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Change in water quality in an Amazonian microbasin: ecological and human health implications

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ABSTRACT

The decline in the quality of water resources in the Amazon is very rapid in cities suffering from unplanned urban growth. The region has two defined seasons, winter (wet) and summer (dry), which directly affect the behavior of contaminants in aquatic ecosystems. The aim of this study was to assess the ecological and human health risks associated with the use of the watershed. In addition, an ecological index was proposed: the Quality Index for Aquatic Life, for the risk of contaminants to aquatic life. Sampling was carried out at six points in the Juá watershed. Physicochemical parameters, major anions, metals and total phosphorus were analyzed at both stations between 2020 and 2021. The highest concentrations of contaminants were found in the rainy season, due to the washing away of the banks. In this sense, Cl presented a concentration more than 307 times higher than that permitted by Brazilian legislation (wet). The ecological index showed that the watershed has a high risk of metals such as Cr III and Cr VI for the biota. The human health risk analysis showed a low risk; however, the lack of basic sanitation in the city indicates that monitoring of urban water resources is necessary.

Key words: eutrophication, major anions Quality Index for Aquatic Life, metals, seasonality

HIGHLIGHTS

- Population growth and a lack of urban planning in Amazonian cities have resulted in a drop in water quality.
- The study of Amazonian microbasins is a way of managing water resources in the region.
- The rainy season is responsible for the highest concentrations of contaminants in the water.
- The high concentrations of Cr III and Cr VI in water are a public health problem in the Amazon region.

1. INTRODUCTION

Water quality is constantly changing owing to advances in anthropogenic activities (Zhang 2018; Wang *et al.* 2021). Several rivers worldwide are experiencing deteriorating water quality due to the discharge of untreated effluents from large cities (Wang *et al.* 2021). The degradation of water quality ecosystems to a lesser extent comes from anthropogenic pressures on water sources, as well as natural factors (Alves *et al.* 2012; Batista *et al.* 2022). However, due to society's demand for quantity and quality, multiple uses of water trigger a series of conflicts associated with inadequate management. Contaminants released without treatment can damage aquatic ecosystems and human health (Nascimento *et al.* 2022).

The Amazon region is important in several dynamics on a global scale, such as water cycling and biodiversity maintenance (Gauthier & Moran 2018; Coura *et al.* 2021). However, the rapid and unplanned urban growth of some cities in the region can interfere with these dynamics, which can lead to global environmental imbalance. Despite being the largest freshwater reservoir in the world, both in surface and groundwater resources (Monte *et al.* 2021b), the Amazon suffers from degradation in the quality of its water resources (Pinheiro *et al.* 2019; Monte *et al.* 2021b; Nascimento *et al.* 2022).

Santarém, located in the state of Pará (Brazilian Amazon), has the worst sanitation index in Brazil (Monte *et al.* 2021a). However, one of the biggest environmental problems faced by the cities in the region is population growth, especially in

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the last three decades, which has not accompanied the implementation of adequate development mechanisms that would provide the minimum conditions of education, health, and salary combined with adequate urban infrastructure (Becker 2010; Monte *et al.* 2021b).

According to Santos *et al.* (2020), in the urban area of the municipality, residential waste flows into septic/rudimentary tanks or is released untreated into streams that are part of the Tapajós watershed, including the microbasins. One of the methods used for water quality management of Amazonian water resources is the study of urban microbasins (Monte *et al.* 2021b; Batista *et al.* 2022; Nascimento *et al.* 2022). Variations in igarapés (Amazonian streams) occur more intensely and rapidly, with possible changes from one type of water to another in a few days or even hours, due to the mixture of rivers that drain different regions or seasons (Monte *et al.* 2021b; Nascimento *et al.* 2022).

Currently, several urban microbasins in Santarém are under anthropogenic pressure due to disorganized urban growth (Monte *et al.* 2021b; Nascimento *et al.* 2022). The development of instruments to evaluate the quality of hydric bodies, such indices have become necessary with the advancement of anthropogenic activities, especially in urban areas. However, the Amazon biome presents particularities in environmental aspects that should be considered when calculating indices for optimizing water quality management (Silva *et al.* 2013; Monte *et al.* 2021b; Nascimento *et al.* 2022). One of the particularities of the Amazon is seasonality: there are two clearly defined seasons, the Amazon summer (dry) and winter (wet) (Ferreira *et al.* 2021; Nascimento *et al.* 2022). Seasonality is controlled by climate dynamics in the equatorial region, causing different interactions between terrestrial and aquatic ecosystems in the region, which influences the availability of contaminants (Coura *et al.* 2021).

Thus, this study aimed to assess the ecological and human health risks associated with the use of microbasins. To achieve this objective, indices such as the human health risk index will be calculated to predict the effects of ingesting contaminated water, as well as the proposition of a new index called the Quality Index for Aquatic Life (QIAL). The hypotheses of this study were as follows: (I) seasonality influences ecological and human health indices. (II) The rainy season presents the highest concentrations of contaminants and, consequently, the worst indices.

2. MATERIAL AND METHODS

2.1. Study area and sampling

The Juá microbasin, represented mainly by the São Brás stream, belongs to the drainage basin of the Tapajós River, which is located in the municipality of Santarém, western Pará (Figure 1). The municipality is located on the right bank of the Tapajós River at the confluence of the Amazon River. In the Juá microbasin, which is located in the peri-urban areas of Santarém, there is an intense process of disorderly occupation with residential construction, bars, agricultural and livestock areas, and restaurants on the banks of the water body, which compromises the integrity of the stream since basic sanitation is nonexistent in these areas. Moreover, in some streams, water is used for recreational purposes by local populations, visitors, and tourists (Batista *et al.* 2022).

2.2. Sampling

Six sampling points were selected and divided along the microbasin (Figure 1) considering the main course and tributaries. Sampling campaigns were carried out during different periods of the year, in the rainy season (February/2020 and January/2021) and dry season (November/2020 and October/2021), making it possible to visualize the influence of seasonal variations on the quality of the water body.

