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

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RESUMO

Levantamento geoquímico nas sub-bacias Vermelho (SBV) e Sororó (SBS) da bacia do Itacaiúnas no sudeste da região Amazônica revela que parâmetros físico-químicos da água superficial não mostram variações acentuadas entre as estações chuvosa e seca. Com exceção de Fe e Mn, em geral os demais metais revelam baixas concentrações na água e não foram observadas evidências significativas de contaminação. Conteúdos comparativamente mais elevados foram obtidos principalmente durante a estação chuvosa. Fe e Mn se distribuem regularmente na água na área estudada e o aumento de seu conteúdo foi favorecido pelo desmatamento. A concentração de Mn aumenta durante a estação seca possivelmente devido a processos biogeoquímicos. Altas concentrações de Fe e Mn em águas superficiais são inerentes às condições locais da região Amazônica. Fatores geogênicos influenciam a distribuição na água de Co, Cr, Cu, Ni, Pb, Sn, V e Zn. Efeitos antrópicos são subordinados, exceto para Fe e Mn ou em áreas localizadas. A definição de valores de *threshold* para As, Co, Cr e Pb, apresentou limitações. Valores de *threshold* puderam ser definidos em pelo menos uma estação nas duas sub-bacias para Cu, Ni, Sn, V e Zn. No caso de Fe total, foram obtidos valores de *threshold* de 5 a 6 mg/L e de 2 a 3 mg/L nas estações chuvosa e seca, respectivamente. Os valores de *threshold* para Mn são de 0,30 a 0,45 mg/L na estação chuvosa e, na estação seca, decrescem para 0,20 a 0,30 mg/L na VSB e aumentam para 1,3 a 1,4 mg/L na SSB.

Palavras-chave: Geoquímica de água fluviais; Valores de threshold; Metais pesados; Bacia do rio Itacaiúnas; Amazônia Oriental.

ABSTRACT

Geochemical survey in the Vermelho (VSB) and Sororó (SSB) sub-basins of the Itacaiúnas basin in southeastern Amazonian region has shown that the physical-chemical parameters of stream water do not display accentuated variations between the rainy and dry seasons. Except for Fe and Mn, in general most metals show low contents in water and evidences of significant contamination were not observed. Higher contents were mostly registered during the rainy season. Fe is regularly distributed in water in the studied area and the increase of its concentration was favored by deforestation. Mn contents increase during the dry season possibly due to biogeochemical processes. High Fe and Mn contents in water are inherent to the specific local conditions prevalent in the Amazonian region. Geogenic influence in metal distribution in water is significant for Co, Cr, Cu, Ni, Pb, Sn, V, and Zn. Anthropic effects are subordinate except for Fe and Mn or in local areas. The definition of threshold values for As, Co, Cr, and Pb, was limited, however, threshold values for Cu, Ni, Sn, V, and Zn were estimated for at least one season in each sub-basin. Threshold values of total iron were obtained (5 to 6 mg/L and 2 to 3 mg/L in the rainy and dry seasons, respectively). Estimated Mn threshold values are 0.30 to 0.45 mg/L in the rainy season and in the dry season they decrease to 0.20 to 0.30 mg/L in VSB and increase to 1.3 to 1.4 mg/L in SSB.

Keywords: Stream water geochemistry, Heavy metals, Threshold limit values, Itacaiúnas River Watershed, Eastern Amazon.

1 INTRODUCTION

Environmental monitoring surveys are increasing not only because of its inherent relevance, but also due to the availability of high standard analytic and computational facilities that allow quick responses (Tercier-Waeber *et al.* 2009, Wade *et al.* 2012, Aubert *et al.* 2014, Halliday *et al.* 2015, Girardi *et al.* 2016). Elemental concentrations in river waters are related to the local geologic setting but are also influenced by various other anthropogenic factors. Changes in land use and land cover can drastically influence natural hydrological regime and quality of stream water and water bodies (Brion *et al.* 2011, Souza-Filho *et al.* 2016, Levy *et al.* 2018). Comparisons of hydrological behavior and elemental concentrations in rivers with different land uses were reported by Neal *et al.* (2012), Wade *et al.* (2012) and Outram *et al.* (2014).

Particularly for toxic heavy metals, the determination of background values or threshold limits of elements is highly relevant to distinguish between natural and anthropogenically-influenced metal concentrations (Urresti-Estala *et al.* 2013, Arpine & Gayane 2016). The imprecise use of the terms background and threshold and the statistical methods for their determination have been discussed (Ander *et al.* 2013, Cembranel *et al.* 2017, Gałuszka & Migaszewski 2012, Gałuszka 2007, Matschullat *et al.* 2000, Nakić *et al.* 2007, 2010, Peh *et al.* 2009, Reimann & Garrett 2005, Reimann *et al.* 2005, 2018, Rodrigues *et al.* 2013, Teng *et al.* 2009, Urresti-Estala *et al.* 2013, Zgłobicki *et al.* 2011). Geochemical background and threshold values are generally used as a reference to distinguish between natural concentrations of a certain element from the concentrations affected by anthropogenic activities, considering temporal and spatial variables of the area under investigation (Gałuszka 2007, Reimann & Garrett 2005). Moreover, statistical methods for the determination of threshold values are a current discussion on literature (Reimann *et al.* 2005, 2018, Cembranel *et al.* 2017, Ander *et al.* 2013, Rodrigues *et al.* 2013, Nakić *et al.* 2007, 2010, Peh *et al.* 2009, Teng *et al.* 2009, Gałuszka 2007, Reimann *et al.* 2005, Reimann & Garrett 2005, Matschullat *et al.* 2000).

Geochemical background surveys of many stream water have been widely conducted in many countries worldwide. However, in Brazil and particularly in the Amazon region, they are still scarce. To fulfill partially this gap of information, the Instituto Tecnológico Vale (ITV) is undertaking, at present, a systematic geochemical background survey in surficial water, stream sediments and soils in the Itacaiúnas River Watershed (IRW). In part of this area, previous geochemical surveys in soil and stream sediments were conducted by Companhia de Pesquisa de Recursos Minerais (CPRM – Brazilian Geological Survey, CPRM 2013, 2012) and Vale S/A (unpublished internal reports). A geochemical study of surface water samples in the Parauapebas area of the IRW was undertaken by the Museu Paraense Emílio Goeldi (MPEG) (Ruivo & Sales 1989). The obtained results by MPEG team are of historical interest but their use is limited for the sampling criteria and analytical method adopted.

The present work is focused on the geochemistry and characterization of surficial water of the sub-basins of the Vermelho (VSB) and Sororó (SSB) rivers, located in the eastern domain of the IRW (Figure 1). This study is related to the Geochemical Background of the Itacaiúnas River Watershed (GBI) project, conducted by ITV. The study area was significantly influenced by land-use and land cover changes over the past decades (Souza-Filho *et al.* 2016), with accentuated expansion of pasturage and cattle production, development of mining projects, and growth of urban areas. As a consequence, the dispute for territory in the region has intensified and the quality of water resources became a serious concern. It is known that monitoring of stream water is an important step to evaluate its quality, to identify the nature and spatial distribution of eventual contaminants and to project environmental mitigation measures, if needed. This study aims to make a general water quality characterization and estimate threshold limit values of some heavy metals, identified as Potentially Toxic Elements (PTEs), in the stream water of the two mentioned sub-basins of IRW (VSB and SSB). This study will contribute to define the stream water geochemical characteristics and to establish a reference picture for it in the eastern domain of the IR.

2 LOCATION AND GENERAL ASPECTS OF THE STUDY AREA

The study area corresponds to the sub-basins of Vermelho and Sororó rivers located in the eastern IRW, North of Tocantins Basin (Figure 1).

