quality index (WQI) variation in both dry and wet periods in the N4WSul and N3 areas.

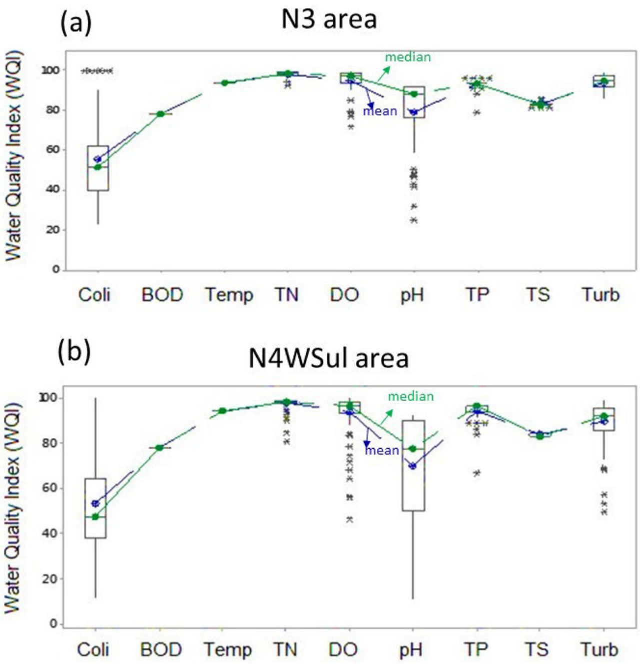

Figure 4. Box plot showing the contribution of individual parameters that make up the WQI in both N3 (a) and N4WSul (b) areas. Coli: coliform thermotolerant, Temp: temperature, TP: total phosphorus, TS: total solid.

comparing seasons, despite the strong contrast in precipitation along the year, WQI data do not indicate significant differences in water quality between the rainy and dry seasons in the studied areas (Table 2; Figure 3). Variations of WQI between good and optimum are observed throughout all the sampling campaigns carried out independent of the period of the year. In Figure 4, the behavior of each individual variable that composes the WQI index can be observed. The variables that make up the WQI with the lowest individual values are dissolved oxygen, thermotolerant coliforms and pH, and, by coincidence, they have the highest weights in the calculation of WQI (0.17, 0.15 and 0.12, respectively). The results obtained for thermotolerant coliforms are consistent with microbiological conditions of

Table 3. Estimated BTVs (mg/L) of elements in the N3 and N4WSul areas compared with CONAMA class 2 and WHO permissible limit.

			Upper limits/BTV			
			N3 (n = 47)		N4WSul (n = 136)	
Elements	Limit of quantification (LQ)	CONAMA II	ProUCL	mMAD	ProUCL	mMAD
Ag_t	0.003	0.01	*	*	*	*
Al_d	0.05	0.1	0.127$^{(4)}$	*	0.23	0.77
As_t	0.01	0.01	*	*	*	*
B_t	0.02	0.5	*	*	*	*
Be_t	0.004	0.04	*	*	*	*
Cd_t	0.001	0.001	*	*	0.004	*
Co_t	0.01	0.05	*	*	*	*
Cr_t	0.01	0.05	*	*	*	*
Cu_d	0.009	0.009	*	*	0.04	*
Fe_d	0.1	0.3	0.323$^{(4)}$	*	0.45	0.62
Fe_t	0.1	0.3$^{\#}$	0.774$^{(5)}$; 0.919$^{(6)}$	0.22	1.3	1.14
Hg_t	0.0002	0.0002	*	*	*	*
Li_t	0.1	2.5	*	*	*	*
Mn_d	0.025	–	0.79	*	0.84	0.05
Mn_t	0.025	0.1	0.79	*	1.02	0.13
Ni_t	0.01	0.025	*	*	0.03	*
Pb_t	0.01	0.01	*	*	0.04	*
Sb_t	0.005	0.005	*	*	*	*
Se_t	0.01	0.01	*	*	*	*
U_t	0.01	0.02	*	*	*	*
V_t	0.02	0.1	*	*	*	*
Zn_t	0.1	0.455	0.104$^{(4)}$	*	0.455	**1.72**

(1)95% USL; (2)95% KM Bootstrap UCL; (3)95% KM (t) UCL; (4)95% KM USL; (5)95% Gamma USL—Wilson Hiferty (WH); (6)95% Gamma USL—Hawkins Wixley (HW); * = Value below DL; BTV: background threshold value; # WHO (1993) permissible limit. In bold = Threshold value > maximum concentration obtained; For elements values below LQ (*), the LQ was considered as their BTVs.

environments without significant anthropic effects. However, this parameter presents large variations, with values between <1 to 780 CFU/100 ml, which is reflected in the values obtained for the WQI. As for pH, the acidic to slightly acidic characteristic is predominant for the surface waters of the region, with at least one determination below the lower limit stipulated for this parameter by CONAMA in each of the monitored points. These values lead to the reduction of WQI values, being represented graphically below the good category (Figure 3). The oxygenation levels of the water at the sampling points are in agreement with CONAMA rules and this reinforces previous evidence of a local environment without significant anthropogenic interference. The dissolved oxygen has the greatest weight in the WQI calculation. Hence, the results obtained for this variable have a great contribution in the final WQI result. The results of WQI values vary between 79 and 99 for N3 and between 66.8 and 99.3 for N4.

