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Distribution and seasonality of potentially toxic elements (PTEs) in the waters of the Negro river in Manaus, Amazonas, Brazil

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Population growth and urbanization have led to critical environmental challenges worldwide. Chemical pollutants, especially Potentially Toxic Elements (PTEs) such as Cd (Cadmium), Cu (Copper), Zn (Zinc), Al (Aluminum) and Mn (Manganese), as well as macroelements like P (Phosphorus), affect physicochemical and ecological parameters, posing risks to both human health and biodiversity. This study evaluates the influence of seasonality on the concentration of these PTEs in the waters of the Negro River, Manaus, Amazonas. Sampling was conducted at 60 sites along the river in January 2023, September 2023, and March 2024. Sampling, storage, and analyses followed the procedures established in the *Standard Methods for the Examination of Water and Wastewater*. Results revealed elevated mean Al and P concentrations (above 1250 µg/L and 250 µg/L, respectively), suggesting significant inputs of organic matter and surface urban pollution. Principal Component Analysis (PCA) revealed distinct patterns in January, higher levels of Na, Mg, Ca, Al, P, Ti, Be, and Cu; in September, predominance of K, Rb, and Ba; and in March, Li and Fe. Contamination by PTEs is multifactorial: although seasonality is a key driver, other factors, such as urbanization, proximity to agricultural areas, and industrial discharges, strongly modulate water quality.

Keywords Amazon river, Potentially toxic elements (PTEs), Seasonality, Water quality, Manaus, Water monitoring

Environmental impacts resulting from population growth and urbanization have intensified globally, requiring integrated responses to preserve urban ecosystems and water resources[1,2]. In metropolitan regions, intensive land use, untreated sewage expansion, and increased surface runoff compromise both the quantity and quality of water resources[3,4]. Furthermore, water management often lags in infrastructure and planning, amplifying impacts on water bodies and leading to consequences for public health, biodiversity, and local economies[5,6].

Water quality is influenced by natural factors such as rainfall regime, geology, and vegetation cover, as well as anthropogenic factors, including industrial and domestic discharges, urban solid waste, and agricultural practices[7,8]. Among the most concerning contaminants are Potentially Toxic Elements (PTEs) such as Cr, Cd, Cu, Pb, Zn, As, Mn, and phosphorus, whose increasing presence has been associated with industrial activities and urban runoff[9,10].

In the Amazonian context, the Negro River displays unique characteristics. It contains blackwater with high concentrations of humic and fulvic acids, low turbidity, and marked acidity (pH between ~ 4.0 and 5.5). These properties influence both the mobility and seasonality of PTEs[11–13]. Seasonality in the Negro River is important for understanding ecological and hydrological processes that shape water quality. It plays a significant role in determining metal concentrations and changes in limnological parameters[14–16].

The proximity of Manaus, particularly the Manaus Industrial Hub (PIM), places the Negro River under strong anthropogenic pressure. Previous studies indicate that industrial and domestic discharges, often carrying heavy metals, contribute to the deterioration of water quality near urban areas[17,18]. Monitoring PTEs is essential for

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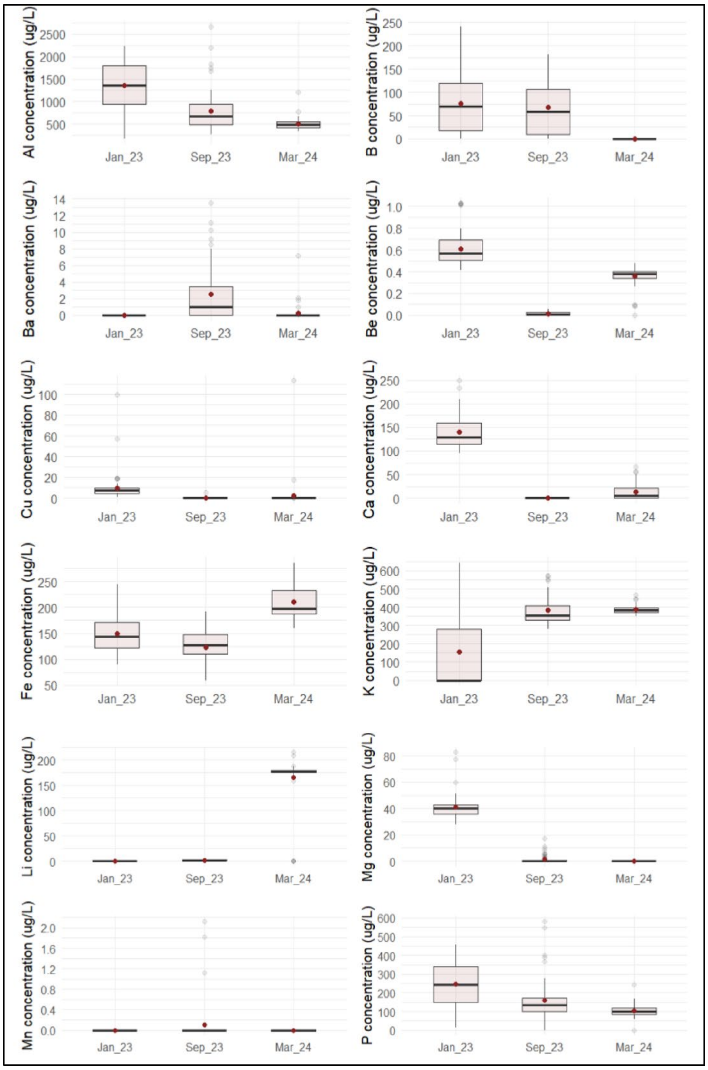

