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Spatial and temporal distribution of potentially toxic elements in the urban area of São Raimundo Basin in Manaus, Brazil

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ABSTRACT

Contamination of surface water by metallic elements is an environmental concern in cities with industrial parks such as Manaus in Amazonas, Brazil. The concerns are related to the bioaccumulation of these elements and their toxicity, which affect the ecology of aquatic environments and human health. The study evaluated the role of seasonality in the concentrations of potentially toxic metals in the São Raimundo Basin in Manaus. Collections were carried out in June 2021, October 2021 and January 2022 at thirty collection points. The physicochemical parameters were analyzed according to the Methods for the Examination of Water and Wastewater of the APHA/AWWA. The metals were analyzed using optical emission spectrometry with inductively coupled plasma (ICP-OES), and the data using analysis of variance (ANOVA), Pearson correlation and Principal Component Analysis (PCA). All presented values outside those established by Brazilian legislation, with an average of 267.2 ug/L. ANOVA showed role of seasonality in the concentrations of the metals, with the periods of flooding in the basin having the lowest concentrations of metals. Such as Barium (Ba) and Beryllium (Be) with averages close to 0.0 ug/L in the flood period, and dry period with average values of 0.50 ug/L. The correlation showed the relationship of Ba, Be and Titanium (Ti) with the Biochemical Oxygen Demand (BOD). PCA indicated the metals Ba, Be and Ti as the most relevant contaminants in the basin. It was possible to develop a map to identify the sampling points where the concentrations of these metals are the highest.

Keywords: Surface water, toxic metals, urban basin, water contaminants.

Distribuição espacial e temporal de elementos potencialmente tóxicos na área urbana da bacia do São Raimundo em Manaus, Brasil

RESUMO

A contaminação de águas superficiais por elementos metálicos é uma preocupação ambiental em cidades com parques industriais, em Manaus - AM, Brasil. As preocupações estão relacionadas à bioacumulação desses elementos e sua toxicidade, que podem afetar a ecologia dos ambientes aquáticos e a saúde humana. O estudo avaliou o papel da sazonalidade nas concentrações de metais potencialmente tóxicos na bacia do São Raimundo, na cidade de Manaus. As amostras foram coletadas em junho de 2021, outubro de 2021 e janeiro de 2022 em trinta e um pontos de coleta. Os parâmetros físico-químicos foram analisados de acordo com os Methods for the Examination of Water and Wastewater of the APHA/AWWA. Os metais foram analisados por espectrometria de emissão óptica com plasma indutivamente acoplado (ICP-OES), e os dados por análise de variância (ANOVA), correlação de Pearson e Análise de Componentes Principais (PCA). Al apresentou valores fora do estabelecido pela legislação brasileira, com média de 267.2 ug/L. A ANOVA mostrou um forte papel da sazonalidade nas concentrações dos metais, com os períodos de inundação na bacia apresentando as menores concentrações de metais. Como Bário (Ba) e Berílio (Be) com médias próximas de 0.0 ug/L no período de cheia, e período de seca com valores de 0.50 ug/L. A correlação mostrou a relação de Ba, Be e Titânio (Ti) com DBO. A PCA indicou os metais Ba, Be e Ti como os contaminantes mais relevantes na bacia. Foi possível desenvolver um mapa para identificar os pontos de amostragem onde as concentrações desses metais são maiores.

Palavras-chave: águas superficiais, bacia urbana, contaminantes da água, metais tóxicos.

1. INTRODUCTION

The accelerated growth of urbanization accompanied by the industrialization of large cities has expanded the use of the most diverse chemical compounds. These recent urban modifications have resulted in an increase of contaminants such as metallic elements, which have become contemporary concerns for health and the environment around the world (Aziz *et al.*, 2023).