Background concentrations estimation

The background values of elements in each mineral body were calculated independently, since their sampling periods were different. Therefore, the results obtained in the two studied areas are not fully comparable. Table 3 presents the BTVs of elements for water bodies of N3 and N4WSul and for each location BTVs were estimated by ProUCL (upper 95% limit of USL, UTL, and UPL) and mMAD techniques (Table 4). However, the results show that in many cases the calculated BTVs by mMAD exceeded the respective maximum values. In ProUCL, it should be noted that in the case of N4WSul area, the anomalous results registered in the sampling point N4-07 would have a strong influence in the integrated results if considered. For this reason, the results from this point were excluded from the calculation of the dataset for that area. Nevertheless, the calculation for point N4-07 was performed separately. In the same way, the upper outlier results for the parameter copper dissolved in the water samples of the N4-02 monitoring point were not considered in determining the background concentration value for this element. It should be noted that in the calculation of BTVs, when the results could not be processed due to the high number of values below Limit of Quantification (LQ), the LQ value was adopted as the concentration value. For total Hg in both areas, and for total Cd, Pb, dissolved Cu and total Ni in N3, background concentration values could not be calculated due to the large number of analyzes with values below limit of detection in relation to the total

Table 4. Estimated geochemical baseline (mg/L) of elements in the N3 and N4WSul areas.

		Background threshold values (BTVs) calculated for each sampling point													
		Ald		Cud		Fed		Fet		Mnd		Mnt		Znt	
Sample location	No. of samples	ProUCL	mMAD	ProUCL	mMAD	ProUCL	mMAD	ProUCL	mMAD	ProUCL	mMAD	ProUCL	mMAD	ProUCL	mMAD
N3-3	8	<0.05	*	*	*	*	*	*	**0.61**	*	0.04	*	0.04	*	*
N3-4	8	*	0.07	*	*	*	*	*	*	*	*	*	*	*	*
N3-5	8	*	*	*	*	*	**0.58**	*	**0.96**	*	0.04	*	0.04	*	*
N3-6	8	*	*	*	*	*	*	*	0.16	*	*	*	*	*	*
N3-7	8	*	0.08	*	*	*	*	*	*	*	*	*	*	*	*
N3-8	7	*	**0.09**	*	*	*	*	*	**0.22**	*	*	*	*	*	*
All points from N3	47	0.127$^{(4)}$	*	*	*	0.323$^{(4)}$	*	0.774$^{(5)}$ 0.919$^{(6)}$	0.22	0.79	*	0.79	*	0.104$^{(4)}$	*
N4-01	12	0.14$^{(4)}$	**0.30**	0.04	0.03	0.34	**0.61**	0.46$^{(4)}$	**0.71**	0.5	*	0.59	0.04	0.1	**0.30**
N4-02	12	0.19$^{(5)}$ 0.19$^{(6)}$	**1.19**	0.03	0.01	0.35$^{(5)}$ 0.38$^{(6)}$	**0.50**	1.05	**0.78**	0.32	*	0.32	0.04	0.13	0.58
N4-03	12	0.06	**0.11**	0.01	*	0.17$^{(5)}$ 0.17$^{(6)}$	**0.25**	**0.74$^{(5)}$** **0.84$^{(6)}$**	**0.35**	0.79	0.20	0.702	0.28	0.0793	**0.60**
N4-04	12	0.12	**0.93**	0.01	0.03	0.20$^{(4)}$	**0.21**	0.34	0.31	0.153$^{(4)}$	**0.23**	0.256$^{(4)}$	**0.29**	0.0739	**0.48**
N4-05	12	0.05	0.48	0.020$^{(5)}$ 0.020$^{(6)}$	**0.05**	0.45	**0.24**	0.48	0.33	*	0.03	0.06	0.04	0.053$^{(4)}$	**1.76**
N4-06	12	0.08	**0.54**	0.022	0.01	0.1	*	0.13$^{(4)}$	**0.18**	0.84	0.11	0.91	0.11	0.1	**1.83**
N4-07	12	0.16$^{(4)}$	**0.73**	0.02	**0.03**	3.54$^{(4)}$	**4.12**	13.11$^{(4)}$	**57.87**	0.333	0.15	0.180$^{(4)}$	**0.51**	0.124$^{(5)}$ 0.130$^{(6)}$	**0.73**
N4-08	4	*	*	*	**0.02**	*	*	*	**0.24**	*	*	*	0.03	*	**0.18**
N4-09	12	0.24$^{(5)}$ 0.26$^{(6)}$	1.06	0.087	**0.23**	0.1	*	0.1	*	0.09	*	0.09	0.03	0.08$^{(4)}$	**0.62**
N4-25	12	0.08$^{(4)}$	**0.26**	0.013$^{(4)}$	**0.02**	0.22 $^{(4)}$	0.17	0.53$^{(4)}$	0.42	0.396$^{(5)}$ 0.436$^{(6)}$	**0.48**	0.551$^{(5)}$ 0.628$^{(6)}$	**0.66**	0.122$^{(4)}$	**0.34**
N4-26	12	0.12	*	0.014	**0.02**	0.35$^{(4)}$	**0.43**	1.88$^{(5)}$ 2.25$^{(6)}$	1.13	0.76	0.07	0.8	0.23	0.1	**0.27**
N6-01	12	0.33$^{(5)}$ 0.36$^{(6)}$	**0.28**	*	**0.02**	0.1	**0.18**	0.25$^{(5)}$ 0.27$^{(6)}$	**0.30**	0.77	*	1.02	0.04	0.0175$^{(4)}$	0.14
All points from N4WSul	136	0.23	0.77	0.04	0.06	0.45	0.62	1.3	1.14	0.84	0.05	1.02	0.13	0.455	**1.72**

$^{(1)}$95% USL; $^{(2)}$95% KM Bootstrap (t) UCL; $^{(3)}$95% KM (t) UCL; $^{(4)}$95% KM USL; $^{(5)}$95% Gamma USL—Wilson Hiferty (WH); $^{(6)}$95% Gamma USL—Hawkins Wixley (HW); '*' = Value below QL; in bold = Threshold value > maximum concentration obtained; N6-01 considered in N4WSul group; For elements values below LQ (*), the LQ was considered as their BTVs.

number of analyzes. This restriction was more accentuated in the background calculation of the individual points in N3 whose number of monitoring campaigns was lower than those performed in N4WSul and in which almost all the results indicated values below the detection limit making it impossible to process the data for background calculation.