The IRW is entirely located in the Carajás region, Pará state, north of Brazil, and the main city in the region is Marabá. The VSB and the SSB cover

an area of 7,000 and 3,600 km^2, respectively, and both represent approximately 25.6% of the IRW (41,342 km^2). The towns of Curionópolis and Eldorado dos Carajás are situated in the study area (Figure 1).

The IRW was originally covered by the Amazon rainforest. However, it suffered intense changes in the land use and land cover, due to accelerated human occupation over the last decades. At present, areas covered by reminiscent tropical rainforest are mostly limited to environmental protected areas and indigenous lands (cf. Figures 1A and 2A) and pasturages are largely dominant. Pristine montane savanna covering ferruginous canga and urban areas are subordinated (Figure 1A; Souza-Filho *et al.* 2016). The region has a monsoon climate (Alvares *et al.* 2013) with a rainy season (November to April; Figure 2B) with precipitation average of 1,550 mm, and a comparatively dry season (May to October; Figure 2C) with precipitation average of 350 mm (Silva Júnior *et al.* 2017).

Along the valleys of Vermelho and Sororó rivers, the relief of the region is flat with altitudes ranging mostly from 80 to 400 m (Figure 2D). It becomes more accentuated in the western part of the VSB, where hilly terrains, associated to highly dissected plateaus, with altitudes ranging from 400 to 780 m, are present. Besides that, local highs are related to mafic-ultramafic intrusions in the central lower lands and to the units of the Parnaíba sedimentary basin, in the eastern border of the Sororó sub-basin.

The geology of the study area is marked by two main geological domains, the Carajás province, restricted to the western part of VSB, and the Araguaia Belt that corresponds to most of it (Figure 2E). The Carajás Province is an Archean domain located in the southeastern part of the Amazonian Craton (Vasquez *et al.* 2008, Almeida *et al.* 2011, Feio *et al.* 2013, and references therein) and it has a remarkable economic relevance due to its active mines of iron, copper (both world-class), manganese and nickel (Docegeo 1988, Moreto *et al.* 2014).
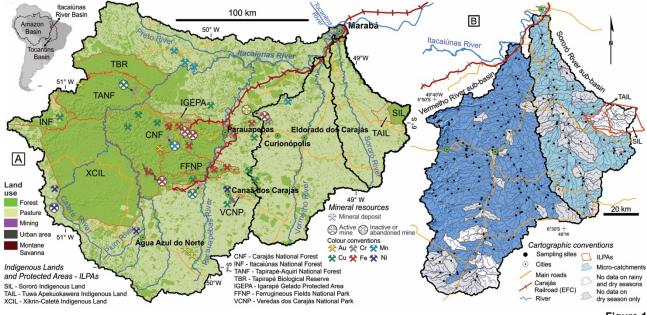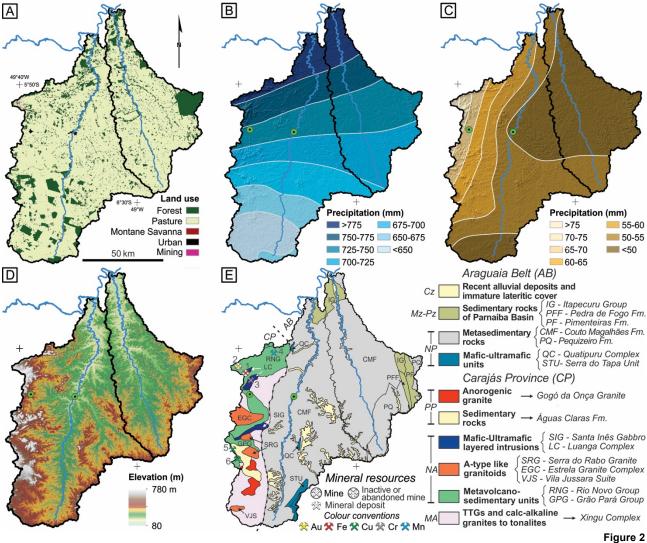

Figure 1

Map of the Itacaiúnas River Watershed in the region of Carajás, northern Brazil (A), highlighting the Vermelho and Sororó rivers sub-basins. The location of main cities, mines, and mineral deposits, and the indigenous lands and protected areas are indicated, as well as main land uses. In the study area map (B), the individualized micro-catchments and the location of sampling sites for stream water are shown.

In the Carajás Province, the main units are Mesoarchean calc-alkaline granites, tonalites and trondhjemites with subordinate gneisses and migmatites and local remnants of greenstone belts (Machado *et al.* 1991, Feio *et al.* 2013, Moreto *et al.* 2014). The granitoid basement is overlain by the Neoarchean Itacaiúnas Supergroup, which is represented by mafic-felsic volcanic sequences of

the Grão Pará (Zucchetti & Lobato 2004, Martins *et al.* 2017), and Rio Novo groups (Gibbs *et al.* 1986, Docegeo 1988, Machado *et al.* 1991, Vasquez *et al.* 2008). These units are crosscut by Archean syntectonic A-type like granitoids (Huhn *et al.* 1999, Barros *et al.* 2001, Sardinha *et al.* 2006, Feio *et al.* 2012, Dall'Agnol *et al.* 2017), layered mafic-ultramafic rocks (Machado *et al.*

1991, Vasquez *et al.* 2008, Teixeira *et al.* 2015), and Paleoproterozoic anorogenic A-type granitic plutons (Teixeira *et al.* 2017). Paleoproterozoic clastic sedimentary rocks cover partially the Archean sequences of the study area (Araújo and Maia 1991, Nogueira *et al.* 1995).

In the Neoproterozoic Araguaia Belt, the low-grade metasedimentary rocks of the Couto Magalhães Formation, composed mainly by phyllites and slates, interlayered with minor amounts of quartzite, meta-arkose and metalimestone (Gorayeb 1981, Hasui *et al.* 1984, Dall'Agnol *et al.* 1988), are dominant. The

metamorphic grade increases towards east where it occurs the schists of the Pequizeiro Formation (Figure 2E). Metamafic-ultramafic bodies are found in the central-southern part of the VSB (Serra do Tapa and Quatipuru units; Vasquez *et al.* 2008). Paleozoic-Mesozoic sedimentary rocks related to the Parnaíba Basin occur in the extreme eastern part of SSB and in the north of the study area, represented by Itapecuru Group, Pimenteiras and Pedra de Fogo formations. Neogene sedimentary deposits of sand, clay and ferruginous crusts, are mainly located at the main water streams of the Vermelho and Sororó rivers.

Figure 2

General aspects of the study area: A) Simplified land cover and land use map of the studied area in 2013 (Souza-Filho *et al.* 2016). Precipitation maps during (B) rainy season, from December to February, and (C) dry season, from June to August. (D) Hypsometric map derived from Shuttle Radar Topography Mission (SRTM) data of the United States Geological Survey (USGS). (E) Simplified geological map of the study area [based on Teixeira *et al.* (2017), Vasquez *et al.* (2008), Pimentel *et al.* (2004) and Alvarenga *et al.* (2000)], exhibiting the main lithostratigraphic units of the Archean Carajás Province (ACP) and Neoproterozoic Araguaia Belt (NAB). Chronostratigraphic conventions: MA=Mesoarchean; NA=Neoarchean; PP=Paleoproterozoic; NP=Neoproterozoic; Pz=Paleozoic; Mz=Mesozoic; Cz=Cenozoic. Mines and mineral deposits: 1=Serra Leste active mine; 2=Serra Pelada abandoned mine; 3=Luanga; 4=Serra do Sereno; 5=Cristalino; 6=Serra Buriti. In figures 2 to 5, the crosses located at the left upper corner and at the lower right corner indicate the latitudes of 5°50' and 6°30' South and longitudes of 49°40' and 49° West, respectively (cf. Figure 1B).