During sampling and before conditioning of the water samples, the concentrations of abiotic limnological variables of electrical conductivity (EC) in mg/L (Hanna-DIST 4, HI98304 SERIES), dissolved oxygen (DO) in mg/L (Microprocessor oximeter/AT-160, E009470 SERIES), temperature in °C, and hydrogen potential (pH) (AKSO-AK103, AKAT08531 SERIES) were determined *in situ*. The water samples were packed in polypropylene bottles and kept refrigerated until they reached the laboratory when they were subjected to conservation methods according to the parameter to be analyzed, as described in Standard Methods for the Examination of Water and Wastewater, 22nd edition (APHA 2012).

Nutrients and major anions (total dissolved solids (TDS), nitrite, nitrate, ammonia, chloride, and total phosphorus (TP)) were analyzed in a Bel spectrophotometer (UV-M51 UV–Visible) using the colorimetric method, while metals (aluminum, iron, manganese, chromium III, chromium VI, copper, and zinc) were analyzed in flame atomic absorption spectrometry (Thermo Scientific iCE 3300) according to procedures of the Standard Methods for the Examination of Water and Wastewater, 22nd edition (APHA 2012).

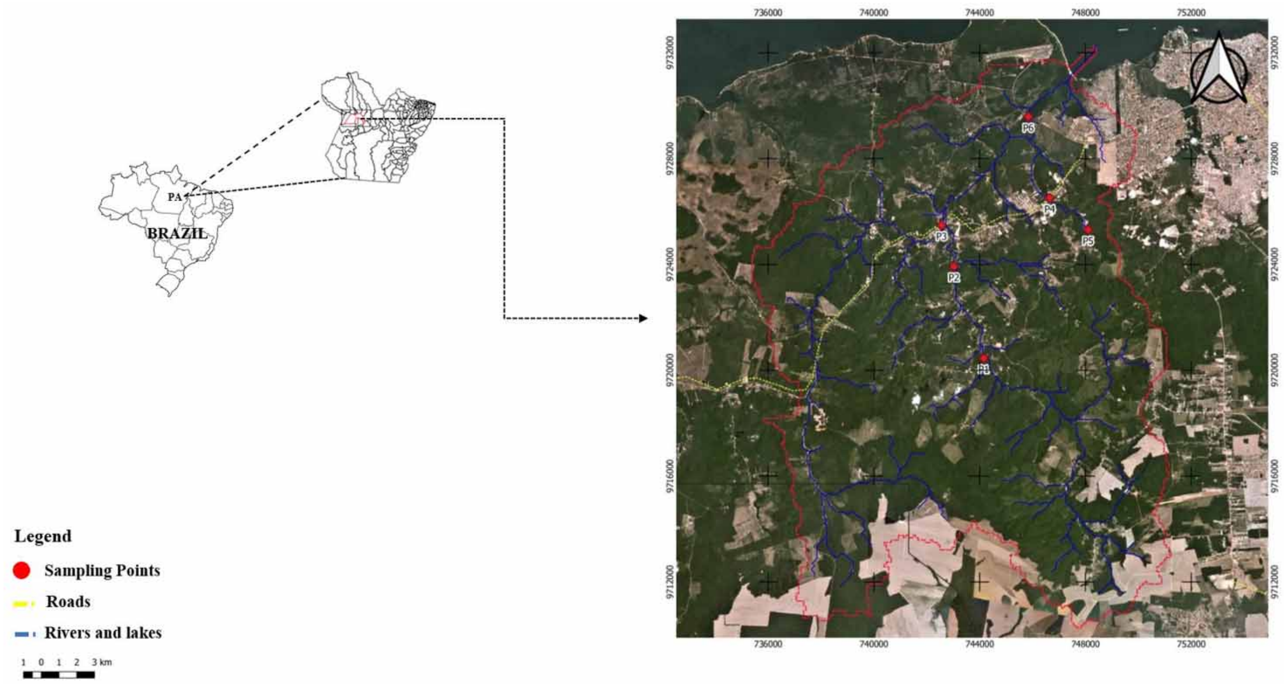

Figure 1 | Study area.

2.3. Statistics

Statistical analyses were performed using STATISTICA 8.0. The Shapiro-Wilk normality test was applied, which classified the distribution as normal. In view of this, the Student's *t*-test ($p < 0.05$) was applied to investigate the influence of seasonality on the dynamics of contaminants. In addition, the principal component analysis (PCA) statistical test was applied ($p < 0.05$) in order to verify the possible relationships between contaminants and physicochemical parameters and the influence of seasonality (Monte *et al.* 2021b; Nascimento *et al.* 2022).

The identification of contaminant sources by distinguishing between anthropogenic sources and the input of elements into the aquatic environment is essential for evaluating environmental processes and the protection of rivers (Deng *et al.* 2021; Ashayeri *et al.* 2023). PCA was performed to group elements that behaved similarly or differently to interpret their possible origins (Ashayeri *et al.* 2023).

2.4. Assessment of potential risk to human health

A potential risk assessment is an important tool for tracking contaminant exposure and possible interference with human health (Castilhos *et al.* 2014; Nascimento *et al.* 2022). In this study, exposure values were selected for the worst-case scenario for direct ingestion and ingestion via swimming, as the Juá stream has several uses such as water abstraction near the source and several bathing sites along its course. The evaluation was performed according to USEPA (1989).

The selection of contaminants for the calculation of the risk to human health is based on the studies of Nascimento *et al.* (2022), who carried out a similar study in another microbasin of the Tapajós River, to compare the degradation and impacts of urban growth in the region. The methodology and equations used are described in Castilhos *et al.* (2014) and Nascimento *et al.* (2022). If the IP exceeds 1, it is characterized as a potential risk to human health (Castilhos *et al.* 2014; Nascimento *et al.* 2022).