Contamination by metallic elements can result from a variety of human activities, from the inadequate disposal of industrial effluents, through the use and disposal of herbicides in the soil and effluents to the tailings of the mining industry (Gevorgyan *et al.*, 2021). The concerns regarding this type of contaminant in surface water are justified by its non-biodegradability, toxicity, bioaccumulation and carcinogenesis. These characteristics are threats to both aquatic ecosystems and human health (Khadse *et al.*, 2015; El-Toony *et al.*, 2019; Hussain *et al.*, 2021).

Although some metals are used as components in essential biological processes, for example as cofactors of proteins, many of them are toxic when in concentrations that exceed a certain limit (Ebrahimpour and Mushrifah, 2008; Maia *et al.*, 2019). We can cite as ecological risks those related to their bioaccumulation in benthic macroinvertebrates that serve as food for various species of fish, thus inserting these chemical elements into the food chain of all other animals (Santos and Jesus, 2014).

Some studies have shown susceptibility to metabolic diseases such as diabetes or cardiovascular diseases in people with prolonged exposure to some types of metals. (Korashy *et al.*, 2017). Another example of the seriousness of this problem for human health was shown in the study by Sahoo and Sharma (2023) the element Fe is associated with disorders such as Parkinson's or Alzheimer's disease.

Regarding the concerns for human health, cultivable foods can be cited as the most exposed to risk, given that they can be contaminated by waters containing these metals in excessive concentrations. In addition, among these metallic elements, heavy metals such as As, Cd and Pb, which when present, cause serious effects even in small concentrations (Tchounwou *et al.*, 2012; Witkowska *et al.*, 2021; Singh *et al.*, 2022).

The rapid growth of industry in developing countries such as Brazil has little or no environmental supervision related to the discharge of waste produced by local industry (Santos and Jesus, 2014). This absence of more frequent monitoring measures and stricter protective measures has resulted in a substantial increase in contaminants in urban rivers, with the presence of metals being observed relatively frequently (Silva *et al.*, 2019; Singh *et al.*, 2022).

The São Raimundo Basin in Manaus is comprised of a network of hydrographic basins that covers the capital of the state of Amazonas. This network is formed by the basins of Educandos, Tarumã and Puraquequara, and others such as Mauá, Mauzinho, Colônia Antônio Aleixo, Refinaria and Ponta Pelada, the latter ones being considered microbasins. This set of basins, due to its location in the vicinity of the urban part of the city of Manaus, are under constant threats of pollution (Duvoisin *et al.*, 2024).

In view of its geographical characteristics and the various types of sources of contamination by metallic elements and other types of contaminants, it is necessary to continuously monitor the São Raimundo Basin in order to subsidize the planning and management of waste that reaches the basin. Similar to what has been happening in other parts of the world, the deterioration of water quality is caused by geological, agrochemical processes and the overexploitation of natural resources and industrial and mining activities (Alexakis, 2020). All of these processes have been occurring in the São Raimundo Basin and without any investigation into the risks to which the population is exposed due to the presence of these contaminants in the basin's waters. These activities need monitoring so as to improve the mitigating measures that are necessary to minimize the environmental problems arising from the contamination caused by them (Lizama-Allende *et al.*, 2022).

Thus, the objective of this study was to evaluate the influence of seasonality on the concentration of metallic elements in the waters of the São Raimundo Basin in Manaus. In addition, mapping of the regions of the basin that have the highest concentrations of metals was performed as a way of indicating the possible sources of contamination distributed throughout the basin. Such results can contribute to adequate planning for decontamination and to the application of mitigating measures that reduce ecological risks and risks to human health.