3 MATERIALS AND METHODS

3.1 WATER SAMPLING: LOCATION AND METHOD

Sampling method followed the procedures defined in the GBI project of ITV. Before sampling, the microbasins present in the entire area of the Itacaiúnas watershed were identified using remote sensing techniques. It was planned to collect one stream water sample in each microbasin, preferentially near the mouth of the tertiary water flow. In the whole Itacaiúnas basin around nine hundred sampling points were visited in each season. Two hundred and twenty-nine sites from that total are located in the eastern part of IRW in the domains of Vermelho and Sororó sub-basins (Figure 1B). Field works were undertaken in two distinct periods, during the rainy (March to April) and dry season (July to August), of 2017. In both seasons, a limited number of microbasins could not be sampled due to access conditions. These include the microbasins located in two indigenous lands of the Sororó Sub-basin (Figure 1B). During the dry season, this number increased significantly because of the intermittent character of part of the local drainage, in particular in the middle and high course of Sororó River and in the high course of Vermelho River. Duplicate samples were collected separately as additional samples immediately after the collection of the representative stream water samples at an approximate rate of one duplicate per each 20 samples collected.

Sampling and preservation of water samples were done following the Standard Methods for the Examination of Water and Wastewater (SMWW, methods 1060 and POP LB 010; APHA 2012). The samples were collected in the middle of the channel, in a location upstream from the collection point of the stream sediments. At each point, physico-chemical parameters were measured in situ with multi-parameter probe and two separated samples were then collected, the first to be stored in a 30 ml high density polyethylene bottle (anions determination / non-purgeable organic carbon - NPOC), and a second of 60 ml high density polyethylene bottle (metal element analysis).

3.2 ANALYTICAL METHODS

The analytical methods adopted for stream water samples were previously determined for the whole sample set of the BGI project. Five physico-chemical parameters (pH, conductivity - EC, dissolved oxygen - DO, temperature, and redox potential – Eh) were measured in situ with a multiparameter probe (HI 98194 from Hanna Instruments®), while TDS and turbidity were measured in the laboratory. The unfiltered water samples were acidified with HNO_3 to pH < 2 at the time of collection and used to analyze total metal concentrations. The total content of twenty-four elements (Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, N, Na, Ni, Pb, Se, V, and Zn) in water were analyzed by inductively coupled plasma mass spectrometry (ICP-MS), except for total P. Anions (fluoride, chloride, nitrate, and sulphate) were determined by ion chromatography. Table 1 summarizes information regarding analytical methods and sample preparation. All analytical procedures were undertaken by the certified laboratory Bioagri Ambiental Ltda. A summary of the analytical results and detection limits of these elements is shown in Table 2.

3.3 GEOGRAPHIC INFORMATION SYSTEM AND SPATIAL ANALYSIS

A specific geochemical database (BDGeoq) was structured by the team of the GBI project initially to guide sample location and store all field data using tablets and gradually additional related information as analytical results and geochemical maps. Programming rules were applied to avoid accidental errors in sampling registering and duplicate collection of samples in a same microbasin. After the conclusion of the project, the intention is to make the BDGeoq available for consultation of enabled users via an online geographic information system platform (SIGGeoq) (*e.g.*, PostGIS or Quantum GIS-QGIS).

For the construction of geochemical maps, and also for other maps presented in this paper, the datum World Geodetic System 1984 (WGS84) was adopted. The delimitation of catchment areas was performed via algorithm-based analysis via QGIS software (Quantum GIS Development Team 2009), based on a digital elevation model (DEM) from Shuttle Radar Topography Mission

(SRTM) conducted by the United States Geological Survey (USGS) (freely available online at https://earthexplorer.usgs.gov/). The contouring and coloring in the maps showing the distribution of elements were defined taking in account the analytical results above the detection limits for each element. The resulting intervals on both rainy and dry seasons are easily comparable.

Table 1 – Physico-chemical parameters and anions in surface water samples

Parameters	Detection limit (DL)	Unit	Specific conditions	Method	Maximum holding time
[1]Dissolved oxygen	0.1	mg/L	In situ	HI 98194 multiparameter probe	-
[2]pH (25°C)	2 to 13	-			
[3]Temperature	-	°C			
[4]Specific electrical conductivity	1.0	µS/cm			
[5]Redox potential	-	mV			
[6]Total Dissolved Solids (TDS)	5.0	mg/L			7 days
[7]Turbidity	0.1	NTU		Nephelometric	-
[8]Phosphorus total (P_{total})	0.01		Cooling at 4°C	Sulfuric acid digestion at pH < 2	28 days
[9]Nitrate (NO_3^-)	2.2	mg/L		Ion chromatography	28 days
[9]Sulfate ($SO_4^{2)}$)	0.5				
[9]Fluoride (F^-)	0.05				
[9]Chloride (Cl^-)	0.5				48 hours

Note: The analytical procedures were adopted accordingly to the SMWW methods (APHA 2012): 4500O G[1]; 4500H+ B[2]; 2550 B[3]; 2510 B[4]; 2580 B[5]; 2540 A, B, C, D, E[6]; 2130 B[7]; 4500 P-E[8]; and to the EPA 300.0: 1993, 300.1: 1999, POP PA 032 - Rev. 12[9].

3.4 STATISTICAL ANALYSIS AND DETERMINATION OF THRESHOLD VALUES

The simple substitution method (Keith *et al.* 1983) was applied for the replacement of analytical values below the detection limit (<DL), similarly suggested by Reimann & Caritat (2017). Descriptive statistics of element concentrations were determined, some before and after removing outliers detected by Grubb's test (Grubbs 1969). Physico-chemical parameters and metal concentration were exhibited via box plot representation in order to drive a better understanding of the overall data distribution. Threshold values were only determined according to the following statistical methods: The Median +

2 Median Absolute Deviation (M_{MAD}), Tukey's inner fences (TIF), the cumulative probability (CP), the iterative 2σ technique (I2σ) and the calculated frequency distribution (DF). Regarding a better understanding on the overall description of these methods see Reimann *et al.* (2005, 2018), Reimann & Caritat (2017), Cembranel *et al.* (2017), Ander *et al.* (2013), Urresti-Estala *et al.* (2013) and Nakić *et al.* (2007). Statistical analyses and calculations were carried out using R (R Development Core Team 2008), Action Stat Pro (Equipe Estatcamp 2014) and the VB Background® freeware (Nakić *et al.* 2007).

4 RESULTS

4.1 PHYSICO-CHEMICAL PARAMETERS AND ANIONS

Boxplots of physico-chemical parameters (temperature, dissolved oxygen, acidity, specific electrical conductivity, redox potential, total dissolved solids, and turbidity) and anions (fluoride, chloride and nitrate) were constructed separately for both Vermelho and Sororó sub-basins (Figure 3). In addition the maximum standard values for fresh water quality of the contemplated in the Brazilian legislation (CONAMA 357/05) are also presented.

The averages of the measured temperature values in the studied sub-basins show a narrow range (Figure 3A). In VSB, when comparing the

rainy and dry periods, the maximum, median and minimum temperatures decreased around 2 ± 1 °C each, with a wider temperature oscillation in the dry period. In SSB, the minimum temperature variation is similar to that observed in VSB, whereas the maximum and median temperatures mildly increased (Figure 3A). However, right and left skewed outliers values were mainly observed in SSB during dry season. By disregarding these anomalous values, it is deduced that the temperature in the SSB is not really discordant of VSB (Figure 3A) and the overall dataset tends to a normal distribution.