2.5. Quality Index for Aquatic Life

The QIAL fills a gap in the literature regarding the assessment of the risk to aquatic life in freshwater bodies in relation to major metals and anions. Uncontrolled urban expansion in cities causes pollution of water bodies due to the discharge of untreated effluents, which release metals and anions (Ferreira *et al.* 2019; Nascimento *et al.* 2022).

The limits used for Cr III, Cr VI, Ni, Pb Zn, and Cl were taken from the acute test concentrations with aquatic organisms used in the National Recommended Criteria for Aquatic Life (USEPA 1995, 1986). The limits adopted are Cr III = 0.57 mg/L; Cr IV = 0.0016 mg/L; Ni = 0.47 mg/L; Pb = 0.065 mg/L; Zn = 0.12 mg/L; and Cl = 0.019. The calculation of QIAL follows Equation (5).

$$\text{Equation}\,5 = \text{CP}/\text{AL}$$

where CP is the concentration of the pollutant and AL is the limit adopted by the USEPA. Values above 1 can cause risk to aquatic life.

3. RESULTS AND DISCUSSION

3.1. Physical–chemical parameters

Water is an extremely important natural resource. This resource is the basic element of all beings and the engine of society's development (Rodrigues & Mendiondo 2013; Batista *et al.* 2022). It is estimated that water pollution causes the death of 2 million people every year, especially in developing countries such as Brazil, which is higher than the deaths caused by conflict and crime combined worldwide (Fuller *et al.* 2019; Marcantonio *et al.* 2021).

The pH values of samples P1 and P2 were below the CONAMA Resolution 357/05 (Table 1) at all stations. The resolution regulates the quality of water in Brazil and divides the water bodies into classes, in this study, as there is no official regulation by the environmental agencies, Class II was adopted according to the use of the water body. A pH below CONAMA 357/05 is typical in the Amazon, mainly in areas with or without low anthropic interference, as in the case of Points 1 and 2, which are characterized by low anthropic interference. Acidic pH in Amazonian pristine areas is expected because of the large input of humic and fulvic acids (Ríos-Villamizar *et al.* 2020; Monte *et al.* 2021b; Nascimento *et al.* 2022), including areas of clear

Table 1 | Physical–chemical parameters for seasons between 2020 and 2021

Season	Samples	DO (mg/L)	EC (μS/cm)	TDS (mg/L)	Temperature (°C)	pH	BOD (mg/L/day)	Turbidity (NTU)
Wet 2020	1	6.26	16	10.24	24	**4.7**	1.54	11.98
	2	6.59	14	8.96	23.7	**4.8**	0.11	31.11
	3	7.01	18	11.52	23.5	5.09	0.34	53.53
	4	6.01	17	10.88	23.5	5.3	0.2	**169.5**
	5	**1.08**	41	26.24	24	6.2	4.92	**322.1**
	6	**4.16**	12	7.68	23.4	5.3	0.1	65.11
Dry 2020	1	7.5	4	2.56	24.4	**4.72**	1.72	1.63
	2	6.86	5	3.86	24.5	**4.56**	0.06	2.29
	3	6.44	3	2.32	24.4	**4.7**	0.46	4.81
	4	**2.86**	2	1.92	25	5.63	1.56	6.01
	5	**0.1**	39	24.96	25.4	7.22	**6.72**	32.8
	6	**4.54**	1	10.72	24.4	**4.93**	2.4	3.5
Wet 2021	1	6.8	12	7.68	23.6	**4.29**	2.52	15.17
	2	6.26	13	8.32	23.5	**4.67**	0.18	15.69
	3	**5.75**	19	12.16	23.3	**4.76**	0.04	31.98
	4	**3.35**	19	12.16	24.4	**4.85**	1.84	**105.93**
	5	**1.38**	380	243.2	23.7	5.42	**5.42**	**345.45**
	6	7.33	14	8.96	23.3	**4.78**	2.18	29.55
Dry 2021	1	6.79	14	8.96	24	**4.47**	0.5	2.93
	2	**5.8**	14	8.96	23.9	**4.56**	0.86	2.71
	3	7.06	12	7.68	24.1	**4.6**	0.54	6.91
	4	6.61	34	21.76	28	**4.49**	0.9	11.32
	5	**2.08**	393	251.52	23.9	6.89	2.04	10.44
	6	6.02	12	7.68	23.9	**4.66**	1.1	5.97
Conama 357/05 Class II	–	6.0–9.0	NA	500	NA	5	5	100

*Concentrations in disagreement with CONAMA 357/05 are in bold.

NA = not applicable.

water rivers, and is related to the forest–water interaction and the lithology of the site (Pinheiro *et al.* 2019; Monte *et al.* 2021b; Nascimento *et al.* 2022).

In addition, the Alter do Chão Geological Formation is composed mainly of yellow ferrasols, which are rich in clay and acids, eroded, and transported to the stream, and may contribute to the acidity of the water (Ferreira *et al.* 2021). However, the increase in pH at P5 was related to the entry of sewage, which was located immediately after the municipal penitentiary, and the discharge of untreated sewage was observed in this part of the watershed, causing a strong odor near the bank. In these effluents, ammonia is formed from the decomposition of organic matter in sewage, which tends to cause an increase in the pH.

Moreover, substances with basic characteristics are present in domestic effluents, such as detergents, which can also contribute to an increase in pH (Sousa *et al.* 2018; Pinheiro *et al.* 2019; Nascimento *et al.* 2022). Concentrations below the legislation do not impact the Amazonian aquatic biota, which is adapted to low DO concentrations due to the forest–water interface in pristine areas (Ríos-Villamizar *et al.* 2020; Nascimento *et al.* 2022). DO concentrations below those allowed by the CONAMA resolution do not indicate aquatic life, demonstrating that the CONAMA resolution does not consider the regional ecological aspects (Silva *et al.* 2013; Monte *et al.* 2021b; Nascimento *et al.* 2022).