2. MATERIAL AND METHODS

2.1. Study area

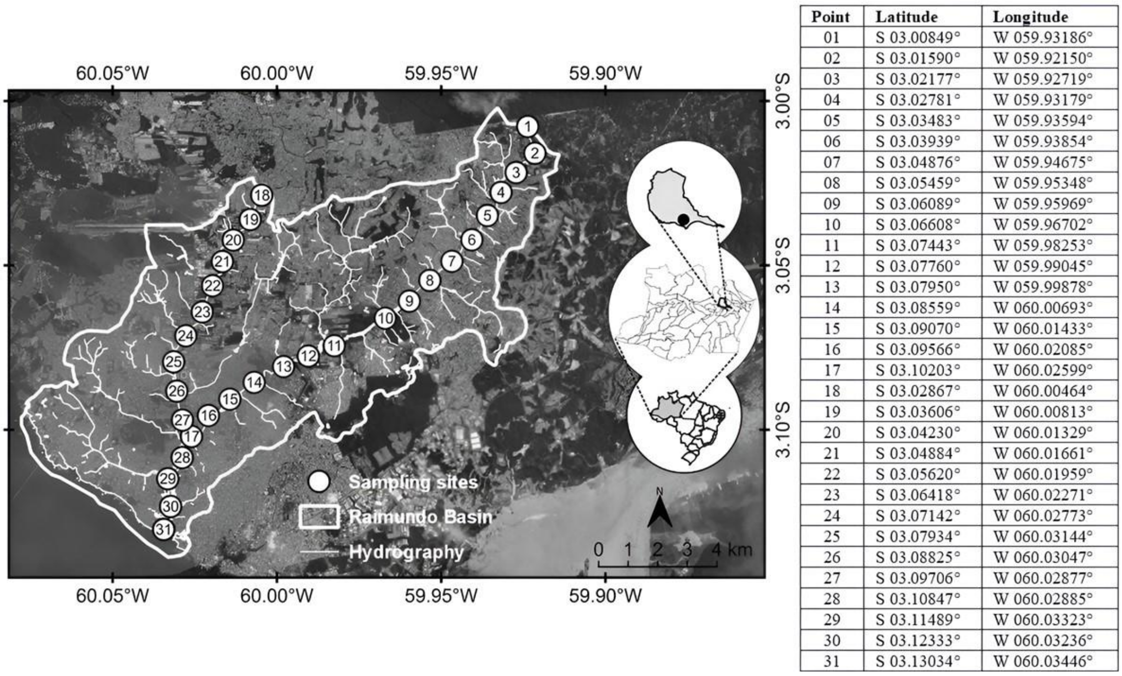
The São Raimundo Basin is located on the left bank of the Negro River and has an area of approximately 119.60 km^2. It covers 16 neighborhoods of Manaus, the capital of the state of Amazonas, from the north to the south of the city (Rocha, 2014). This region is characterized by a period of the year with a large volume of rainfall that fills the headwaters of its rivers. This characteristic, combined with mutual energy exchanges between the forest and the climate, are strong determinants for the fluvial regime of the great Amazon basin (Fernandes, 2016).

The basin is also be characterized by land that has an undulating relief, marked unevenness along its extension, with steep areas near the bank of the Negro River. The soil near the basin is nominally consolidated, constituting sedimentary packages of great amplitude (Marinho *et al.,* 2022). According to Rocha (2014), the São Raimundo Basin has an area of 11,961.80 hectares, which, in 2011, had a total of 603,212 inhabitants of which 111,541 resided in riparian areas of the basin. It is a basin that is totally contained in the urban area of the city of Manaus.

2.2. Sample collection

Water samples from the São Raimundo Basin were collected in June and October 2021, and January 2022, using 31 sample points, 1,000 m apart (Figure 1). The months for collecting the samples were selected as a way of guaranteeing replicas of the periods of low rainfall, also known as the dry season (October 2021), the transition period (July 2021) and the period of heavy rainfall (January 2022).

Likewise, the distance between the sampling points was established as a way of obtaining a significant number of sampling points that represent the current reality of the basin with respect to the concentration of metallic elements. These ensure the mapping that is closest to the reality of what is happening in the basin throughout this period.