Table 2 - Descriptive statistics of stream water analyses of samples from Vermelho (VSB) and Sororó (SSB) sub-basins during rainy (-R) and dry (-D) seasons. n: number of samples; DL: detection limit; LOL: lower outlier limit; Min: minimum concentration; M: 50th percentile of the data set, also known as median; and Max: maximum concentration. Mean (σ) and standard deviation (SD) were calculated before (BRO) and after (ARO) removing outliers

Element	SB - Season	n	DL	n<DL	%<DL	LOL	n≥LOL	%≥LOL	Min	M	Max	BRO σ	BRO SD	ARO σ	ARO SD
As	VSB-R	143	1	130	90.9	1.03	13	9.1	<1	<1	4.37	0.62	0.50	0.50	0
	VSB-D	123	1	114	92.7	1.26	4	3.3	<1	<1	2.8	0.61	0.42	0.50	0
	SSB-R	75	1	54	72.0	1.19	21	28.0	<1	<1	3.99	0.92	0.79	0.50	0
	SSB-D	50	1	34	68.0	2.69	3	6.0	<1	<1	3.39	0.90	0.71	0.76	0.45
Co	VSB-R	143	1	66	46.2	4.90	5	3.5	<1	1.11	9.58	1.53	1.51	1.36	1.10
	VSB-D	123	1	62	50.4	6.67	5	4.1	<1	<1	17.7	1.74	2.38	1.38	1.32
	SSB-R	75	1	58	77.3	2.07	3	4.0	<1	<1	4.29	0.77	0.62	0.68	0.38
	SSB-D	50	1	33	66.0	3.44	2	4.0	<1	<1	4.04	0.87	0.71	0.75	0.40
Cr	VSB-R	143	1	82	57.3	3.94	15	10.5	<1	<1	32.7	1.85	3.45	0.99	0.76
	VSB-D	123	1	86	69.9	1.76	20	16.3	<1	<1	85.7	2.38	8.84	0.63	0.29
	SSB-R	75	1	30	40.0	4.64	2	2.7	<1	1.24	11.6	1.49	1.53	1.30	0.90
	SSB-D	50	1	42	84.0	1.07	8	16.0	<1	<1	37.8	1.57	5.42	0.50	0.00
Cu	VSB-R	143	1	45	31.5	11.4	6	4.2	<1	1.66	19.3	2.94	3.41	2.44	2.40
	VSB-D	123	1	44	35.8	5.84	9	7.3	<1	1.35	45.9	2.48	5.03	1.52	1.11
	SSB-R	75	1	19	25.3	7.35	5	6.7	<1	1.46	40.4	2.66	5.36	1.50	0.85
	SSB-D	50	1	27	54.0	-	0	0	<1	<1	4.02	1.17	0.93	1.17	0.93
Fe	VSB-R	143	0.02	0	0	9.45	5	3.5	0.82	3.56	19.1	3.99	2.44	3.63	1.45
	VSB-D	123	0.02	0	0	7.73	4	3.3	0.36	1.55	16.3	2.27	2.18	1.98	1.37
	SSB-R	75	0.02	0	0	11.90	2	2.7	1.81	4.28	14.9	4.54	1.92	4.30	1.22
	SSB-D	50	0.02	0	0	5.53	3	6.0	0.57	1.94	7.12	2.27	1.40	2.01	0.95
Mn	VSB-R	143	0.001	0	0	1.04	8	5.6	0.03	0.22	3.74	0.33	0.42	0.25	0.18
	VSB-D	123	0.001	0	0	0.61	27	22.0	0.02	0.17	5.90	0.62	1.09	0.18	0.12
	SSB-R	75	0.001	0	0	0.71	5	6.7	0.03	0.20	2.12	0.28	0.30	0.21	0.13
	SSB-D	50	0.001	0	0	2.64	4	8.0	0.02	0.62	9.14	0.99	1.48	0.64	0.46
Ni	VSB-R	143	1	53	37.1	6.25	15	10.5	<1	1.51	16.8	2.40	2.88	1.57	1.24
	VSB-D	123	1	56	45.5	5.01	11	8.9	<1	1.09	20.7	1.88	2.72	1.20	0.88
	SSB-R	75	1	14	18.7	5.25	1	1.3	<1	1.61	5.25	1.68	0.87	1.63	0.77
	SSB-D	50	1	31	62.0	11.2	1	2.0	<1	<1	11.2	1.15	1.59	0.94	0.66
Pb	VSB-R	143	1	103	72.0	2.70	2	1.4	<1	<1	9.21	0.83	0.86	0.76	0.46
	VSB-D	123	1	110	89.4	1.07	13	10.6	<1	<1	3.65	0.65	0.51	0.50	0
	SSB-R	75	1	36	48.0	6.57	2	2.7	<1	1.13	9.52	1.28	1.34	1.09	0.69
	SSB-D	50	1	43	86.0	1.0	7	14.0	<1	<1	1.69	0.62	0.31	0.50	0.00
Sn	VSB-R	143	1	83	58.0	6.07	14	9.8	<1	<1	22.4	2.30	3.62	1.26	1.23
	VSB-D	123	1	37	30.1	25.3	1	0.8	<1	1.88	25.3	2.25	2.59	2.07	1.53
	SSB-R	75	1	53	70.7	3.84	3	4.0	<1	<1	5.91	1.00	1.05	0.83	0.64
	SSB-D	50	1	8	16.0	13.3	3	6.0	<1	2.51	19.3	3.40	3.54	2.62	1.62
V	VSB-R	143	1	53	37.1	7.58	8	5.6	<1	1.66	18.9	2.19	2.42	1.75	1.42
	VSB-D	123	1	48	39.0	5.80	10	8.1	<1	1.42	31.1	2.24	3.62	1.46	1.09
	SSB-R	75	1	14	18.7	5.20	2	2.7	<1	1.52	8.67	1.72	1.19	1.58	0.77
	SSB-D	50	1	31	62.0	-	0	0	<1	<1	2.89	0.92	0.63	0.92	0.63
Zn	VSB-R	143	1	51	35.7	52.7	4	2.8	<1	7.12	517.0	14.41	44.35	9.78	11.00
	VSB-D	123	1	4	3.3	61.0	3	2.4	<1	9.03	109.0	14.39	15.60	12.53	9.76
	SSB-R	75	1	2	2.7	63.6	5	6.7	<1	15.30	151.0	22.54	24.00	17.47	11.74
	SSB-D	50	1	0	0	68.4	5	10.0	1.2	11.25	170.0	26.28	38.88	14.79	14.34

Note: Concentration values of Fe and Mn are expressed in mg/L, and for the other elements in μg/L. Data below DL were replaced by ½ of the DL value. Cd, Hg and Mo were not exhibited because they presented more than 98% of the overall data <DL. '-' Value not applicable.

In general, in both sub-basins, except for a few lower outliers, pH values are higher than 6 (Figure 3C). Stream water tends to be more acidic during rainy than dry season, and VSB exhibited wider distribution of pH values in comparison to SSB. When comparing between rainy and dry periods, VSB and SSB showed increasing values for median and first and third quartiles in the dry season. The obtained values indicate a near neutral character for stream water of both sub-basins. High-pH values (>8.35; alkaline water) are outliers and were reported during the rainy period in both sub-basins. Comparatively lower pH values (<6,15; acid to near neutral water) correspond to outliers and extremes and were mostly reported during dry period, especially in SSB.