Fig. 1. Boxplot graphs of PTEs concentrations in the Negro River during the evaluated periods.

water quality management, as it enables the identification and control of contaminants that threaten ecosystems and public health. Tracking these pollutants enables the implementation of effective mitigation measures, ensuring water security and environmental Sustainability[19,20].

The Negro River is of enormous importance not only to the Amazon region but also to Brazil and, consequently, to the rest of the world. Its role in climate and environmental balance is indisputable, given its large volume of water, which directly influences rainfall and temperature regulation in the Amazon region and much of Brazil[21,22]. This information about the Negro River underscores the study's relevance, as it is a pioneering effort to monitor PTEs in these waters, which could pave the way for future research on this topic (Fig. 1).

One of the major issues surrounding the Negro River lies in its size and its essential role as a nutrient supplier for all living beings along its banks—microorganisms, plants, animals, and, therefore, humans. Until this study, no other study of this scale and quantity of samples had been conducted, making this pioneering work address not only a local but also a global need: understanding the role of this river in the distribution of this chemical element. Therefore, the information on PTEs obtained in this study is completely new, never before seen or analyzed from the perspective of the region's seasonality.

Considering this mix of natural and anthropogenic factors, the objective of this study is to evaluate how seasonality influences the spatiotemporal distribution of PTEs in the Negro River, Manaus, Amazonas. The specific objectives are: 1—Evaluate which PTEs are in higher concentrations and outside the limits established by Brazilian legislation. 2—Verify which PTEs are correlated and how these relationships can influence the environment. 3—Assess how flooding and drought influence PTE concentrations in the Negro River. The findings aim to offer insights for public policies that focus on monitoring and managing water quality in the region.

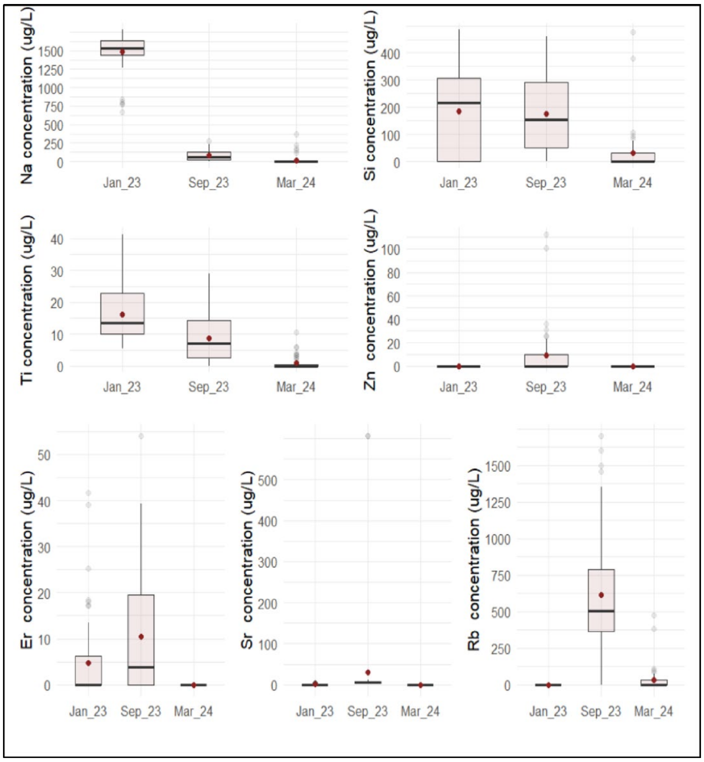

Fig. 1. (continued)

Results and discussion

Descriptive statistical analysis

The results revealed significant variations in the concentrations of the analyzed chemical elements in the Negro River across the three sampling periods: January 2023 (low-water season), September 2023 (transition from low to high water), and March 2024 (intermediate high-water season), consistent with the region's characteristic hydrological seasonality[23]. The ANOVA shows statistically significant differences in the concentration of PTEs in the analyzed sampling periods, revealing that Al ($p = 0.107$), B ($p = 0.201$), Be ($p = 0.098$), phosphorus ($p = 0.102$), Ca ($p = 0.048$), K ($p = 0.307$), Li ($p = 0.091$), Mg ($p = 0.109$), Na ($p = 0.003$), Rb (p = 0.341) showed differences between the flood and dry periods for the Negro River.