For both areas, it was noted that the natural background concentrations of the evaluated elements are equal to or greater than the legal limits established in CONAMA Resolution No. 357/2005 for freshwater class 2 (Tables 3 and 4). Comparing the results for N3 and N4WSul areas, the higher background concentrations were noted for the N4WSul area, even with the exclusion of the anomalous Fe results obtained in the N4-7 point and of the dissolved copper values of the point N4-2.

Discussion

Water quality and seasonal influence

The surface water quality of the N3 and N4WSul areas shows that most of the analyzed physico-chemical parameters are in conformity with the legislation limits. Differences between the two studied areas are also evident with higher concentrations of metals in N4WSul compared to N3. The concentrations of most analyzed elements (e.g., B, Cd, Pb, Cl, Co, Cr, F, P, Ni) are below detection limits which are, in turn, lower than the legislation limit recommended in CONAMA Resolution 357/2005. However, Al, Fe, Mn, Zn, and Cu contents, the latter only in N4WSul area, are commonly above detection limits and, in some cases, also above the legislation limits. The calculated water quality index indicates that superficial water in the studied areas can be classified as ‘good’ and ‘optimum’ categories. Hence, they are satisfactory and reflect the pristine characteristics of the studied environment.

Seasonal variation exerted influence in the obtained results. The pH values are largely superposed in both seasons, but during the dry season they tend to be a little lower. As for metals (mainly for Fe_d, Fe_t, Al_d), the highest concentrations were mostly obtained during the raining season and this can be related to the increase of erosion, weathering, leaching and transport associated with larger rainfall and more intense run-off (Panday et al. 2015; Menezes 2017; Levy et al. 2018; Nóbrega et al. 2018). The effect of these processes should compensate the water dilution due to the volume increase of the superficial waters during the wet season. This is a relevant conclusion that was also verified in other domains of the Itacaiúnas watershed (Salomão et al. 2018; Sahoo et al., 2019a). Some local exceptions to this general behavior were indicated by the occurrence of upper outlier values in the dry period for Mn, Zn, and Cu(d) in the N4WSul area and for Pb, Ni, and Cu(d) in the N3 area. In relation to the parameters related to solid fractions, some higher anomalous values for total dissolved solids and turbidity were registered in N4WSul in both seasons and only in the wet period in N3. It is concluded that the general tendency is the increase of metals and solid fractions by more catchment weathering and surface runoff during the raining season compared to the dry season, but local exceptions to this dominant behavior are also observed.

A general conclusion is that the occurrence in the studied areas of some values higher than those admitted in the CONAMA Resolution 357/2005 for freshwater class 2 is related to specific characteristics of the local environment. In other words, the influence of geological, geomorphological, pedological, and climatological factors is more relevant to explain the variations in the concentration of different elements and of physical parameters in the superficial waters than anthropogenic effects. This conclusion is valid for the studied areas situated in a protected area covered by tropical forest, but there is evidence that it can be extended to other areas of the Itacaiúnas watershed. However, in those affected by intense deforestation, during the rainy season the intense precipitation and the absence of tropical forest tend to increase the surficial run-off and the transport of elements to the local drainage (Levy et al. 2018; Nóbrega et al. 2018; Salomão et al. 2018; Sahoo et al., 2019a).

Geochemistry of Fe and Mn

Iron and Mn occur naturally in waters in varying quantities depending on the geology of the area and local environmental factors (Abouhend and El-Moselhy 2015). The wide variation of Fe in the study area is likely related to the differences in geology, soil type, transport and geochemical behavior (Raiswell and Canfield 2012). The higher contents of Fe (dissolved and total) in the rainy period indicates more intense catchment weathering rates, leading to increase the concentration of this element in surficial waters. Although, Fe and Mn contents originate from catchment erosion, the poor correlation between Fe