The specific electrical conductivity and total dissolved solids (TDS) show similar behavior. It is clear that, in a same period, the stream waters of

the VSB tend to present higher and more variable values for both parameters in comparison to SSB (Figures 3G, H). When comparing the rainy and dry seasons in each sub-basin isolated, it is observed a similar picture for total dissolved solids, with higher and more variable values in the dry season for both, VSB and SSB. On the other hand, specific electrical conductivity shows also a larger variation interval in the dry season, but values obtained in the two seasons are superposed. Outliers of electrical conductivity are more common in VSB in both seasons, and TDS outliers are only observed in VSB (Figures 3G, H). By removing outliers, VSB and SSB exhibited similar right-skewed conductivity distribution in both seasons.

Dissolved oxygen (DO) presents similar trend in both sub-basins during the rainy period, while in the dry period, VSB displays mostly higher values and a much larger variation of DO in comparison to SSB (Figure 3B). DO in SSB has little variation when comparing to the rainy and dry periods, but boxplot indicates that lower values are dominant in the interval Q1-Q3 and the median value is significantly lower compared to that of the raining season (Figure 3B).

When evaluating the turbidity, it is clear that stream water in VSB and SSB presents substantially higher turbidity values during the rainy season in comparison to the dry period (Figure 3D). Moreover, SSB has a little higher turbidity during the rainy period in comparison to VSB, contrasting with the dry season when the reverse is observed. Outliers and extremes are far more common in VSB than in SSB (Figure 3D).

In regard to the analyzed anions, in both sub-basins, Chloride (Cl^-) and Fluoride (F^-) show similar patterns than specific electrical conductivity and TDS (Figure 3H, I and J). For nitrate (NO_3^-), few analyses presented values above the detection limit. VSB tends to have higher concentrations of nitrate in comparison to SSB. Moreover, VSB exhibited higher concentrations during the rainy season compared to the dry period (Figure 3K).

4.2 DESCRIPTIVE STATISTICS OF HEAVY METALS

In this study, only 11 elements (As, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sn, V, and Zn) that presented substantial amount of analytical data > DL will be discussed in detail, and Cd, Hg, and Mo (> 98% of the overall data was < DL) will not be considered. It can be observed that the proportion of values <DL is also high for As and Pb, the latter mainly during the dry season (Table 2). For statistical analysis, values <DL were replaced by 1/2 DL. Table 2 summarizes the statistics of analytical results of stream water samples from VSM and SSB during the rainy and dry seasons.

The boxplots for the 11 mentioned elements (Figure 4) show some relevant aspects: (1) As, Co, Cu, Ni, Pb, Sn, and V, do not present any result exceeding the maximum tolerated limits as defined by CONAMA 357/05. (2) Cr and Zn both have only one result corresponding to extreme outlier values above that limit and the anomalous Cr value was obtained in an area in the proximities of the Quatipuru mafic-ultramafic unit. (3) Independent of the period of the year, Mn behavior is entirely distinct from those of the previous elements. It displays dominance of values above the maximum of CONAMA 357/05, with median, 25th and 75th quartiles values being higher than it. (4) In the case of total Fe, there is no reference value by CONAMA 357/05, but the Fe contents in water are high (median values > 1.50 mg/L; minimum values > 0.35 mg/L; maximum values attaining 7.12 to 19.1 mg/L; Table 2). It can be concluded that Fe contents in water are elevated and its behavior is similar in this perspective to Mn.

Contents of most elements, including Cr, Cu, Fe, Ni, Pb, and V, decrease in water in the dry season compared to the rainy one in both VSB and SSB (Table 2, Figure 4). On the contrary, Sn contents in water increase in both sub-basins during the dry season. Mn contents increase in the dry season in the SSB and decrease in the VSB and Zn shows an opposite behavior. In general, there is a tendency to higher metal content in water during the rainy season. In the SSB, Fe and Mn show distinct behavior.

4.3 SPATIAL DISTRIBUTION OF HEAVY METALS

The spatial distribution of nine selected elements in VSB and SSB is shown in Figure 5. Arsenic and Pb were not illustrated because on an average they show more than 70% of results <DL (Table 2). Cobalt and Cr also show a large number of results <DL (Table 2) and this can be seen in the corresponding geochemical maps (Figure 5). In general, the higher contents of most metals in water during the rainy season is indicated by the contrast between the corresponding geochemical
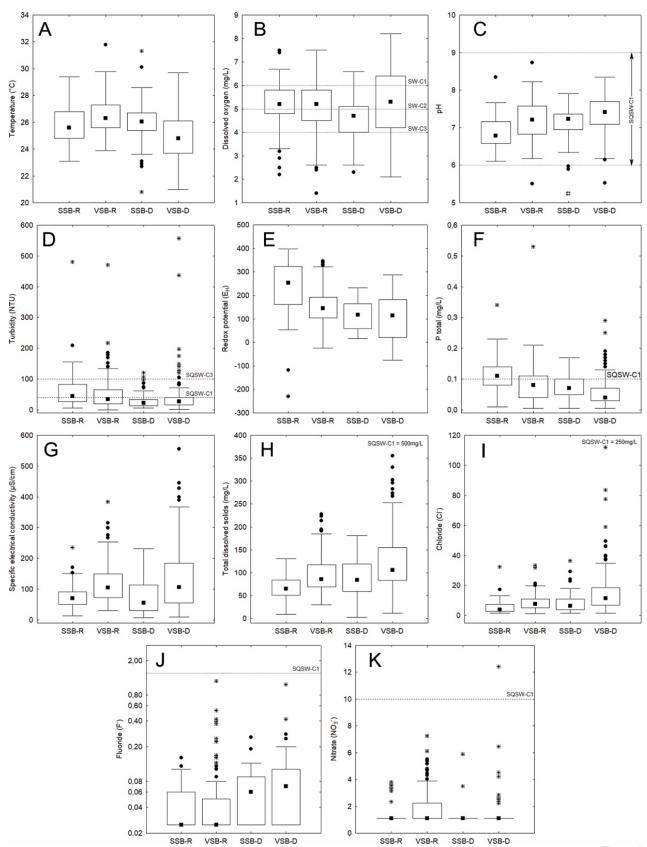
Figure 3