Among the determined elements, those with reference values established by CONAMA Resolution 357/2005 (Al, B, Ba, Be, Cu, Fe, Li, Mn, phosphorus, and Zn) were highlighted, enabling an assessment of environmental compliance. It was observed that B, Ba, Be, Cu, Fe, Li, Mn, and Zn had mean concentrations below the established thresholds, indicating compliance with water quality standards. In contrast, Al and P exceeded maximum permissible values in all analyzed periods.

Aluminum (Al):

According to CONAMA Resolution 357/2005, the maximum permissible value for Al in Class 1 and 2 freshwater is 100 $\mu g \cdot L^{-1}$. In all campaigns, observed concentrations exceeded this threshold, with the highest values recorded during the low-water season (January 2023) and a gradual reduction in subsequent periods, evidencing seasonal dilution associated with increased water volume. Statistically, no significant differences in Al concentrations were observed across the sampling periods ($p = 0.107$). Despite this, the pattern confirms the strong influence of the hydrological regime on Al mobility and availability.

The Negro River, classified as a blackwater system, presents acidic pH, low dissolved solids, and high dissolved organic matter (DOM), which forms stable complexes with metals such as aluminum[24,25]. Studies show that even at the confluence with the Solimões River, dissolved Al remains in solution due to its strong association with organic compounds, with little removal by flocculation or sedimentation. Thus, although values exceed legal limits, they reflect natural system conditions rather than anthropogenic contamination. Nevertheless, such concentrations are relevant when considering the river's use for public supply, as Al can compromise potability without proper treatment.

Phosphorus (P)

The P concentrations exhibited marked seasonality. During the low-water season (January 2023), elevated concentrations (250 $\mu g \cdot L^{-1}$) were recorded, exceeding thresholds for Class 1 waters (100 $\mu g \cdot L^{-1}$) and Class 2 waters (150 $\mu g \cdot L^{-1}$). During the transition (September 2023) and high-water (March 2024) periods, progressive dilution was observed, with values gradually approaching legal standards.

This behavior is consistent with studies linking phosphorus fluxes in Amazonian rivers to the flood pulse[26]. Additionally, in black water systems, naturally poor in phosphorus, fauna play an important role in nutrient cycling and redistribution between flooded and upland environments, reinforcing the natural character of the observed variation[27]. However, the relationship between P and eutrophication of river waters has been known for quite some time[28]. In this sense, it is possible and even probable that during the dry season, the waters of the Negro River become more conducive to the proliferation of eutrophic microbiological agents. These occurrences may explain a higher P concentration during the dry season than during the rainy season.

The concentration of *P* in the Rio Negro, although not statistically significant ($p = 0.102$), clearly demonstrates the relevance of seasonality, particularly the increase in water during rainy periods compared to the dry period.

Elements without reference values in CONAMA

For Ca, K, Mg, Na, Si, Ti, Er, Sr, and Rb, no thresholds are established by CONAMA Resolution 357/2005. Even so, statistical analysis revealed relevant seasonal variations, particularly for Ca, K, Li, and Rb.

Calcium (Ca): Concentrations remained within the ranges observed in natural waters (1–135 $mg{\cdot}L^{1}$)[29], consistent with the WHO's recommended ideal range of 40–80 $mg{\cdot}L^{-1}$[30]. Despite seasonal oscillations, no risks to human health were identified.

Potassium (K): Displayed greater spatial heterogeneity during the low-water season (January 2023), including values close to zero and others elevated. In subsequent periods, concentrations stabilized (350–400 $\mu g{\cdot}L^{-1}$). This pattern suggests the influence of local processes such as leaching of flooded soils and organic matter decomposition, in addition to hydrological regime effects[31,32]. Although essential, elevated concentrations may pose risks to vulnerable populations, but no official guideline values exist[33]. Regarding vulnerable individuals, excess potassium can compromise renal function in patients with renal insufficiency or even elderly people with compromised renal function. Therefore, it is necessary to evaluate water quality with respect to the concentration of this element.[33]

Magnesium (Mg) and Sodium (Na): Both presented low concentrations, typical of blackwater rivers[34]. For Na, values were far below the WHO's alert threshold of 200 $mg{\cdot}L^{-1}$[35], not representing an immediate risk. In the case of Mg, reports of neurological problems due to excessive magnesium exposure have already been reported. Other studies have been inconclusive in analyzing the effects of this element on rodents, partly because the effects of this element on different animals may not be reproducible. Thus, the element demonstrates relative potential and therefore deserves to be investigated in abundant water sources such as the Rio Negro[35].

Strontium (Sr) and Rubidium (Rb): Both showed seasonal variations at low concentrations. Sr can replace Ca in bone metabolism, with potential implications at elevated levels[36], while Rb, generally considered non-toxic under typical environmental conditions, may compete with K in ion channels[37].

Silicon (Si) and Titanium (Ti): Detected at low concentrations without relevant seasonal variation. Si, mostly as dissolved silica, may benefit bone health (Exley, 2009), while Ti has low mobility and toxicity in aquatic systems[38].