When analyzing the PCA (Figure 2), pH showed a behavior opposite to that of DO at some stations, suggesting a negative correlation between the parameters. This behavior indicates that anthropogenic interference contributed to the behavior of these parameters. However, in this study, the low concentration of DO at points P4 and P5, and consequently, the increase in pH, were related to untreated effluent discharges. pH showed a positive correlation with biochemical oxygen demand (BOD) only in the dry season (Figure 2), suggesting that oxygen consumption in the aquatic ecosystem directly interferes with pH. This may be related to the higher speed of organic matter (OM) decomposition as the water temperature increases in the dry season (2020 and 2021) (Table 1), which accelerates OM decomposition (Muller *et al.* 2018). High BOD concentrations can cause deaths of aquatic organisms and increase eutrophication (Dede *et al.* 2013).

Similar to other studies conducted in Amazonian microbasins, EC was higher in both rainy seasons in the present study. According to Nascimento *et al.* (2022) and Monte *et al.* (2021b), the higher EC is related to the input of sewage and debris carried to the microbasin bed, and to the clay that is eroded from rocks and sediments of the Alter do Chão Geological Formation, where the microbasin is located (Mendes *et al.* 2012; Pinheiro *et al.* 2019), which directly impacts the amount of TDS. In the case of sample P5, the high CE came mainly from untreated sewage from the penitentiary and adjacent areas.

3.2. Nutrients and contaminants

TP concentrations were generally higher during the rainy season (Table 2); however, only one sample (P6) in the rainy season of 2020 showed compliance with CONAMA 357/05, whereas all other samples showed non-compliance with the resolution in all seasons during the years studied. Sample P5 in the rainy season of 2021 was 77 times higher than the standard, indicating that the watershed is severely impacted by anthropogenic activities, with a risk of eutrophication, as phosphorus is one of the main factors controlling algal blooms (Han *et al.* 2016).

The increase in TP during the rainy season can be explained by increased surface water runoff, which carries nutrients into the water body from sewage, fertilizers from gardens and leaves in urban areas, and agricultural management and fertilizer use in rural areas. Some studies have attributed the higher phosphorus concentrations during the rainy season to the higher amount of suspended sediments due to higher surface runoff (Sousa *et al.* 2018; Pinheiro *et al.* 2019). Regarding the statistics (PCA), TP showed an inverse relationship with DO at all stations, indicating a negative correlation (Figure 2). This suggests that TP may be associated with organic matter (Paula Filho *et al.* 2012), and that the decomposition of OM consumes DO in the water.

Al concentrations were higher during the rainy season, a behavior similar to that found by Nascimento *et al.* (2022). The metal showed nonconformity with CONAMA 357/05 only in the rainy seasons for samples P3 (2021), P4 (2020), and P5 in both years. In the case of P5, the concentration was 38 times higher than that allowed by the standard. Although rocks, soils, and sediments are characterized as sources of Al in the aquatic environment, in this study, the highest concentrations were in P5, indicating that the main source is related to untreated sewage, while in the rainy season, surface runoff increases the concentration (Angelova *et al.* 2020; Senze *et al.* 2021; Nascimento *et al.* 2022).

Fe concentrations were higher in the rainy season (Table 2), and P5 in the rainy season of 2021 was 21 times higher than allowed by the standard. At most stations, Fe showed significant correlations with some parameters; however, in the rainy season of 2021, Fe was one of the most abundant chemical elements in the Earth's crust. High Fe concentrations in water