Boxplots of main physico-chemical parameters in stream water of Sororó (SSB) and Vermelho (VSB) sub-basins, analyzed during rainy (-R) and dry (-D) seasons: Temperature (A); dissolved oxygen (B); pH (C); turbidity (D); redox potential (E); P total (F); specific electrical conductivity (G); total dissolved solids (H); and anions: chloride (I) fluoride (J); and nitrate (K). Dashed line represents standard quality for sweet water (SQSW) based in CONAMA 357/05 and the reference class is indicated. The box indicates approximately the 25th, 50th (median=black square) and 75th percentile; outliers are defined according to: (upper whisker, lower whisker) = (upper hinge, lower hinge) ± 1.5*hinge width. Filled circles and asterisks represents respectively outliers and extremes.
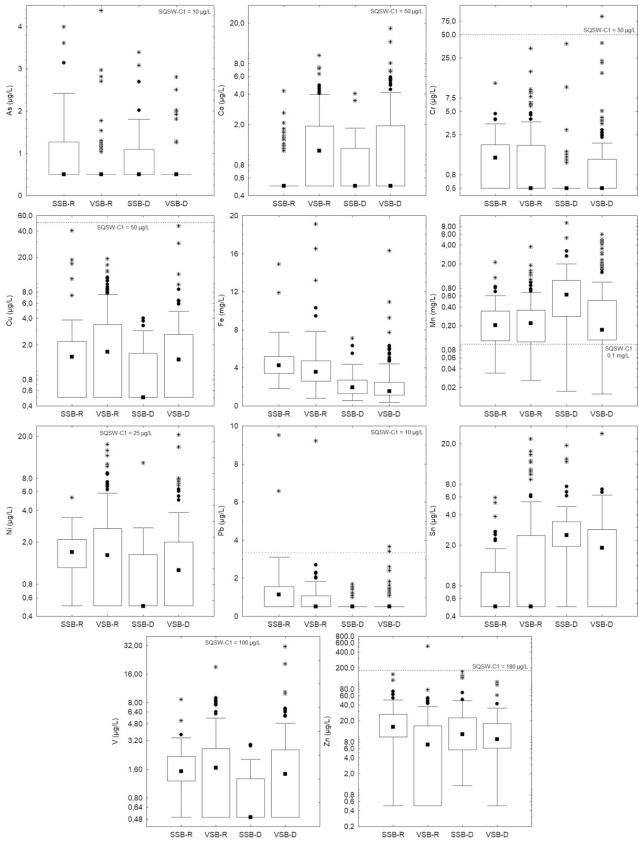
Figure 4
Boxplots of metal contents in stream water of the Sororó (SSB) and Vermelho (VSB) sub-basins, obtained during rainy (-R) and dry (-D) seasons. Standard quality for sweet water (SQSW) is given or represented by dashed lines and are based in CONAMA 357/05 for the reference classes indicated. The box indicates approximately the 25th, 50th (median=black square) and 75th percentile; outliers are defined according to: (upper whisker, lower whisker) = (upper hinge, lower hinge) ± 1.5*hinge width. Filled circles and asterisks represents respectively outliers and extremes.

maps and those for the same metals in the dry season. Some metals, as exemplified by Cu, Ni, Co, and V, tend to be more abundant in the area situated on or under influence of the Amazonian craton. In some cases, the geochemical imprint of local geological setting is also evident, *e.g.* the preferential relationships of copper and cobalt with metavolcanosedimentary units and Cristalino deposit, as well as of nickel, chromium and vanadium with mafic-ultramafic units. The areal distribution and higher anomalous values of Sn in the raining season could be apparently related to the occurrences of A-type granites (Gogó-da-Onça, Estrela and Serra do Rabo granites, Figure 2E). However, they cannot be explained in this way in the dry season that shows higher values in the SSB, without any influence of the mentioned granites.

Spatial distribution of Fe and Mn in water of the VSB and SSB is relatively uniform compared to those of other studied metals and cannot be attributed to lithological control (Figure 5). It is not affected by the presence in the studied area of the remarkable tectonic limit between the Amazonian craton and the Araguaia Belt. Hence, it should be explained in other way.

4.4 THE ESTABLISHMENT OF THRESHOLD VALUES

Calculation of threshold values for metal contents in stream water of the Vermelho (VSB) and Sororó (SSB) sub-basins is strongly dependent of the number of analytical results larger than DL for each element (Table 3).

For those elements with dominance of <DL values, the statistical methods are generally not able to define a strict value for threshold. This is the case for As, Co, Cr, and Pb that presented none or only few significant statistical values for threshold. These elements show also variations in the two sub-basins and in the seasons of the year. Arsenic data do not allow definition of threshold values, except for SSB during the dry season by TIF method which indicated a threshold value for it < 1 µg/L, the DL value. For Co, the picture is a little distinct because it shows a clear contrast between the VSB and SSB with significant threshold values in the former during both seasons. The statistical data available allow to estimate threshold values of 2 to 4 µg/L for this element in the VSB and < 1 µg/L in the SSB. The geochemical contrasts between VSB and SSB are almost certainly related to the influence of geological setting and obtained results put in evidence that this is an essential aspect to be considered for threshold or background definition (Galuszka 2007, Reimann & Garrett 2005, Reimann *et al.* 2005, Matschulat *et al.* 2000). In the case of Cr, statistical data are consistent only for SSB during the raining season (Table 3) and suggest values of ~3 µg/L for threshold in stream water. In VSB and during the dry season in SSB, values of < 1 µg/L should be considered. The increase of threshold values in SSB (D) is apparently not related to the influence of mafic-ultramafic units that are concentrated in the VSB (Figure 5) and there is not a clear explanation for it. Lead behavior is similar to that of Cr and Co, with threshold values of 2-3 µg/L being estimated in both VSB and SSB during the rainy season whereas during the dry season it should be < 1 µg/L.

Nickel and Sn results for threshold values are apparently better defined than for the previous metals, but they could be estimated only partially (Table 3). For Ni, threshold values are defined by different methods in the dry season in VSB and in the rainy season in SSB and can be estimated to be of 2-4 µg/l (Table 3). For Sn, threshold values are better constrained in the dry season for VSB and SSB and can be estimated in 3-5 µg/l (Table 3).

The five remainder metals, Fe, Mn, Cu, V, and Zn compared to those metals previously discussed show lower number of results < DL (Table 2), thus they have been able to give significant threshold values in stream water, except for Cu and V during the dry season (Table 3). For Cu, the methods CF, I2σ and DF indicate values of 2-3.5 µg/l and for V between 2.0 and 3.0 µg/l (Table 3). For Zn the situation is more complex because, taking as reference the three mentioned methods, there are significant variations in threshold values between the raining and dry seasons, with variation of 18 to 23 µg/l and 24 to 32 µg/l in the raining season and 9 to 17 µg/l and 9 to 24 µg/l in the dry season, respectively in VSB and SSB (Table 3). Overall, values between 15 and 30 µg/l can be seen as a reasonable threshold limit for Zn in the studied area.

Concentrations of Fe and Mn do not show analytical data <DL (Table 2). Thereby the estimation of threshold values for these elements is more consistent. The results obtained are similar for the different methods employed (Table 3), except for Fe and Mn. In most cases, the methods I2σ and DF that removed outliers produced similar results and are generally admitted as more suitable for geochemical threshold and background estimation (cf. Raimann and Caritat 2017, Urresti-Estala *et al.* 2013).
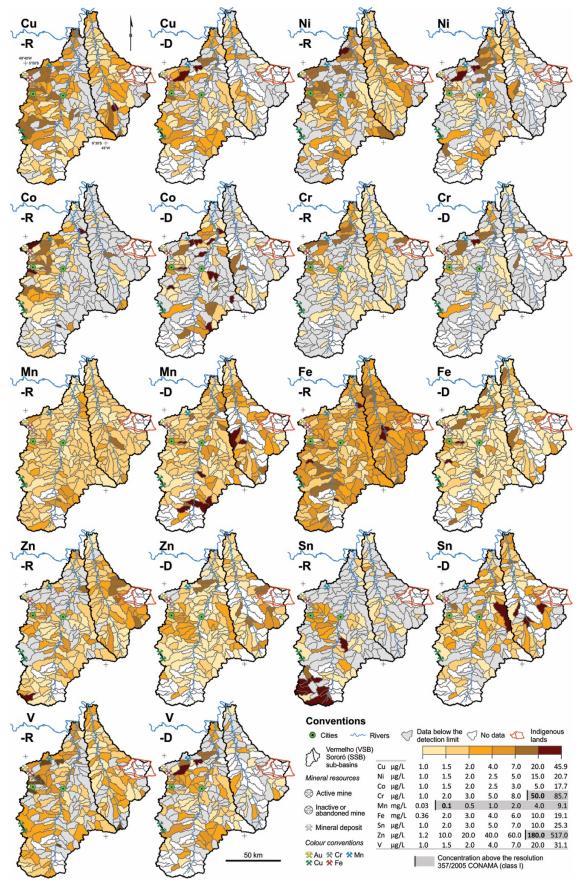
Figure 5

Geochemical distribution of Cu, Ni, Co, Cr, Mn, Fe, Sn, Zn, and V in stream water of the Vermelho and Sororó sub-basins of the Itacaiúnas River Watershed. The samples were collected during rainy (-R) and dry (-D) seasons along 2017. Refer to Figure 2 for the remarks applied, and to Table 2 for the detection limit.