We know that physicochemical parameters such as pH can influence the greater or lesser adsorption of metallic elements in river waters[39]. However, considering that one of the peculiar characteristics of the Negro River is its acidic pH between 5.1 and 5.5, we can infer that this played some role in the presence of EPTs in the Negro River water. However, since this physicochemical characteristic is present throughout the river, and since these pH values fluctuate little even in different seasons, we can expect little influence of this parameter on the concentration of metals in different periods of the year.

In summary, results demonstrate that hydrological seasonality exerts a direct influence on the mobility and distribution of analyzed elements, particularly Al and P, whose concentrations exceeded legal thresholds but reflect natural system conditions. The other elements, although variable, remained within ranges compatible with Amazonian environments, reinforcing the chemical uniqueness of the Negro River and its implications for water quality.

Correlation analysis

The correlation matrix (Fig. 2) presents the Pearson correlation coefficients (r) calculated between the analyzed chemical elements. Each cell of the matrix represents the strength and direction of the relationship between two elements, with values ranging from −1 (perfect negative correlation, blue) to + 1 (perfect positive correlation, red). Values near zero indicate no correlation. The strongest correlations ($r > 0.90$) were observed between Al–P, Ca–Mg, Ca–Na, and Na–Mg. Additionally, a relevant association was identified between Be–Ca ($r = 0.78$). These patterns suggest that certain elements exhibit coupled geochemical behavior, reflecting both local dynamics and the influence of external sources.

The strong positive correlation between Al and P can be attributed to the high affinity between these elements in Amazonian environments. Regional soils, intensely weathered and acidic, are rich in aluminum oxides, which act as important phosphorus adsorbents[40]. Part of this phosphorus is mobilized and transported to the aquatic system associated with Al, favoring the formation of Al–P complexes. In the acidic, nutrient-poor blackwaters of the Negro River, naturally enriched in Al, this process explains the persistence of the observed association[41].

Positive correlations between Ca–Mg and Ca–Na indicate common sources or similar mobilization processes. The strong Ca–Mg association confirms the co-weathering of carbonate and silicate rocks, a process widely documented in large tropical rivers[42]. The Ca–Na correlation, however, extends beyond local weathering, since the region's intensely leached soils are poor in easily weatherable primary minerals. In this context, atmospheric deposition plays a central role: sea salts from the Atlantic and mineral dust from the Sahara, rich in Ca, Na, and Mg, are regularly deposited over the Amazon[43]. This external input has been linked to changes in cation balances in nutrient-poor tropical soils[44], reinforcing that in oligotrophic systems like the Negro River, the combination of limited weathering and atmospheric deposition explains the observed correlation patterns.

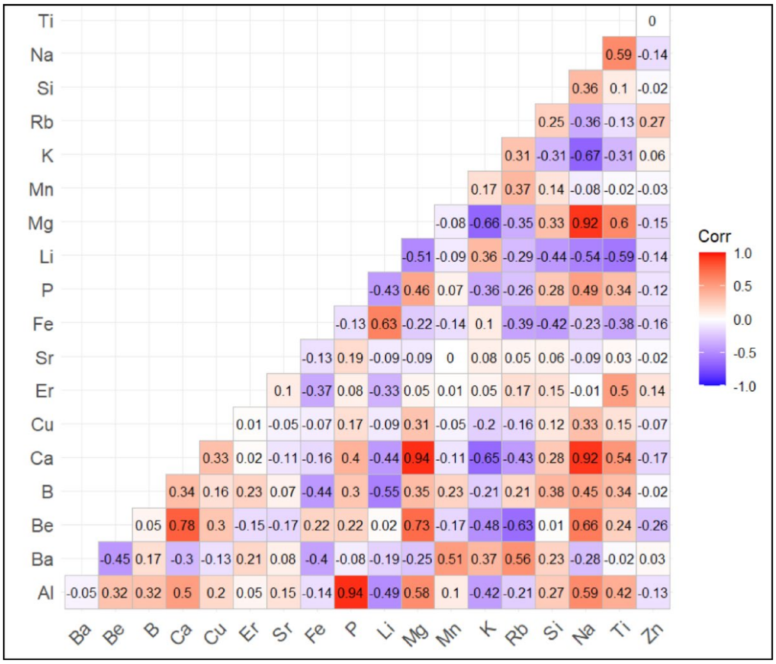

Fig. 2. Pearson correlation matrix of PTEs in Negro River waters. Cophenetic correlation coefficient = 0.86.

Similarly, the positive correlation between Na and Mg reflects the joint influence of atmospheric deposition of sea salts and mineral dust rich in cations. Since their primary local mineral sources do not coincide and weathering release is limited, atmospheric inputs emerge as the most plausible explanation[43].