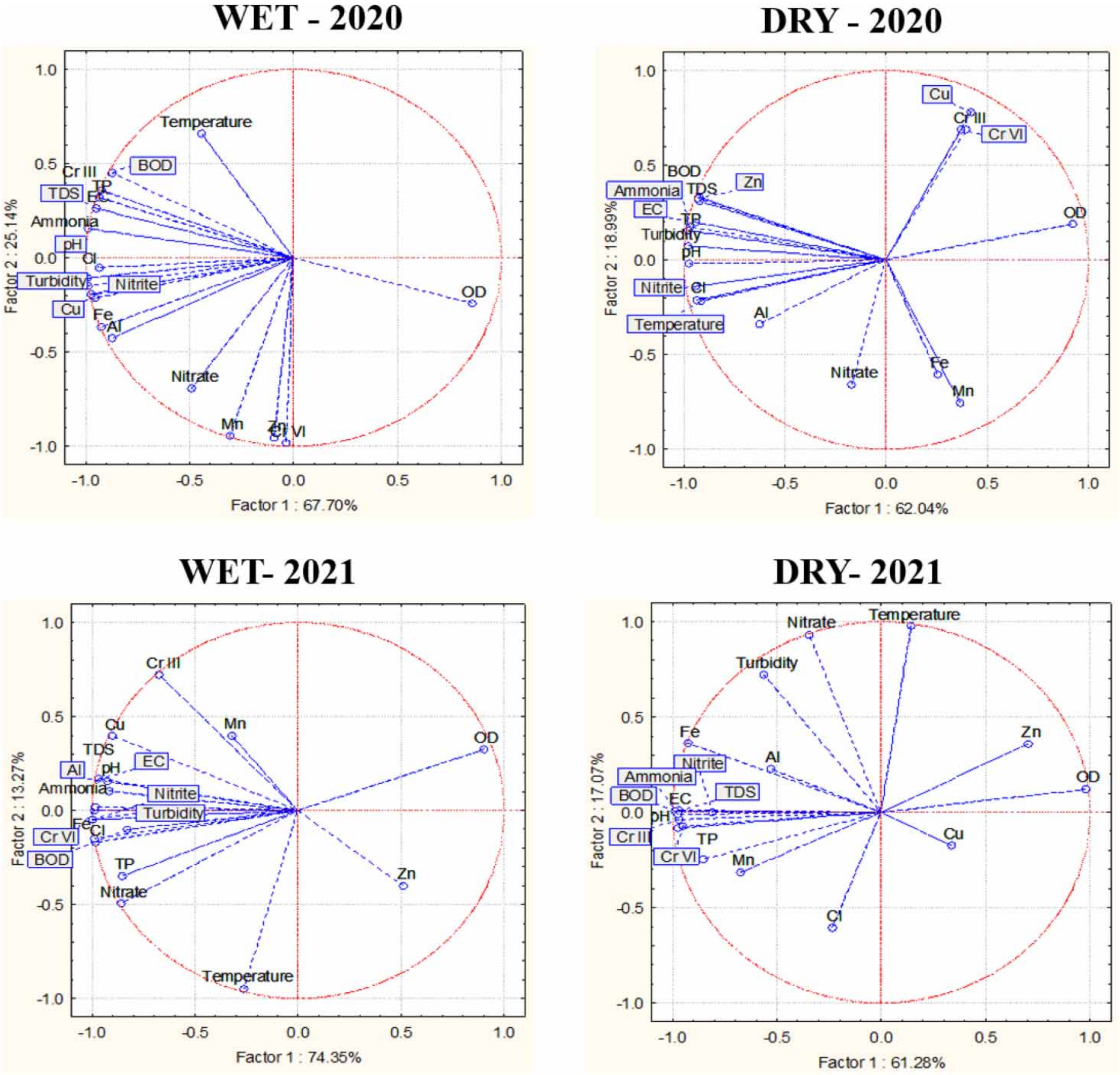

Figure 2 | PCA plot – The plot of the wet and dry seasons between physical–chemical parameters, metals, TP, and major anions.

can cause health problems in humans, including respiratory and cardiovascular diseases (Dede *et al.* 2013; Yuvaraja *et al.* 2022). The higher Fe concentrations during the rainy season may be related to natural sources. The Alter do Chão Formation is composed of a superficial laterite layer dating back to the Cretaceous (Mendes *et al.* 2012) that can reach aquatic environments through weathering.

Mn showed concentrations above the standard at most of the points in both seasons in the 2 years of the study. However, the highest concentrations of Mn were observed during the rainy season (Table 2). Mn is a metal that can cause neurological diseases at high concentrations in water (Nascimento *et al.* 2022), and it is very important to monitor its concentrations in the aquatic environment, due to the risk to human health when there is ingestion or contact with water contaminated by the metal.

Although most studies point out that the main source of Mn in the aquatic ecosystem is industrial sewage, in the case of this study, there was no industrial agglomeration along the watershed, indicating that the natural source of Mn is the main source. The laterite of the Alter do Chão Formation is composed of Mn oxides (Costa 1991) that reach the microbasin through

Table 2 | Concentrations of metals and phosphorus (mg/L) for seasons between 2020 and 2021

Season	Samples	Al (mg/L)	Fe (mg/L)	Mn (mg/L)	Cr III (mg/L)	Cr VI (mg/L)	Cu (mg/L)	Zn (mg/L)	TP (mg/L)
Wet 2020	1	0.03	**0.79**	0.05	0.08	0.02	**0.37**	0.07	**0.69**
	2	0.1	**0.78**	**0.24**	0	0.02	**0.45**	0	**0.63**
	3	0.06	**1.28**	**0.4**	0.16	0.68	**0.72**	0.13	**0.32**
	4	**0.24**	**3.87**	**1.64**	0	3.56	**1.41**	**0.81**	**0.615**
	5	**0.27**	**4.87**	**0.55**	1.37	0.07	**2.23**	0.05	**3.7**
	6	0.08	**1.58**	**0.55**	0	1	**1**	0.13	0.01
Dry 2020	1	0	**0.77**	0.08	5.83	2.72	**0.45**	**0.2**	**0.15**
	2	0.02	0.06	**0.16**	0.01	0.03	**0.18**	0.06	**0.68**
	3	0.01	**0.99**	**0.38**	0.06	0	**0.12**	0.05	**0.11**
	4	0.01	**1.94**	**0.24**	0.01	0.05	**0.18**	0.03	**0.52**
	5	0.02	0.11	0.04	0.02	0.07	**0.15**	**3.04**	**4.7**
	6	0.01	0.04	0.01	0.04	0	**0.38**	**0.99**	**0.54**
Wet 2021	1	0.02	**0.65**	0.05	0.02	0.1	**0.35**	0.11	**0.72**
	2	0.01	**0.47**	**0.56**	0.05	0.01	**0.23**	0.07	**0.65**
	3	**0.17**	**0.77**	**0.82**	0.06	0.08	**0.89**	0.11	**1.42**
	4	0.09	**2.79**	**0.38**	0	0.36	**0.03**	0.1	**3.19**
	5	**0.38**	**6.37**	**0.6**	0.1	1.79	**3.38**	0.02	**3.85**
	6	0.02	**1.1**	**0.24**	0.04	0.02	**1.03**	0.01	**2.01**
Dry 2021	1	0.02	0.27	**0.37**	0.02	0	**0.24**	0.11	**1.33**
	2	0.03	**0.4**	**0.54**	0.03	0.02	**0.29**	0.07	**0.57**
	3	0.02	**0.36**	**0.24**	0	0.01	**0.03**	0.11	**0.54**
	4	0.03	**1.22**	**0.32**	0.03	0.02	**0.11**	0.1	**0.7**
	5	0.03	**2.32**	**0.57**	2.77	0.07	**0.89**	0.02	**3.02**
	6	0.03	**0.49**	**0.38**	0.01	0.04	**0.29**	0.01	**2.05**
Conama 357/05 Class II		0.1	0.3	0.1	NA	NA	0.009	0.18	0.050

*Concentrations in disagreement with CONAMA 357/05 are in bold.
NA = not applicable.

weathering and erosion. Cr III and Cr VI were higher in the dry seasons (Table 2), which may indicate an anthropogenic source. The most toxic Cr species to humans is Cr VI, as it can penetrate biological membranes (Bakshi & Panigrahi 2018), and is known to be carcinogenic, mutagenic, teratogenic (Mamyrbaev *et al.* 2015), highly soluble, and mobile in aquatic ecosystems (Bakshi & Panigrahi 2018).