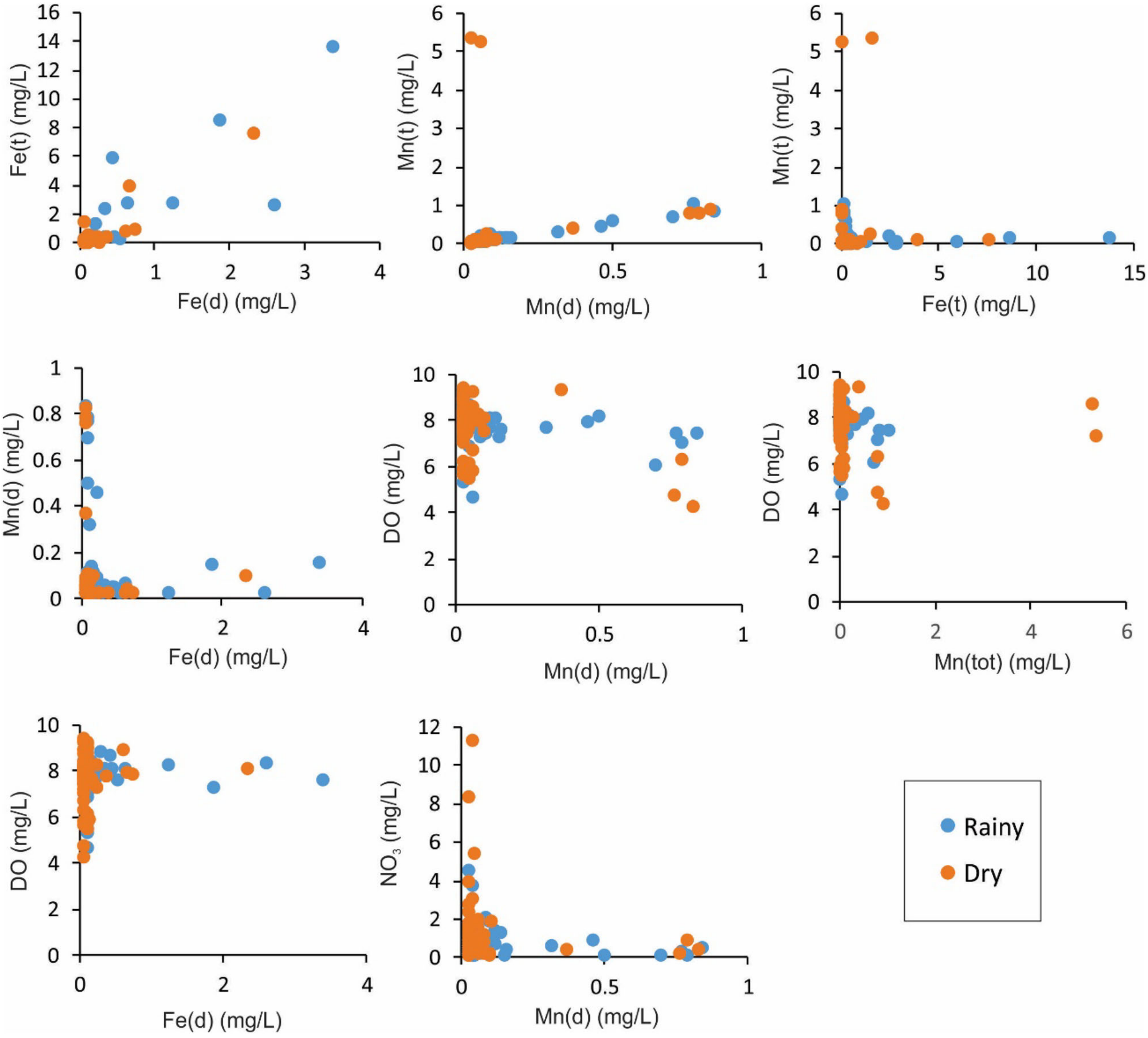

Figure 5. Geochemical relationship between Fe and Mn and other water quality parameters.

and Mn (Figure 5) in surficial water bodies indicates they were affected by different transport and biogeochemical processes (Raiswell and Canfield 2012), as well as dispersal and sedimentation and in-situ redox conditions (Hamilton-Taylor and Price, 1983). The oxidation states as well as mobility of the two elements will control the precipitation and/or dissolution of Fe and Mn oxides (Balistrieri, Murray, and Paul 1992; Voelker, Morel, and Sulzberger 1997; Aucour et al. 2003). If the total concentration of Fe and Mn exceeded their respective Fe/Al and Mn/Al ratios of 1.2 and 0.06, then there would be presence of some colloidal and/or complexed Fe and Mn particles (see Price and Calvert 1973; Sholkovitz and Copland 1982). A close positive relationship (Figure 5) between dissolved Fe and total Fe is clearly related to the particulate Fe in water. Although, a similar trend was observed for Mn (Figure 5), the maximum concentration of Mn was not following this trend. This indicates that the higher concentrations of Mn could be due to influence of biogeochemical processes occurring at the sampling sites. The elevated level of dissolved Mn linked with lower DO content (Figure 5) suggest reductive dissolution of Mn oxides via bacterial decomposition of OM releasing Mn ions into solutions (Sunda and Kieber 1994). The slow oxidation of the released Mn(II) would be responsible for the temporary increase of the Mn concentration in the early stage of the mixing between water and sediments. Aucour et al. (2003) also reported that reductive dissolution of MnO_2 colloids with OM could exert influence in the distribution of Mn in aquatic systems. In oxidizing environment, Mn mobility is highly influenced by NO_3. Therefore, the increase of NO_3 in surface water could likely exert influence in Mn content in waters.

Anomalous Fe concentrations in N4-07 point

The results obtained in point N4-07, mainly the Fe, are markedly higher in relation to the other points and this indicates a local source of metal enrichment. The most plausible hypothesis to explain this anomaly is related to road opening and reconditioning. The point N4-07 is located near the outflow of an inactive lake and a road used for environmental and exploratory activities was reconditioned and a small road was created connecting the main access to the filled lake. This may have produced a significant amount of detritic materials that were subsequently incorporated into the local water stream. This process should be more intense during the raining season due to elevated precipitation and increase of run-off.