The Be–Ca correlation (r = 0.78) also suggests joint mobilization controlled by sources external to the basin, particularly atmospheric deposition of mineral dust. While Ca may originate from both restricted weathering of carbonate and silicate minerals and atmospheric inputs, Be occurs only as a trace element in silicate minerals and has no known agricultural sources, reinforcing its natural origin[45]. In acidic waters like those of the Negro River, Be mobility tends to be slightly higher; however, concentrations remain extremely low (typically 0.01–0.1 μg L^{-1}), reflecting the same geochemical pulse controlling Ca, with no evidence of anthropogenic contribution[46,47].

EPTs assessment in the waters of the Rio Negro is not a frequently conducted investigation, making comparison with other studies carried out in these waters impossible. However, the recent work of[16,48] evaluated the presence of these elements in the Educandos and São Raimundo basins. Even considering that these are not blackwater rivers, and that both run through the urban area of Manaus, placing them under significant impact from urban waste contaminants, some comparisons can still be made, considering the influence of the region's seasonality. The high concentration of Al in the Negro river and in both basins mentioned is noteworthy. This indicates that geomorphological characteristics of the region influence the presence of this element in the waters of local tributaries. Furthermore, the high concentration of P in the urban basins can be explained by the high contaminant potential of urban waste in both basins.

Principal component analysis (PCA)

Principal Component Analysis (PCA) proved effective in reducing the dimensionality of trace element (PTEs) data. The first two components (PC1 and PC2) explained approximately 50% of the total variance (Fig. 3).

When considering up to the fourth component (PC4), cumulative variance exceeded 60%, which is satisfactory for representing data patterns and trends without significant information loss[49]. Table 1 presents the eigenvalues of the principal components, with PC1 and PC2 highlighted (2.38 and 1.87, respectively). Additionally, PC6 showed relevance for Cu (0.93), while PC4 highlighted Sr (0.69), according to the classification criteria proposed by Finkler et al.[41].

The biplot (Fig. 4) illustrates the relationship between PC1 and PC2 scores, highlighting groupings of elements associated with different seasonal periods in the Negro River. PC1 (Dim1), which explained 32.3% of the total variance, grouped Na, Mg, Ca, Al, P, Ti, Si, and Be, with the greatest contributions recorded in January 2023 (rainy season).

In contrast, K, Rb, and Ba were located at the negative end of Dim1 and were predominant in the dry season (September 2023). In March 2024, during the rainy season, the distribution was more homogeneous, with Li and Fe standing out.

During the high-water period (January 2023), Na, Mg, Ca, Al, P, Ti, and Si presented higher concentrations, reflecting the large inflow of water from precipitation and surface runoff. This seasonal variation marks the start of significant geochemical changes.

This inflow enhances ionic dilution, mobilizes elements associated with natural weathering and particulate matter, and favors the export of dissolved organic matter, a key feature of Negro River blackwaters[34]. However,

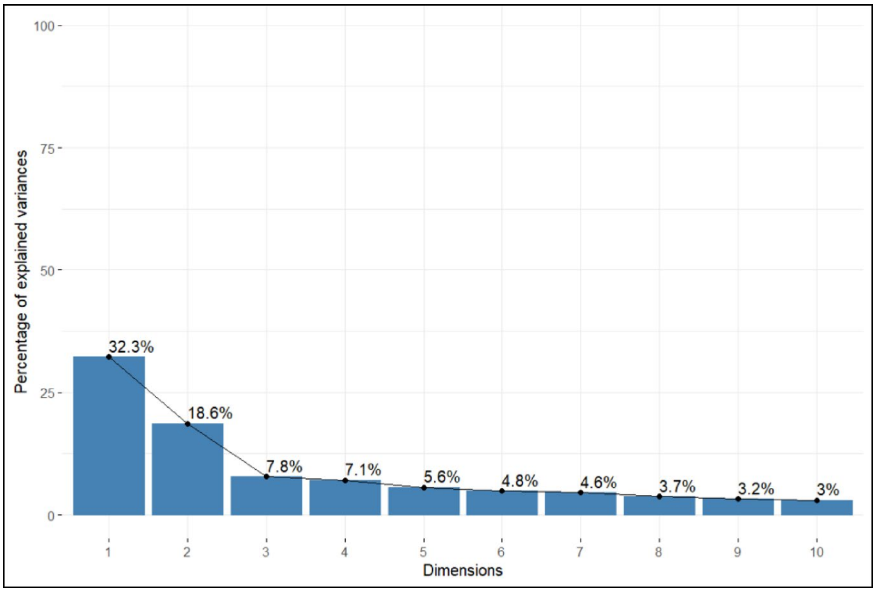

Fig. 3. Percentage of variance explained by the first ten principal components.