The sources of Cr include untreated industrial sewage, wood processing waste, tanneries, mining, and alloy steel manufacturing (Jones *et al.* 2019; Tumolo *et al.* 2020). In the Amazon, tanneries and lumber mills are the main sources of Cr in aquatic ecosystems (Sousa *et al.* 2016). The study region has wood processing activity, which could be the source, as well as small tanneries. Although the effluent mainly contains Cr III, the presence of Mn oxides can cause the oxidation of Cr III to Cr VI, which is more toxic and bioavailable (Szalinska *et al.* 2010). In this study, Cr VI showed a positive correlation with Mn during the 2020 rainy season (Table 2), indicating that it may be associated with Mn oxides.

The highest concentrations of Cu were observed during the rainy season (Table 2); however, all points in all seasons were above the legal limit, indicating anthropogenic input throughout the watershed. Student's *t*-test showed a significant difference between Cu concentrations in the dry and rainy seasons of 2020 ($T = 2.4$; $p < 0.05$). This result suggests that seasonality occurs between seasons, which may be related to sources. In the dry season, the main source was untreated sewage dumped along the microbasin; however, in the rainy season, the source was diffuse and influenced by the washing of the margins.

According to Sodré *et al.* (2012), watersheds that suffer anthropic pressure have high Cu concentrations in the water because of the input of domestic and industrial sewage. The highest concentrations of Zn occurred in the dry season of 2020, with only P5 and P6 being above that allowed by legislation (Table 2). According to Costa *et al.* (2017), the concentration of Zn in the sediment increases when the water column is acidified; therefore, a less acidic water column decreases the incorporation of Zn into the sediment in aquatic environments. Zinc is an essential microelement found in water and food in the form of salts or organic complexes (Ulniković & Kurilić 2020). In this study, the dry season of 2021 was characterized by the highest pH levels (Table 1), which may explain this behavior. The main sources of Zn in aquatic environments are anthropogenic activities, such as untreated domestic and industrial sewage discharge.

Cl showed higher concentrations in the dry season (Table 3), and only P1 in the rainy season of 2021 was in accordance with the CONAMA 357/05. During the dry season of 2021, the concentration of Cl in P3 was 307 times higher than that allowed by legislation, indicating intense anthropogenic pressure in the watershed. This is contrary to the findings of Nascimento *et al.* (2022), who found higher concentrations of chloride during the rainy season in the Irurá microbasin. The main sources of Cl in aquatic ecosystems are agricultural activities, and domestic and industrial sewage (Dede *et al.* 2013).

The concentrations of nitrite and nitrate were higher during the rainy season but were all below the CONAMA 357/05 limit. The negative correlations between nitrite and DO at some stations showed that these nitrogenous forms contributed to the decline in water quality in the microbasin. Nascimento *et al.* (2022) found higher concentrations of nitrite and nitrate in the rainy season and attributed it to fertilizers used in agriculture and the discharge of untreated domestic sewage. When applying Student's t-test, the nitrite content of the 2020 dry season was different from that of the 2020 rainy season ($T = 2.4$, $p < 0.05$). This suggests that there is a difference in nitrite input into the microbasin between the seasons.

Nitrate is the final product of the decomposition of organic matter and is naturally found in the environment. However, nitrite is naturally found in small amounts and is formed in reducing environments. Low amounts of nitrite in the aquatic environment indicate pollution, and the reduction of DO causes microbiological reduction of nitrate to nitrite (Dede *et al.* 2013).

Ammonia concentrations were highest at P5 at all stations (Table 3). The negative correlations between ammonia and DO suggest that in addition to contributing to the decline in water quality, higher ammonia concentrations may cause increased consumption of DO, which may cause anoxia in the aquatic ecosystem (Dede *et al.* 2013). Although ammonia has no

Table 3 | Concentrations of Cl, nitrate, nitrite, and ammonia (mg/L) for seasons between 2020 and 2021

Season	Samples	Cl (mg/L)	Nitrate (mg/L)	Nitrite (mg/L)	Ammonia (mg/L)
Wet 2020	1	**0.02**	0.07	0.05	0.09
	2	**0.05**	0.5	0.05	0.05
	3	**0.13**	1.12	0.05	0.07
	4	**0.96**	1.66	0.14	0.41
	5	**2.04**	1.06	0.21	1.86
	6	**0.13**	0.09	0.06	0.05
Dry 2020	1	0.01	0.06	0.02	0.04
	2	**0.02**	0.07	0.02	0.05
	3	**0.03**	0.07	0.02	0.06
	4	**0.13**	0.75	0.03	0.11
	5	**0.22**	0.18	0.04	1.83
	6	**0.03**	0.07	0.02	0.13
Wet 2021	1	**0.1**	0.08	0.02	0.19
	2	**0.04**	0.09	0.02	0.04
	3	**0.21**	0.1	0.03	0.13
	4	**0.86**	0.87	0.07	0.34
	5	**2.03**	1.04	0.2	1.76
	6	**0.15**	0.12	0.03	0.04
Dry 2021	1	**0.03**	0.07	0.03	0.06
	2	**2.15**	0.05	0.01	0.06
	3	**3.07**	0.05	0.02	0.05
	4	**0.1**	0.45	0.02	0.14
	5	**2.29**	0.25	0.05	1.81
	6	**3**	0.05	0.02	0.12
Conama 357/05 Class II		0.01	10.0	1.0	NA

*Concentrations in disagreement with CONAMA 357/05 are in bold.

NA = not applicable.

reference in the current Brazilian legislation, it can harm human health and aquatic biota (Dede *et al.* 2013; Nascimento *et al.* 2022).

3.3. Multivariate analyses

PCA factors 1 and 2 were responsible (combined) for more than 80% of the variation in the two seasons during the sampling period (Figure 2). In this sense, the PCA results indicate that the contaminants (organic and inorganic) have the same anthropogenic source, originating from domestic and industrial effluents. In the dry season of 2020, Cr III and VI and Cu showed correlation and opposite behavior to nitrate in the PCA, suggesting that in this season, Cr and Cu have a different source in relation to domestic sewage, which may be related to the use of preservatives and biocides for leather, which contain metals in their composition, such as Cu (Ashayeri *et al.* 2023).