Table 3 - Threshold values obtained from various statistical methods [Median + 2 MAD, Tukey's inner fences (TIF), cumulative probability (CP) distribution diagrams, iterative 2σ technique (I2σ) and calculated distribution function (DF)] for 11 elements in stream water of the Vermelho (VSB) and Sororó (SSB) sub-basins during rainy (-R) and dry (-D) seasons of 2017.

Element	SB - Season	Regul. SWC1	Possible threshold values based on GBI data					Number of exceedances above					
			M_{MAD}	TIF	CP	I2σ	DF	SWC1	M_{MAD}	TIF	CP	I2σ	DF
As	VSB-R	10	<1	<1	-	-	-	0	13	13	-	-	-
	VSB-D		<1	<1	-	-	-	0	9	9	-	-	-
	SSB-R		<1	-	-	-	-	0	21	-	-	-	-
	SSB-D		<1	2.00	-	-	-	0	16	4	-	-	-
Co	VSB-R	50	2.68	3.80	2.31	-	2.28	0	22	12	24	-	25
	VSB-D		<1	3.66	3.46	-	-	0	61	14	14	-	-
	SSB-R		<1	<1	-	-	-	0	17	17	-	-	-
	SSB-D		<1	2.04	-	-	-	0	17	2	-	-	-
Cr	VSB-R	50	<1	-	-	-	-	0	61	-	-	-	-
	VSB-D		<1	-	-	-	-	1	37	-	-	-	-
	SSB-R		3.28	3.66	1.59	1.94	2.57	0	5	4	23	16	10
	SSB-D		<1	-	-	-	-	0	8	-	-	-	-
Cu	VSB-R	50	4.62	7.45	3.56	1.47	3.56	0	28	16	33	76	33
	VSB-D		3.53	4.64	2.95	2.00	2.80	0	14	11	22	40	25
	SSB-R		3.46	4.36	2.6	2.61	2.82	0	6	5	12	12	12
	SSB-D		<1	3.27	-	-	-	0	23	3	-	-	-
Fe	VSB-R	-	6.50	7.87	6.22	5.74	5.95	-	10	5	10	15	13
	VSB-D		3.23	4.13	1.99	2.07	2.67	-	20	17	39	39	28
	SSB-R		6.93	7.89	5.16	6.21	6.57	-	3	2	24	6	4
	SSB-D		3.61	4.24	2.49	2.84	3.41	-	8	4	13	11	8
Mn	VSB-R	0.1	0.50	0.66	0.44	0.37	0.44	112	20	14	24	33	24
	VSB-D		0.28	-	0.22	0.20	0.30	96	42	-	50	52	40
	SSB-R		0.42	0.50	0.22	0.31	0.40	60	12	7	35	19	14
	SSB-D		1.45	1.94	0.67	1.32	1.39	43	6	5	24	7	7
Ni	VSB-R	25	3.65	-	4.36	1.88	-	0	25	-	18	54	-
	VSB-D		1.49	3.76	2.97	-	2.22	0	46	13	16	-	24
	SSB-R		2.90	3.58	1.81	3.10	-	0	6	1	33	2	-
	SSB-D		<1	2.76	-	-	-	0	19	1	-	-	-
Pb	VSB-R	10	<1	1.90	1.82	-	-	0	40	7	7	-	-
	VSB-D		<1	-	-	-	-	0	13	-	-	-	-
	SSB-R		2.48	3.08	1.60	1.87	2.37	0	5	4	16	11	6
	SSB-D		<1	-	-	-	-	0	7	-	-	-	-
Sn	VSB-R	-	<1	4.05	6.28	-	-	-	60	22	12	-	-
	VSB-D		5.91	6.26	3.3	3.16	-	-	4	4	24	26	-
	SSB-R		<1	1.87	-	-	-	-	22	9	-	-	-
	SSB-D		4.38	5.22	3.43	4.44	5.07	-	8	6	12	8	6
V	VSB-R	100	4.47	5.13	2.12	2.31	-	0	16	11	42	41	-
	VSB-D		3.59	4.25	2.26	2.18	3.06	0	17	12	30	33	22
	SSB-R		2.75	3.34	2.08	2.79	2.83	0	6	4	20	6	6
	SSB-D		<1	2.45	-	-	-	0	19	2	-	-	-
Zn	VSB-R	180	25.00	37.00	23.3	-	18.68	1	19	8	19	-	28
	VSB-D		18.66	34.82	9.17	12.08	17.27	0	30	7	60	41	34
	SSB-R		31.13	44.23	32.2	24.75	29.90	0	14	9	12	20	16
	SSB-D		29.51	-	24.5	19.0	23.75	0	11	-	11	14	12

Note: Concentration values of Fe and Mn are expressed in mg/L, and for the other elements in µg/L. Data below detection limit (DL) were replaced by ½ of the DL value. Regul. – Regulations; SWC1 = maximum values for Class 1 fresh water (CONAMA 357/05). '-' technique not applicable to the analyzed data set.

Using these methods, it is possible to estimate the threshold values of 5 to 6 mg/L and of 2 to 3 mg/L for total iron in both VSB and SSB in the rainy and dry seasons, respectively. This is apparently allowed by CONAMA 357/05. Mn, however, shows a distinct variation between VSB and SSB. In VSB, Mn behavior is similar to that of Fe, with decreasing threshold values from the rainy to the dry season. The opposite is seen in SSB, where threshold values for Mn show an accentuate independent of the geological setting as put in evidence by the similar threshold values in the two sub-basins.

Mn is the only metal that shows systematically values above the maximum valueincrease during the dry season (Table 3). In VSB, Mn threshold

values can be estimated to be 0.35 to 0.45 mg/L in the raining season and 0.20 to 0.30 mg/L in the dry season. In SSB, threshold values increase from 0.3 to 0.4 mg/L in the rainy season to 1.3 to 1.4 mg/L in the dry season (Table 3).
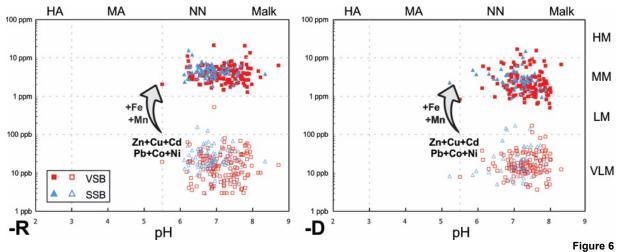
5 DISCUSSION

5.1 GEOCHEMICAL CHARACTERISTICS OF WATER

During the rainy season, higher values of conductivity in the western part of VSB are probably related to a more intense leaching of nutrients and salts from multi-sources and are mainly controlled by the geology of the area (eastern border of the Amazonian Craton) through which the water flows. During the dry season, low conductivity stream waters occur mostly in the SSB, reflecting the combination of low rainfall with the local bedrock in this sub-basin dominated by geochemically depleted (meta)sedimentary rocks.

In relation to acidity (pH), no significant trends were observed in stream water during both the rainy and dry seasons. The pH values are mostly neutral and fall within the admitted normal range for drinking water (Figure 3C). Few samples show accentuated acidity (pH < 6.0) in the SSB during the dry season. These abnormal values were identified in four micro-catchments right next to each other, near an industrial area to the south of Marabá. This indicates that industrial activities possibly resulted in pollution emission that lowered the pH of water around that area.