Point	Latitude	Longitude
01	S 03.00849°	W 059.93186°
02	S 03.01590°	W 059.92150°
03	S 03.02177°	W 059.92719°
04	S 03.02781°	W 059.93179°
05	S 03.03483°	W 059.93594°
06	S 03.03939°	W 059.93854°
07	S 03.04876°	W 059.94675°
08	S 03.05459°	W 059.95348°
09	S 03.06089°	W 059.95969°
10	S 03.06608°	W 059.96702°
11	S 03.07443°	W 059.98253°
12	S 03.07760°	W 059.99045°
13	S 03.07950°	W 059.99878°
14	S 03.08559°	W 060.00693°
15	S 03.09070°	W 060.01433°
16	S 03.09566°	W 060.02085°
17	S 03.10203°	W 060.02599°
18	S 03.02867°	W 060.00464°
19	S 03.03606°	W 060.00813°
20	S 03.04230°	W 060.01329°
21	S 03.04884°	W 060.01661°
22	S 03.05620°	W 060.01959°
23	S 03.06418°	W 060.02271°
24	S 03.07142°	W 060.02773°
25	S 03.07934°	W 060.03144°
26	S 03.08825°	W 060.03047°
27	S 03.09706°	W 060.02877°
28	S 03.10847°	W 060.02885°
29	S 03.11489°	W 060.03323°
30	S 03.12333°	W 060.03236°
31	S 03.13034°	W 060.03446°

Figure 1. Location of the São Raimundo Basin in Manaus and the respective collection points with the latitudes and longitudes of the sampling points.

The sample collections were carried out following the recommendations of the National Guide for the Collection and Preservation of Samples: Waters, Sediments, Aquatic Communities and Liquid Effluents of the National Water Agency (ANA) and the Environmental Company of the State of São Paulo (CETESB, 2015).

The samples were collected in inert polymer bottles and, at the time of sample collection, the pH was checked and adjusted to less than 2, adding a 1:1 (v/v) $HNO3$ solution to preserve the samples. The bottles were packed in a Styrofoam® box with ice packs and then refrigerated at 4°C (ANA, 2009; CETESB, 2015). For the filtration step, 0.45 µm PTFE filters (Millipore®) were used. An aliquot of 50 mL of each sample was filtered in three replicates for further analysis to determine the soluble elements.

All samplings and laboratory analyses were performed by the Chemistry Applied to Technology (QAT) research group and followed the practices recommended by the Standard Methods for the Examination of Water and Wastewater of the APHA/AWWA (APHA *et al.*, 2017). The analyses were carried out at the Higher School of Technology of the Amazonas State University (UEA/EST).

2.3. Analysis of physicochemical parameters

All the analyses of physicochemical parameters were performed as described in Duvoisin *et al.* (2024) and obeyed the recommendations of the Standard Methods for the Examination of Water and Wastewater of the APHA/AWWA (APHA *et al.*, 2017). Table 1 presents the parameters analyzed, their respective units of measurement, the abbreviations used and their methods of analysis.

Table 1. Methodologies for determining the physicochemical parameters of the waters of the São Raimundo Basin.

Parmeter	Unit	Abbreviation	Methodology
Hydrogen Potential	-	pH	Probe - HI-9146 (Hanna Instruments)
Temperature	ºC	Temp	Probe - HI-9146 (Hanna Instruments)
Turbidity	UNT	Turb	Probe - HI-98703-02 (Hanna Instruments)
Dissolved Oxygen	$mg.L^{-1}$	DO	Probe - HI98198 (Hanna Instruments)
Biological Oxygen Demand	$mg.L^{-1}$	BOD	Incubation 20ºC, 05 days.
Total Phosphorus	$mg.L^{-1}$	Ptotal	Method 4500 B (APHA *et al.*, 2017)
Total Nitrogen	$mg.L^{-1}$	Ntotal	Method 4500 ABC (APHA *et al.*, 2017)
Total Solids	$mg.L^{-1}$	Solid_T	Gravimetric Method