The anthropogenic input of metals into the aquatic environment is dangerous for biota, which in the Amazon environment is consumed on a large scale. Thus, PCA corroborates the use of QIAL as an important tool to manage metal contamination in aquatic environments. Therefore, these analyses reinforce the influence of seasonality and the previously found correlations. Nascimento *et al.* (2022) found similar results and attributed the effect of seasonality to the characteristics of the rainy season in the Amazon, which is characterized by a higher contribution of urban and rural contaminants, in addition to sediments from areas that suffer erosion.

In this sense, in the rainy season, the forest–water interface has a greater influence, which directly influences physicochemical parameters (Monte *et al.* 2021b). In addition to seasonality, the analysis showed a strong interaction between contaminants and physicochemical parameters, reinforcing the need to consider the ecoregional aspects of water quality legislation in the country.

3.4. Assessment of potential risk to human health

The population was divided into children and adults in two seasons (dry and rainy) for 2020 and 2021. The non-carcinogenic contaminants studied were Cl, Fe, Mn, nitrate, and nitrite. In both seasons, none of the contaminants exceeded the hazard index value of 1 for direct ingestion (Table 4) or ingestion via swimming (Table 5). Although no result exceeded the value of 1, the analysis of human health risks is very important in the Amazon because the rate of degradation of urban microbasins in the region is high. Unlike other regions, the Amazonian population depends on water resources for transportation, food, and entertainment (Nascimento *et al.* 2022).

Nascimento *et al.* (2022) performed a study on human health risk in another urban microbasin in Santarém and all the results of the hazard ratio were below 1. However, in this study, the results were one order of magnitude higher than those reported by Nascimento *et al.* (2022), suggesting that anthropogenic input is higher in the Juá microbasin, which suffers greater urban pressure.

An increase of one order of magnitude among the urban microbasins of Santarém shows that investment in basic sanitation in the municipality is very important. Santarém is an Amazonian city that is in full demographic growth (Monte *et al.* 2021a); however, this growth does not accompany the increase in infrastructure, the decline in water quality of the microbasins, or the consequent ingestion of contaminated water, which can lead to higher public health costs due to diseases that have water as a vector.

Table 4 | Hazard index for direct ingestion for seasons between 2020 and 2021

Season	**Individual**	**P1**	**P2**	**P3**	**P4**	**P5**	**P6**
Wet 2020	Adults	6.4×10^{-5}	1.2×10^{-4}	2×10^{-4}	8.4×10^{-4}	9.7×10^{-4}	2.3×10^{-4}
	Kids	2×10^{-4}	3.7×10^{-4}	6×10^{-4}	2×10^{-3}	1.6^{-3}	7×10^{-4}
Dry 2020	Adults	5.7×10^{-5}	4.8×10^{-5}	1.3×10^{-4}	1.9×10^{-4}	9×10^{-5}	2×10^{-5}
	Kids	1.9×10^{-4}	1.5×10^{-4}	4.4×10^{-4}	5.4×10^{-4}	1.2×10^{-4}	4×10^{-5}
Wet 2021	Adults	7.2×10^{-5}	1.5×10^{-4}	2.7×10^{-4}	4.7×10^{-4}	1×10^{-4}	1.5×10^{-4}
	Kids	1.6×10^{-4}	5×10^{-4}	7.5×10^{-4}	8.8×10^{-4}	1.8×10^{-3}	3.8×10^{-4}
Dry 2021	Adults	1×10^{-4}	7.4×10^{-4}	9.5×10^{-4}	1.6×10^{-4}	8.8×10^{-4}	9.5×10^{-4}
	Kids	3.4×10^{-4}	6.7×10^{-4}	5.5×10^{-4}	4.6×10^{-4}	1×10^{-3}	6.6×10^{-4}

Table 5 | Hazard index for ingestion via swimming for seasons between 2020 and 2021

Season	Individual	P1	P2	P3	P4	P5	P6
Wet 2020	Adults	6.4×10^{-6}	1.2×10^{-5}	2×10^{-5}	8.4×10^{-5}	9.7×10^{-5}	2.3×10^{-5}
	Kids	2.3×10^{-6}	4.1×10^{-5}	7.2×10^{-5}	3×10^{-4}	3.4^{-4}	8.1×10^{-5}
Dry 2020	Adults	5.7×10^{-6}	4.8×10^{-6}	1.3×10^{-5}	1.9×10^{-5}	9×10^{-6}	2×10^{-6}
	Kids	2×10^{-5}	1.7×10^{-5}	4.7×10^{-5}	6.5×10^{-5}	3.2×10^{-5}	6.7×10^{-6}
Wet 2021	Adults	7.2×10^{-6}	1.5×10^{-5}	2.7×10^{-5}	4.7×10^{-5}	1×10^{-4}	1.5×10^{-5}
	Kids	2.5×10^{-5}	5.3×10^{-5}	9.4×10^{-5}	1.6×10^{-4}	3.6×10^{-4}	5.1×10^{-5}
Dry 2021	Adults	1×10^{-5}	7.4×10^{-5}	9.5×10^{-5}	1.6×10^{-5}	8.8×10^{-5}	9.5×10^{-5}
	Kids	3.7×10^{-5}	2.6×10^{-4}	3.3×10^{-4}	5.5×10^{-5}	3×10^{-4}	3.3×10^{-4}

3.5. Quality Index for Aquatic Life

The development of a water QIAL life is important, especially in regions that are dependent on fishing, and where the diet is based on the consumption of fish and other aquatic animals, such as the Amazon region. In recent years, the annual per capita consumption of fish in traditional Amazonian communities has been 7.7 times higher than the global average (Viana *et al.* 2024). High rates of contamination in aquatic life alert the population to the risk of consuming these animals. Only P1 and P5 presented results above 1 for Cr III (Table 6): P1 only in the dry season of 2020, and P5 in the rainy season. However, for Cr VI, all points showed results above 1 in all the seasons.