Elements	Principal components					
	CP1	CP2	CP3	CP4	CP5	CP6
Al	0.29	−0.06	0.40	−0.23	−0.06	−0.21
Ba	0.11	0.37	−0.28	0.08	−0.27	−0.03
Be	−0.28	−0.30	−0.11	−0.04	−0.17	0.00
B	−0.20	0.28	−0.15	0.00	0.01	0.08
Ca	−0.39	−0.09	−0.05	−0.07	−0.08	−0.05
Cu	−0.16	−0.05	−0.10	−0.07	−0.08	**0.93**
Er	−0.06	0.27	0.44	0.16	−0.38	0.10
Sr	0.02	0.11	0.11	**0.69**	0.39	0.13
Fe	0.12	−0.40	−0.11	0.08	−0.05	−0.07
P	−0.24	0.06	−0.10	0.43	0.18	−0.08
Li	0.25	−0.34	−0.13	0.05	−0.11	0.12
Mg	−0.40	−0.04	−0.04	−0.06	−0.05	−0.09
Mn	0.04	0.24	−0.53	0.02	−0.29	−0.12
K	0.31	0.09	−0.01	0.16	−0.29	0.14
Rb	0.16	0.39	−0.08	−0.26	0.11	0.02
Si	−0.17	0.25	−0.24	−0.12	0.40	0.07
Na	−0.40	−0.03	−0.06	−0.07	0.01	−0.06
Ti	−0.28	0.15	0.33	0.13	−0.39	−0.09
Zn	0.07	0.14	0.42	−0.41	0.23	0.03
Eigen value	**2.38**	**1.87**	1.18	1.08	1.04	0.94
% of variance	0.31	0.19	0.07	0.06	0.05	0.04
Cumulative %	0.31	0.50	0.58	0.65	0.71	0.76

Table 1. Principal Component Analysis (PCA) of PTEs concentrations in the Negro River, Manaus.

elevated Mg, Ca, Al, and P concentrations in specific areas may also be linked to surface runoff from agricultural lands due to fertilizer use[51,52].

Transitioning to the dry season (September 2023), K, Rb, and Ba predominated. This pattern may be attributed to three main factors: (i) natural rock weathering, (ii) accumulated atmospheric deposition mobilized by sporadic rains, and (iii) sediment influence, as lower water volumes favor dissolved ion concentration[53,54].

In March 2024, although also within the rainy season, the distribution differed from that of January 2023, with Li and Fe predominating. This peculiarity may be associated with redox dynamics, particularly the mobility of dissolved iron, strongly influenced by low turbidity and the presence of organic ligands that promote transport in complexed colloidal forms. Although Li does not directly participate in redox processes, it may be transported

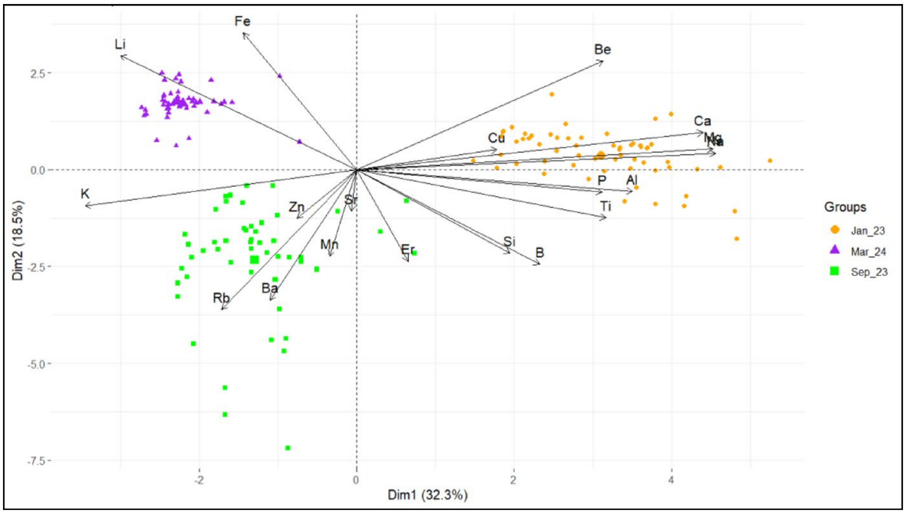

Fig. 4. Graphical analysis of principal components of PTEs. Eigenvalues of PC1 and PC2 variables.

through similar mechanisms. Both elements may originate from natural weathering processes or anthropogenic sources linked to aquifers in the upper Negro River basin[55].

Overall, PCA results show that Amazonian seasonality strongly affects the geochemical composition of the Negro River. Specifically, increased water volume during the flood season—along with greater substrate transport and particulate matter—directly drives the mobilization, dilution, and deposition of PTEs[51].

This study evaluated how seasonality affects spatiotemporal variation of Potentially Toxic Elements (PTEs) in the Negro River, Manaus (Amazonas, Brazil). The research is justified by rising anthropogenic pressure, especially in urban stretches where unplanned urbanization and effluent discharges harm water quality. Statistical and laboratory analyses were used to understand these elements' dynamics throughout different phases of the Amazonian hydrological cycle.

Descriptive statistics identified aluminum (Al) and phosphorus (P) as the most critical PTEs, both exceeding the thresholds established by CONAMA Resolution 357/2005. Al peaked in January (rainy season), surpassing 1250 µg L^{-1}, while P reached concentrations of up to 250 µg L^{-1}, suggesting significant inputs of organic matter and possible diffuse pollution sources such as urban surface runoff. These results further demonstrate how seasonality directly affects contaminant availability, accentuating their presence during certain periods.