Geochemical background and its environmental application

Although, the mMAD has been widely reported as one of the best performer methods for deriving BTVs (Reimann et al. 2005; Salomão et al. 2018; Sahoo et al., 2019b), in the present study, it overestimated the BTVs in several cases as it exceeded the respective maximum concentrations and in some cases it was not even able to calculate BTVs values. This is possibly due to the presence of multiple DL and significant number of BDL values in the dataset making that the method not assuming the presence of outliers depending on the data distribution. Therefore, mMAD method is not suitable for the present study. On the other hand, ProUCL technique, a robust statistical package recommended by EPA (2013), was considered effective for this study as it better worked with and without below DL values and was able to give estimates of the BTV for individual points and set of points in each studied area. The calculation of the BTVs was based on the statistical measure of USL 95%, which deals with the concentrations at 95% of statistical confidence interval. Nevertheless, the prior knowledge of the intrinsic characteristics of the region to be studied is fundamental for making subjective decisions in the treatment of the data obtained statistically. In both areas, it was noted for most analyzed elements that their contents were below detection limit and it was not possible to define their background values. However, it can be concluded that they are certainly lower than the DL and in conformity with CONAMA regulations. For some metals, e.g. Fe, Al, Cu, Mn, and Zn, that commonly show concentrations higher than detection limits, the BTVs were estimated and were equal to or greater than the legal limits established in CONAMA (Figure 6). This was verified even with the purge of data that presented indications of potential external interferences, such as data obtained for iron at point N4-7, or dissolved copper in point N4-2.

In studies carried out in other regions of Brazil (Rodrigues et al. 2013) and other countries (Reimann et al. 2005), it has been registered concentrations of elements above the limits established by the applicable legislation, for reasons not related to human activity. Langmuir (1997) mentioned the identification of natural or geogenic concentrations of one or more substances exceeding the limits established by the USA Environmental Protection Agency (EPA) in surface and groundwater in the United States. In Brazil, and more specifically in the Amazon region, even in areas without evidence of significant anthropogenic action, it was identified concentrations of Fe and Mn in surface waters above the values established in 357/2005 CONAMA resolution (SEMAS/PA 2012). This was also verified in the Vermelho and Sororó sub-basins of the Itacaiúnas watershed (Salomão et al. 2018).

Therefore, as evidenced in the present work, in-depth geochemical studies of the distribution of trace elements and their concentrations in natural ecosystems are fundamental for the definition of water quality standards and hydric resources management in the region. It is unrealistic to attribute reference values lower than background values in different geological areas and environments and the particularities of each region should be taken into account for their correct definition. The two studied areas are representative of preserved pristine areas and the obtained results demonstrate the strong influence of the natural setting in the background values. The background results obtained in this study will be useful as a reference in the region prior to their exploration to assess future anthropogenic impacts. Furthermore, since the study area is situated in a protected area covered by preserved tropical forest, the results of this study can also be useful as a background in the areas of occurrence of Fe-ore deposits/Fe-mining in the Itacaiúnas basin, either if derived from natural sources or from anthropogenic influence.