According to Sousa *et al.* (2016), Cr contamination in the Amazon is an alarming problem related to the tanneries and wood industry. However, this problem has not been addressed because of the high Hg contamination in Amazonian rivers. The authors highlighted that the consumption of fish in regions contaminated by Cr is extremely dangerous to human health because of the carcinogenic, mutagenic, and teratogenic effects of Cr. Zn showed the highest results, above 1, in the 2020 dry season (P3,

Table 6 | QIAL for Cr III, Cr VI, Zn, and Cl for seasons between 2020 and 2021

	Cr III					
	P1	P2	P3	P4	P5	P6
Wet 2020	0.14	0.00	0.28	0.00	**2.40**	0.00
Dry 2020	**10.2**	0.0	0.1	0.0	0.0	0.1
Wet 2021	0.0	0.1	0.1	0.0	0.2	0.1
Dry 2021	0.04	0.05	0.00	0.05	**4.86**	0.02
Cr VI						
Wet 2020	**12.5**	**12.5**	**425**	**2,225**	**43.75**	**625**
Dry 2020	**1,700.0**	**18.8**	0.0	**31.3**	**43.8**	0.0
Wet 2021	**62.5**	**6.3**	**50.0**	**225.0**	**1,118.8**	**12.5**
Dry 2021	0	**12.5**	**6.25**	**12.5**	**43.75**	**25**
Zn						
Wet 2020	0.58	0.00	**1.08**	**6.75**	0.42	**1.08**
Dry 2020	**1.7**	0.5	0.4	0.3	**25.3**	8.3
Wet 2021	0.4	0.8	0.0	0.0	0.3	0.1
Dry 2021	0.92	0.58	0.92	0.83	0.17	0.08
Cl						
Wet 2020	**1.05**	**2.63**	**6.84**	**50.53**	**107.37**	**6.84**
Dry 2020	0.5	**1.1**	**1.6**	**6.8**	**11.6**	**1.6**
Wet 2021	**5.3**	**2.1**	**11.1**	**45.3**	**106.8**	**7.9**
Dry 2021	**1.6**	**113.2**	**161.6**	**5.3**	**120.5**	**157.3**

*Results above 1 are in bold.

P4, and P6). Meanwhile, Cl (only P1) was below 1 during the dry season of 2020. High concentrations of Cl in water can cause problems in freshwater fish, possibly leading to death due to osmotic imbalance (Evans *et al.* 2004).

Waichman *et al.* (2024) in a study of several species of commercial fish bought in various markets in the Amazon, including Manaus and Santarém, found that in the muscles of several species, including carnivores, there were high concentrations of Cr. According to the authors, the sources of Cr may be related to lowland areas, which are subject to seasonal flooding, where Cr leaches into the aquatic environment due to high rainfall.

In addition, Cr may be adsorbed to clay particles in the soil, which reach the aquatic environment during floods, and this process has intensified over the years due to deforestation and mining. Deforestation due to slash-and-burn for agricultural expansion in the region contributes to the enrichment of Cr in the sediments of the Amazonian rivers (Ribeiro *et al.* 2017).

Viana *et al.* (2024) in a study on the risk to human health from the bioaccumulation of metals in carnivorous fish species in an Amazonian river, showed that large quantities of metals such as Cd and Pb were found in the fish tissues and that consumption represents a high risk to human health. These results reflect the high concentrations of Cd and Pb in the water of the Araguari River, which exceeded the CONAMA 357/05 level 2 limit for freshwater (Viana *et al.* 2020). The results of the studies on the bioaccumulation of metals in Amazonian fish corroborate the results obtained by the QIAL, showing that the index is another tool in the management of aquatic ecological risk.

High concentrations of contaminants and nutrients are expected in the Amazon region during the rainy season (Monte *et al.* 2021b; Nascimento *et al.* 2022). Although the rainy season contributes to the greater influence of the dilution effect, which decreases contaminant concentrations in most aquatic ecosystems, the opposite occurs in the Amazon. The rainy season in the region increases the concentration of contaminants in the rivers, which may be related to the increase in runoff, which washes away the banks and carries greater quantities of contaminants into the rivers but can also be attributed to the sediment resuspension effect, which increases due to the greater flow and can release contaminants that were adsorbed to the sediment into the water column.

4. CONCLUSION

In this study, the ecological risk analyses applied to the watershed showed worrying results. Although the highest concentrations of contaminants were concentrated during the rainy season, as expected for the region, this was not reflected in the application of the indices, indicating that the current levels of contamination were high, regardless of the season. The rainy season carries contaminated sediment, agricultural waste, and mining waste to the riverbed, which increases the concentrations of metals in Amazonian rivers.

High concentrations of Cr III and Cr VI are a warning about the disposal of effluents by anthropogenic activities without adequate treatment. Similar to Hg, Cr species are highly toxic to humans and biota, and could become a new public health problem in the Amazon.

The QIAL showed worrying results for the maintenance of aquatic life, being a potential risk for a biome such as the Amazon, in which part of the population's diet is based on fish consumption. The results of this index were alarming for some contaminants, such as Cr, Zn, and Cl species, especially in the rainy season, indicating that the biota may suffer a deleterious effect after exposure to contaminants. The high concentrations of Cr in water affect the biota, some of which have high concentrations of metals in their muscles.

Although the risk to human health is still low, the results show greater degradation in this microbasin than in others in Santarém. High concentrations of Cr III and VI are of concern because of their effects on human health, which is a relevant contamination problem in Amazonian rivers and streams.

The lack of investment in basic sanitation, together with unplanned demographic growth in the Amazon, can become a major public health problem in the region. Future studies on the dynamics of contaminants in sediment are necessary to investigate the processes occurring in this environmental compartment to better understand the influence of seasonality on contaminants in sediment and water.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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