Correlation analysis revealed strong associations among Ca, Mg, Na, and P ($r > 0.9$), as well as a significant Al–P interaction, suggesting interconnected biogeochemical processes and common sources, both natural and anthropogenic. Principal Component Analysis (PCA) further identified distinct seasonal patterns: January showed higher concentrations of Na, Mg, Ca, Al, P, Ti, Be, and Cu; September was dominated by K, Rb, and Ba; while March, although also a rainy period, exhibited a more homogeneous distribution, with Li and Fe prevailing. The difference between January and March suggests that, beyond seasonality, localized factors such as human activities and irregular discharges influence PTEs' variability.

Regarding water quality parameters, Duvoisin et al.[10] recently published a study developing a new water quality index (WQI) for blackwater rivers. In this study, the Negro River was investigated to optimize the assessment of blackwater quality, accounting for its distinctive characteristics, such as pH and electrical conductivity. The approximately 60 points evaluated in this study generally showed good water quality in the Negro River, with a slight decrease at sampling points closer to Manaus. Therefore, we can conclude that in the case of the Negro River, water quality was not a determining factor in the higher or lower concentration of PTEs, but rather the factors already presented and discussed in this work.

It is concluded that PTE contamination in the Negro River is multifactorial. Seasonality plays a decisive role but interacts with anthropogenic factors such as urbanization, proximity to agricultural areas, and industrial waste discharges. This combination reinforces the environmental complexity of the river's urban section and highlights the need for continuous, integrated monitoring strategies.

Study limitations include the restricted spatial scope to urban stretches and the temporal limitation to three sampling campaigns, while the absence of flow and meteorological variability data also constrained more detailed hydrological analyses. Nonetheless, the findings significantly contribute to understanding the interactions between seasonality and anthropogenic pressures in the Amazonian context. To deepen understanding of geochemical dynamics and support public policies to protect and sustainably manage the region's water resources, future research should incorporate sediment analyses, bioindicator organisms, and spatial modeling.

Methods

Study area

The Negro River is in the Amazon region, known for a hot, humid equatorial climate and strongly seasonal rainfall. The rainy season runs from December to May. The dry season runs from June to November, causing

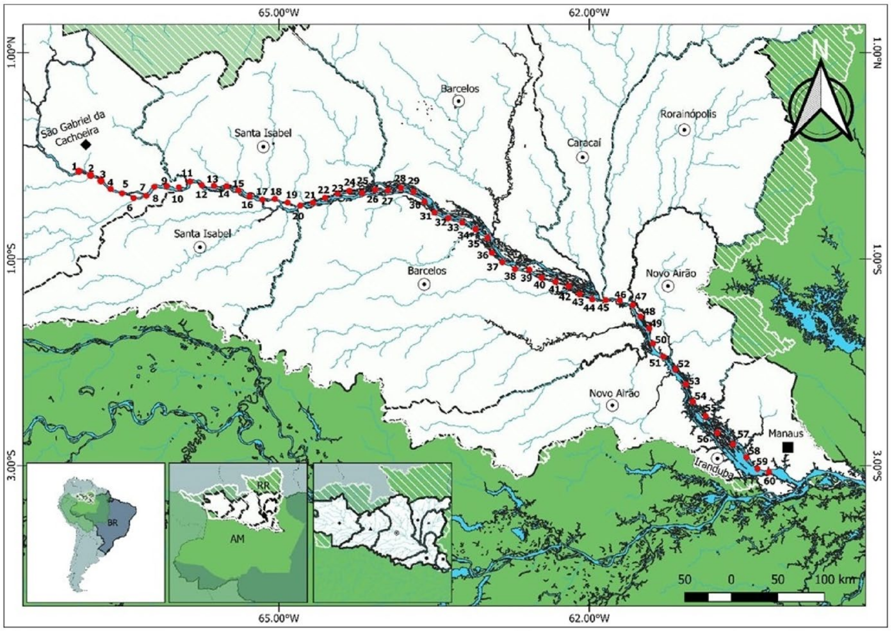

Fig. 5. Location of sampling points along the perimeter of the Rio Negro. All georeferenced collection points are available in Supplementary Table 3 (S3). The map was produced by one of the co-authors (Rafael Lopes e Oliveira), and generated using georeferencing information obtained by the field team at each collection point. To generate the map, all layers were processed using the open-source Geographic Information System software version QGIS 3.41(Link: https://qgis.org/download/). QGIS is licensed under the GNU General Public License, which allows the acquisition of its source code through tar files or the Git repository. The coordinates of the study sites were collected using a GARMIN® eTrex Legend® Hcx handheld GPS device. The data were converted to a digital format and transmitted as a shapefile.

marked changes in river levels[56]. The main geological formation is Tertiary and Quaternary sediments from the Amazon Basin. These determine drainage patterns and the availability of nutrients and minerals[57].