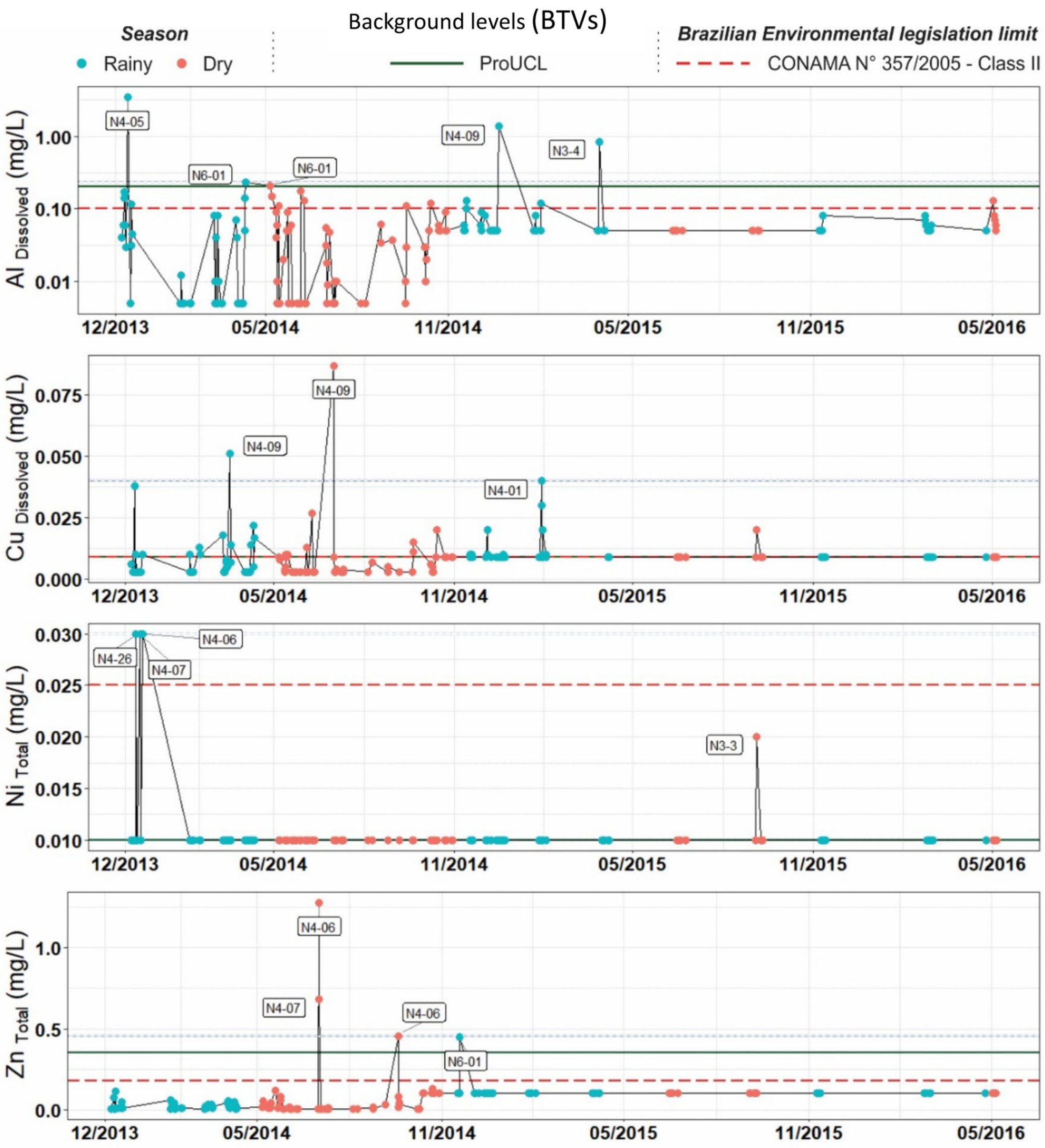

Figure 6. Comparison elemental concentrations in N3 and N4Wsul áreas with respect to BTVs (ProUCL) and CONAMA limits.

Conclusions

Water quality results indicate that surface waters of N4WSul and N3 areas, situated near iron deposits in Serra dos Carajás, were between "good" and "optimal" during the monitored periods. Some of the parameters (Fe_d, Al_d, Mn_t, Zn_t) exceeded the legal limits set in Resolution 357 of CONAMA, a higher number in N4WSul. Seasonal variation was significant for pH, water temperature, coliform, and metal contents (such as Fe_d, Fe_t, Ba, Al_d) with a tendency to higher concentrations in the rainy season. Poor correlations between Fe and Mn indicate that their geochemical behavior and transport processes are different and the elevated dissolved Mn concentration is more likely related to dissolution of Mn-oxides via bacterial decomposition of organic matter. The results show that the ProUCL was appropriate for determination of BTVs in the present study. Compared with the Resolution 357 of CONAMA, the BTVs of the metallic elements that presented systematically higher levels than the minimum limits of analytical detection were equal to or superior to the legal limits set in. This implies that concentrations superior to the normalized limits of these elements occur naturally in the studied region. It should be noted that, although the most discrepant data (Fe in N4-7 and copper dissolved in N4-2) have been purged, the contrast between the N4WSul and N3 areas are evident with significantly higher values in N4WSul (mainly Fe_d, Fe_t, Mn, and Ba). The results obtained in this study demonstrates that the influence of geological, geomorphological, and climatological factors is more relevant to explain the background concentration of different elements in the superficial waters. The outcome of this study is particularly significant in the case of pristine areas prior to their exploration, especially in the region and in other Fe-ore mineralized areas in the Itacaiúnas basin that are beyond the reach of the general legislation limits, which are more restrictive to enforce the precautionary principle of the environmental law.

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References

APHA. 2005. *Standard Methods for the Examination of Water and Wastewater*. 22nd ed. Washington DC: American Public Health Association.

Arpine, H., and Shahnazaryan, G. 2016. Determination of background concentrations of hydrochemical parameters and water quality assessment in the Akhuryan River Basin (Armenia). *Physics and Chemistry of the Earth* 94: 2–9.

Abouhend, A. S., and El-Moselhy, K. M. 2015. Spatial and seasonal variations of heavy metals in water and sediments at the Northern Red Sea coast. *American Journal of Water Resources* 3 (3):73–85.

Aucour, A. M., Tao, F. X., Moreira-Turcq, P., Seyler, P., Sheppard, S., and Benedetti, M. F. 2003. The Amazon River: Behaviour of metals (Fe, Al, Mn) and dissolved organic matter in the initial mixing at the Rio Negro/Solimões confluence. *Chemical Geology* 197: 271–285.

Balistrieri, L. S., Murray, J. W., and Paul, B. 1992. The cycling of iron and manganese in the water column of Lake Sammamish, Washington. *Limnology and Oceanography* 37:510–528.

Beisiegel, V. R. 1982. Distrito Ferrífero de Carajás. *Simpósio de Geologia da Amazônia* 1:21–46.

BRASIL. 2005. Ministério do Desenvolvimento Urbano e Meio Ambiente. Conselho Nacional do Meio Ambiente—CONAMA. Resolução n 357. de 17 de março de.

CETESB (Companhia de Tecnologia de Saneamento Ambiental). 1988. *Guia de coleta e preservação de amostras de água*. São Paulo: CETESB, 150 p.

CETESB. 2003. *Companhia de Tecnologia de Saneamento Ambiental. Relatório de Qualidade Das Águas Interiores Do Estado de São Paulo 2002*. São Paulo: CETESB (Série Relatórios).

CETESB (Companhia de Tecnologia de Saneamento Ambiental) 2016. *Relatório de Qualidade das Águas Interiores do Estado de São Paulo. Apêndice D – Índices de Qualidade das Águas*. Disponível em: http://cetesb.sp.gov.br/aguas-interiores/wp-content/uploads/sites/12/2013/11/Ap%C3%AAndice-D-%C3%8Dndices-de-Qualidade-das-%C3%81guas-1.pdf (accessed June 02, 2016).

Choi, S. H., Kim, J. Y., Choi, E. M., Lee, M. Y., Yang, J. Y., Lee, G. H., et al. 2019. Heavy metal determination by Inductively Coupled Plasma- Mass Spectrophotometry (ICP-MS) and Direct Mercuty Analysis (DMA) and arsenic mapping by femtosecond (fs). *Analytical Letters* 52(3):496–510. doi:10.1080/00032719.2018.1471484.

Daniel, D. L. 2015. A case study perspective on working with ProUCL and a state environmental agency in determining background threshold values. *International Journal of Environmental Research and Public Health* 12(10):12905–12923.