The characteristics of the stream water for each catchment basin are better visualized in a plot of pH vs. the sum of base metals (Zn, Cu, Pb, Cd, Co, and Ni). Stream waters of Vermelho and Sororó sub-basins are mostly near neutral and, except for a few samples, have low dissolved concentrations of these metals (Figure 6). However, if we consider Fe and Mn, the total metal concentrations are classified as medium range, which demonstrates the strong influence of these two metals in local aqueous environment.

Figure 6
Modified Ficklin diagram of stream water samples showing the sum of dissolved base metal concentrations as a function of pH during the rainy (-R) and dry (-D) seasons in Vermelho (VSB) and Sororó (SSB) sub-basins. HA=High acid; MA=Medium acid; NN=Near neutral; Malk=moderate alkalinity; HM=High metallic; MM=Moderate metallic; LM=Low metallic; VLM=Very low metallic (modified from Macías *et al.* 2012)

5.2 HIGH CONTENTS OF Fe AND Mn IN SURFICIAL WATER

Irrespective of the season of the year, the concentrations of Fe followed by Mn in water of VSB and SSB were much higher when compared to the maximum value of CONAMA 357/05. Despite the occurrence of the Serra Leste iron mine in the extreme northeast of VSB (Figure 1), in the VSB and SSB, the influence of iron mines or deposits does not look relevant. The main course of Vermelho and Sororó rivers flows from south to north and their water characteristics are certainly more related to the geologic setting of the Araguaia Belt than to that of the Amazonian craton (Figures 1 and 2E). Hence, the anomalous geochemical behavior of Fe and Mn in the VSB and SSB and their high contents in the water cannot be explained by the influence of mining or banded-iron-formations, which are widespread only in the Archean terrains of the craton, and should be explained in other way. High Fe contents in surficial waters were also observed

around the N3 and N4WSul areas in the Serra dos Carajás, studied by Teixeira (2016), but they are less common than in the VSB and SSB. Those areas are situated near the Fe mines of Serra Norte in the Carajás National Forest but water sampling was done in areas without direct influence of mining. Therefore, the higher Fe contents in water of those areas are also more likely related to local geogenic influence.

We admit that the enrichment in those elements in water is due to a sum of the conditions prevalent in most of the Amazonian region, thoroughly related to geologic setting associated with climatic and geomorphologic conditions. However, beside the mentioned factors, land use and land cover also exert influence in the geochemical distribution and mobility of these elements. Deforestation caused increase of water flow in the Itacaiúnas basin (Souza-Filho *et al.* 2016) and in the Amazonian region in general (Levy *et al.* 2018, Nóbrega *et al.* 2018) and it was particularly intense in the VSB and SSB (Figure 2A). It should favor the transport of metals

concentrated in weathered rocks and ferruginous crusts to the water stream and this process should be particularly active during the rainy season, as put in evidence by our results. A similar situation was observed in other areas of the Itacaiúnas basin (Teixeira 2016). On the other hand, the increase of Mn content in water during the dry season could be due to release of Mn via biogeochemical processes that might be facilitated by low flows and consequent lesser water dilution during this period.

It is concluded that the maximum values proposed as reference in the Brazilian environmental legislation (CONAMA 357/05) for Fe and Mn are not realistic for the Amazonian region or at least for some regions of it. This contradictory situation is not specific of the Amazonian region and was verified also for several metals in other regions of Brazil (Rodriguez *et al.* 2013) or in other continents (Reimann *et al.* 2005). It suggests a need of more flexibility or adjustments of the legislation to the conditions prevailing in the Amazonia.

5.3 NATURAL INFLUENCE VS. ANTHROPIC INFLUENCE AND ENVIRONMENTAL IMPLICATIONS

For most elements, including Co, Cr, Cu, Ni, Pb, Sn, V, and Zn, the geogenic influence is clear as indicated by the contrast in metal distribution in the western area of the VSB included in the Archean Carajás Province of the Amazonian craton and other parts of the VSS and the entire SSB that corresponds to the Neoproterozoic Araguaia Belt. At the same time, for this same group of elements, the dominance of low metal contents in stream water is demonstrated by values <DL. This aspect and the restrict number of analytical values above the maximum metal contents according to CONAMA 357/05 point to a subordinate anthropogenic influence in the studied area. In the cases of Fe and Mn, the general picture is similar, but there is a significant difference. The intense change of land cover around the Vermelho and Sororó catchments with

large scale replacement of tropical forest for pasturage has probably contributed to the increase of Fe and Mn contents in the stream water. In our view, the deforestation and replacement of tropical forest by pasturage lead to a remarkable anthropogenic effect that accentuated the natural influence of geological setting and lithologies associated with climatic and weathering processes that are characteristic of the Amazonian region. The contrast in Fe and Mn contents between the Vermelho and Sororó catchments located in the deforested eastern part of the Itacaiúnas basin and those obtained in stream water in areas situated in the Carajás National Forest, a preserved area (Teixeira 2016) are strong evidence of significant anthropic effects related to deforestation in the studied   area.

6 CONCLUSIONS

- There are no accentuated variations in the physico-chemical parameters of water during the rainy and dry seasons in the VSB and SSB.
- For most of the analyzed metals, including As, Co, Cr, Cu, Ni, Pb, Sn, V, and Zn, the contents in surficial water are quite low and there is no evidence of significant contamination in the studied sub-basins. However, in general, these metals show higher contents in water during

the rainy season. This could be due to the increase of surficial flow that favors leaching and transport of metals to the local drainage.
- Fe and Mn contents in surficial water are high and their behavior differ from those of the other metals. The Fe distribution is not controlled by the occurrence of iron mines and banded-iron formations in the studied area. However, it was accentuated by the extensive

deforestation in the VSB and SSB that favored intense leaching of exposed soils and weathered rocks. The increase of Mn contents during the dry season should be related to biogeochemical processes that were facilitated by the decrease of flow and water dilution during this period. High Fe and Mn contents in water are inherent to the natural conditions prevalent in the entire Amazonian region.

• The geogenic or natural influence in metal distribution in water is significant as indicated by differences in the concentrations of Co, Cr, Cu, Ni, Pb, Sn, V, and Zn, in the domain of the Amazonian craton compared to those in the Araguaia belt. Anthropogenic influence looks subordinate for most metals but it could be more significant in the case of Fe and Mn, probably affected by the changes in land use and vegetation. Decrease in pH in areas near the industrial district of Marabá could also possibly result of anthropic influence.

• For those elements that presented a large proportion of data lower than DL, *e.g.* As, Co, Cr, and Pb, the definition of threshold values was limited and only indicative values were obtained. For Cu, Ni, Sn, V, and Zn threshold values for at least one season were estimated in each sub-basin. In the case of Fe and Mn, the methods I-2σ and DF were selected for geochemical threshold estimation. Values of 5 to 6 mg/L and of 2 to 3 mg/L for total iron were obtained in both VSB and SSB in the rainy and dry seasons, respectively. Mn behavior is distinct in VSB and SSB. In VSB, estimated Mn threshold values are 0.35 to 0.45 mg/L in the raining season and 0.20 to 0.30 mg/L in the dry season. In SSB, threshold values increase from 0.3 to 0.4 mg/L in the rainy season to 1.3 to 1.4 mg/L in the dry season. It is concluded that threshold values for metals are mostly low, except for Fe and Mn which behavior is controlled by the regional environment.

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8 REFERENCES

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