The Negro River's distinct physicochemical properties define its status as a blackwater river. It exhibits low suspended-solids concentrations, high acidity (pH 4.0–5.5), and elevated levels of humic acids from decaying organic matter[13]. These hydrological and climatological features drive the river's biogeochemistry and influence the seasonal movement of Potentially Toxic Elements (PTEs).

The Negro River is one of the main left-bank tributaries of the Amazon River, with approximately 2250 km of navigable length[58]. Its proximity to the urban center of Manaus gives it economic, social, and environmental significance, as it serves as a water supply, a transportation hub, and a recreational area. However, this close relationship with the city also leads to impacts from domestic and industrial discharges[59]. Therefore, understanding the river's regional setting and specificities is essential for linking hydrological fluctuations to spatial and temporal patterns in the distribution of these contaminants.

Sampling sites and collection

Three sampling campaigns were carried out in the Negro River, representing distinct phases of the hydrological pulse: January 2023 (low-water season), September 2023 (transition from low to high water), and March 2024 (intermediate high-water season). The campaigns covered 60 sampling sites distributed along the river, as illustrated in the map below (Fig. 1). The spacing between sampling sites was defined to ensure both statistical and spatial representativeness of PTEs concentrations, allowing a more accurate mapping of environmental variability throughout the study period (Fig. 5).

The sampling procedures followed the protocols established in the National Guide for Sample Collection and Preservation: Water, Sediments, Aquatic Communities and Liquid Effluents[51,52]. For the preservation of samples for analysis of potentially toxic elements (PTEs), these were collected in inert polymer bottles, and five replicates were collected at each sampling point. To ensure sample preservation, the pH was checked and adjusted to less than 2, with the addition of a 1:1 (v/v) aqueous HNO_3 solution. Furthermore, the bottles were then placed in a styrofoam box with ice and refrigerated at 4 °C[51,52], thus maintaining the sample at a low temperature and ensuring its preservation. For filtration, 0.45 µm PTFE filters (Millipore®) were used. From each sample, a 50 mL aliquot was filtered in triplicate to determine soluble elements.

All collection and laboratory analyses were conducted by the Applied Chemistry to Technology Research Group (QAT) according to the Standard Methods for the Examination of Water and Wastewater[60]. Analyses took place at the School of Technology, State University of Amazonas (UEA/EST).

Analysis of potentially toxic elements (PTEs)

The quantification of metallic trace elements was performed using inductively coupled plasma optical emission spectrometry (ICP-OES, Shimadzu 9820)[61]. Operating conditions are detailed in Supplementary Table 1(S1). Initially, qualitative readings were conducted to estimate concentrations and support quantification. For quantification, calibration curves were constructed with multielement reference standards from LGC Standards (lots 999,925–22 and 1,000,997–14), covering the range from 0 to 30,000 µg L^{-1}.

After data acquisition, wavelengths (λ) with the highest signal intensity and lowest spectral interference were selected for each metallic element. Supplementary Table 2 (S2) presents the detected elements, corresponding wavelengths, calibration curves, correlation coefficients (R^2), as well as detection limits (LOD) and quantification limits (LOQ).

Statistical analysis

Descriptive statistical analyses were first used to evaluate the central tendency and dispersion of metal concentrations in the three sampling periods. Differences between groups were tested using analysis of variance (ANOVA) at the $p<0.05$ significance level. Tukey's test followed. Boxplots showed the mean, extreme values, and outliers. Concentrations were also compared to the thresholds established by CONAMA Resolution No. 357/2005 for Class 2 freshwater. To investigate relationships between physicochemical parameters and trace elements, a Pearson correlation matrix was constructed, with significant correlations set at 0.5 or higher[62].

Before Principal Component Analysis (PCA), Bartlett's test of sphericity and the Kaiser–Meyer–Olkin (KMO) test were used. KMO values near 1 showed that the data were suitable. A $p<0.05$ in Bartlett's test also confirmed that PCA was appropriate [50]. PCA was used to reduce data dimensionality and facilitate the interpretation of element behavior as a function of seasonality. The procedure included the calculation of covariance and correlation matrices, eigenvalues and eigenvectors, and the construction of the factor-loading matrix[63,64]. Following Finkler et al.[41], factor loadings were classified as: relevant (>0.75), intermediate (0.50–0.75), and irrelevant (<0.50).

Because water quality data varied widely, an accumulated variance threshold of ≤75% was set as the acceptance criterion for principal components. All statistical analyses and graphical representations were carried out in RStudio (R version 4.3.1) using *ggplot2*, *vegan*, *tidyverse*, *readr*, and *patchwork* packages[65,66].

Data availability

All data used in this research are available in the cited articles, in the supplementary data, and in the Supporting Information. All data related to the water quality parameters of the Negro river are available at: [https://www.gp-qat.com/c%C3%B3pia-projetos-acad%C3%AAmicos] (https:/www.gp-qat.com/c%C3%B3pia-projetos-acad%C3%AAmicos).

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Declarations

Competing interests
The authors declare no competing interests.

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