Demirak, A., Yilmaz, F., Tuna, A. L., and Ozdemirc, N. 2006. Heavy metals in water, sediment and tissues of Leuciscus cephalus from a stream in southwestern Turkey. *Chemosphere* 63:1451–1458.

DOCEGEO. 1988. Revisão litoestratigráfica da Província Mineral de Carajás—Litoestratigrafia e principais depósitos minerais. In *35 Congresso Brasileiro de Geologia*. Belém: Anais.

EPA. 2013. ProUCL statistical software for environmental applications and documentation. Download software and obtain User Guide, Technical Guide, Fact Sheet, and archived webinars at http://www.epa.gov/esd/tsc/software.htm

Galuszka, A. 2007. A review of geochemical background concepts and an example using data from Poland. *Environmental Geology* 52:861–870.

Hamilton-Taylor, J., Price, N. B., 1983. *The geochemistry of iron and manganese in the waters and sediments of Bolstadfjord*, S.W. Norway.

Langmuir, D. 1997. *Aqueous Environmental Geochemistry*. Upper Saddle River, New Jersey, USA: Prentice-Hall, 600 pp.

Levy, M. C., Lopes, A. V., Cohn, A., Larsen, L. G., and Thompson, S. E. 2018. Land use change increases streamflow across the arc of deforestation in Brazil. *Geophysical Research Letters* 45:3520–3530.

Nóbrega, R. L. B., Lamparter, G., Hughes, H., Guzha, C. A., Amorim, R. S. S., and Gerold, G. 2018. A multi-approach and multi-scale study on water quantity and quality changes in the Tapajós River basin, Amazon. *Proceedings of the International Association of Hydrological Sciences* 377:3–7.

Machado, N., Lindenmayer, Z., Krogh, T. E., and Lindenmayer, D. 1991. U-Pb geochronology of Archean magmatism and basement reactivation in the Carajás área, Amazon shield, Brazil. *Precambrian Research* 49: 329–354.

Menezes, R. S. 2017. *Avaliação sazonal da qualidade da água em lagoas dos platôs da Serra Sul de Carajá, Sudeste da Amazônia, Brasil*. Dissertação de Mestrado. Instituto Tecnológico Vale—ITV.

Muniz, D. H. F., Moraes, A. S., Freire, I. S., Cruz, C. J. D., Lima, J. E. F. W., and Oliveira-Filho, E. D. 2011. Evaluation of water quality parameters for monitoring natural, urban, and agricultural áreas in the Brazilian Cerrado. *Acta Limnologica Brasiliensia* 23:307–317.

NBR 9897. 1987. Planejamento de amostragem de efluentes líquidos e corpos receptores—Procedimento.

NBR 9898. 1987. Preservação e técnicas de amostragem de efluentes líquidos e corpos receptores—Procedimento.

Nogueira, A. C. R., Truckenbrodt, W., and Pinheiro, R. V. L. 1995. Formação Águas Claras, Pré-Cambriano da Serra dos Carajás: redescrição e redefinição litoestratigráfica. *Boletim Museu Paraense Emílio Goeldi* 7:177–277.

Oliveira-Filho, E. C., and Parron, L. M. 2007. Avaliação de qualidade das águas no Brasil: o Rio Preto examinado. *Espaço & Geografia* 10:279–294.

Osté, L. A., Klein, J., and Zwolsman, G. J. 2011. Inventory and evaluation of methods to derive natural background concentrations of trace metals in surface water, and application of two methods in a case study. Deltares report. 1206111.005, Utrecht.

Panday, P. K., Coe, M. T., Macedo, M. N., Lefebvre, P., and Castanho, A. D. A. 2015. Deforestation offsets water balance changes due to climate variability in the Xingu River in eastern Amazonia. *Journal of Hydrology* 523: 822–829.

Price, N. B., and Calvert, S. E. 1973. A study of the geochemistry of suspended particulate matter in coastal waters. *Marine Chemistry* 1:169–189.

R Core Team. 2018. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna. https://www.R-project.org.

Reimann, C., Filzmoser, P., and Garrett, R. G. 2005. Background and threshold: critical comparison of methods of determination. *Science of the Total Environment* 346:1–16.

Reimann, C., Fabian, K., Birke, M., Filzmoser, P., Demetriades, A., Négrel, P., et al. 2018. GEMAS: Establishing geochemical background and threshold for 53 chemical elements in European agricultural soil. *Applied Geochemistry* 88:302–318.

Reimann, C., and Garrett, R. G. 2005. Geochemical background—Concept and reality. *Science of the Total Environment* 350:12–27.

Rodrigues, A. S. L., Malafaia, G., Costa, A. T., and Nalini, J. H. A. 2013. Background values for chemical elements in sediments of the Gualaxo do norte river basin, MG, Brazil. *Revista de Ciência Ambientais* 7:15–32.

Raiswell, R., and Canfield, D. E. 2012. The Fe biogeochemical cycle past and present. *Geochemical Perspectives* 1: 1–220.

Sahoo, P. K., Tripathy, S., Equeenuddin, Sk. Md., Panigrahi, M. K., 2012. Geochemical Characteristics of Coal Mine Discharge vis-à-vis Behavior of Rare Earth Elements at Jaintia Hill Coalfield, Northeastern India. *Journal of Gechemical Exploration*, *112*, 235–243.

Sahoo, P. K., Kim, K., Equeenuddin, Sk. Md., Powell, M. A., 2013. Current Approaches for Mitigating Acid Mine Drainage. *Reviews of Environmental Contamination and Toxicology*, *226*, 1–32.

Sahoo, P. K., Dall'Agnol, R., Salomão, G. N., Junior, J. S. F., Silva, M. S., Souza Filho, P. W. M., et al. 2019a. High resolution hydrogeochemical survey and estimation of baseline concentrations of trace elements in surface water of the Itacaiúnas River Basin, southeastern Amazonia: Implication for environmental studies. *Journal of Geochemical Exploration* 205:106321. doi:10.1016/j.gexplo.2019.06.003.

Sahoo, P. K., Tripathy, S., Equeenuddin, Sk. Md., Panigrahi, M. K., 2012. Geochemical Characteristics of Coal Mine Discharge vis-à-vis Behavior of Rare Earth Elements at Jaintia Hill Coalfield, Northeastern India. *Journal of Gechemical Exploration*, *112*, 235–243.

Sahoo, P. K., Dall'Agnol, R., Salomão, G. N., Junior, J. S. F., Silva, M. S., Martins, M. G. C., et al. 2019b. Source and background threshold values of potentially toxic elements in soils by multivariate statistics and GIS-based mapping—a high-density sampling survey in the Parauapebas basin from Brazilian Amazonia. *Environmental Geochemistry and Health* 42:1–28. doi:10.1007/s10653-019-00345-z.

Salomão, G. N., Dall'Agnol, R., Sahoo, P. K., Júnior, J. S. F., Silva, M. S., Sousa-Filho, P. W. M., et al. 2018. Geochemical distribution and threshold values determination of heavy metals in stream water in the sub-basins of Vermelho and Sororó rivers, Itacaiúnas River watershed, Eastern Amazon, Brazil. *Geochimica Brasiliensis* 32: 180–198.

Salomão, G. N., Figueiredo, M. A., Dall'Agnol, R., Sahoo, P. K., Filho, C. A., da Costa, M. F., et al. 2019. Geochemical mapping and background concentrations of iron and potentially toxic elements in active stream sediments from Carajás, Brazil–implication for risk assessment. *Journal of South American Earth Sciences* 92: 151–166.

Salminen, R., and Tarvainen, T. 1997. The problem of defining geochemical baselines. A case study of selected elements and geological materials in Finland. *Journal of Geochemical Exploration* 60:91–98.

Schneider, P., Nilius, U., Gottschalk, N., Sub, A., Schaffrath, M., Loser, R., et al. 2017. Determination of the Geogenic Metal Background in Surface Water: Benchmarking Methodology for the Rivers of Saxony-Anhalt, Germany. *Water* 9:75.

Silva Júnior, R. O., Queiroz, J. C. B., Ferreira, D. B. S., Tavares, A. L., Souza-Filho, P. W. M., Guimarães, J. T. F., et al. 2017. Estimativa de Precipitação e Vazões médias para a Bacia Hidrográfica do Rio Itacaiúnas (BHRI)—Amazônia Oriental, Brasil—Estimation of precipitation and average flows for the Itacaiúnas River

Watershed (IRW)—Eastern Amazonia, Brazil. *Revista Brasileira de Geografia Física* 10:1638–1654.

Sholkovitz, E. R., and Copland, D. 1982. The chemistry of suspended matter in Esthwaite Water, a biologically productive lake with seasonally anoxic hypolimnion. *Geochimica et Cosmochimica Acta.* 46:393–410.

SEMAS/PA (Secretaria Estado Meio Ambiente). 2012. *Sistema de Gerenciamento de Recursos Hídricos do Estado do Pará—Brasil*. Brazil: Secretaria de Estado de Meio Ambiente—SEMA.

Shah, M. H., Iqbal, J., Shaheen, N., Khan, N., Choudhury, M. A., and Akhter, G. 2012. Assessment of background levels of trace metals in water and soil from a remote region of Himalaya. *Environmental Monitoring and Assessment* 184:1243–1252.

Smith, R. A., Alexander, R. B., and Schwarz, G. E. 2003. Natural background concentrations of nutrients in streams and rivers of the conterminous United States. *Environmental Science & Technology* 37(14):3039–3047.

Souza-Filho, P. W. M., Souza, E. B., Silva Júnior, R. O., Nascimento Jr., W. R., Mendonça, B. R. V., Guimarães, J. T. F., Dall'Agnol, R. and Siqueira, J. O. 2016. Four decades of land-cover, land-use and hydroclimatology changes in the Itacaiúnas River watershed, southeastern Amazon. *Journal of Environmental Management* 167:175–184. doi: 10.1016/j.jenvman.2015.11.039

Sunda, W. G., and Kieber, D. J. 1994. Oxidation of humic substances by manganese oxides yields low-molecular-weight organic substrates. *Nature* 367:62–64.

Tiburtius, E. R. L., Peralta-Zamora, P., and Leal, E. S. 2004. Contaminação de águas por BTXS e processos utilizados na remediação de sítios contaminados. *Química Nova* 27: 441–446.

Vasquez, L. V., Rosa-Costa, L. R., Silva, C. G., Ricci, P. F., Barbosa, J. O., & Klein, E. L. 2008. Geologia e recursos minerais do estado do Pará: Sistema de Informações Geográficas – SIG: Texto explicativo dos mapas geológico e tectônico e de recursos minerais do estado do Para. http://rigeo.cprm.gov.br/jspui/handle/doc/10443.

Voelker, B. M., Morel, F. M. M., and Sulzberger, B. 1997. Iron redox cycling in surface waters: effects of humic substances and light. *Environmental Science & Technology* 31:1004–1011.

VALE/amplo. Estudo de Impacto Ambiental – EIA: *Projeto Ferro Serra Norte – Mina N4 e N5 / Estudo Global das Ampliações.* Volumes 1 a 5, 2010.