2.4. Procedures for the analysis of metals

For the analysis of the metals, the samples were collected in inert polymer bottles and, at the time of sample collection, the pH was checked and adjusted to less than 2, adding a 1:1 (v/v) HNO_3 solution to preserve the samples. The bottles were packed in a Styrofoam® box with ice packs and then refrigerated at 4°C (ANA, 2009; CETESB, 2015). For the filtration step, 0.45 µm PTFE filters (Millipore®) were used. An aliquot of 50 mL of each sample was filtered in three replicates for further analysis to determine the soluble elements.

The determination of the metals in the samples was performed by inductively coupled plasma optical emission spectrometry (Shimadzu ICP-OES 9820), which has multi-element characteristics and high sensitivity and reliability for the determination of metals in the samples and is based on the detection of the amount of radiation emitted by the molecules or atomic species of interest (Boss and Freedeen, 2004). The equipment and the operating conditions of the ICP-OES used for metal analysis are described in Supplementary Material 1.

Qualitative readings were performed that allowed us to obtain the possible concentrations of metals and served as the basis for the quantification step. For the quantification of the metals, analytical curves were elaborated using the multi-element reference standards of LGC Standards (batches: 999925-22 and 1000997-14) and the analytical curves comprised points between 0 and 30,000 $\mu g.L^{-1}$.

After reading the samples in the analytical curves, the wavelength (λ) with the best signal intensity and lowest spectral interferences of each metallic element detected by the technique was chosen. Supplementary Material 2 presents the detected elements, the wavelengths, the points of the analytical curve, the correlation coefficient (R^2) and their respective limits of detection (LoD) and quantification (LoQ).

2.5. Statistical analysis

Descriptive statistics were used to compare the measures of central tendency and data dispersion for metal concentrations in the three periods evaluated. Differences in metal concentrations were evaluated using analysis of variance ANOVA with $p<0.05$, followed by Tukey's test. Boxplot charts were used for the visualization of averages, maximums, minimums and possible outliers. In addition, it was possible to evaluate the variations between the parameters in the three selected seasonal periods comparing them with that established by CONAMA resolution 357/2005, for Class 4 freshwater, which is consistent with the standards proposed for the São Raimundo basin (CONAMA, 2005).

A Pearson's correlation matrix was used to evaluate the relations between water quality parameters and metallic elements, as a way to understand how the physicochemical parameters relate to the metals identified in the basin samples. It is also possible to assess whether seasonality has a modifying role in these relationships between the parameters. In this work, as a significant correlation level, we assume the one that presents ≤ 0.5, and that these values can be negative or positive (Neves *et al.,* 2021).

The Bartlett sphericity test and the Kaiser-Meyer-Olkin (KMO) test were performed prior to the Principal Component Analysis - PCA to verify the possibility of applying this type of analysis to the data. In the KMO, a result close to 1 indicates that the data are suitable for PCA analysis. For the Bartlett test, a significance level of 0.05 would indicate that the analysis should be performed (Chen *et al.*, 2018; Finkler *et al.*, 2015).

A PCA was used to transform and reduce the complexity of the data so as to facilitate the understanding of the behavior of the metal elements identified in the work as a function of seasonality. The PCA involves the coding of the variables, the calculations of the covariance matrix, the correlation matrix, the eigenvalues, the classification of the corresponding eigenvalues and eigenvectors by the order of the numerical value and, finally, the development of the variable load matrix (Dimri *et al.*, 2021; Souza *et al.*, 2021).

For this study, we chose to adopt the criterion presented by Finkler *et al.* (2015), which classifies the values of the variable loads of the parameters corresponding to the absolute composition of the principal components (PC) into relevant (>0.75), average (>0.50 and <0.75) and irrelevant (<0.50). In addition, since these are water quality data, i.e., data with great variability, we defined ≤75% as the limit for the accumulated variance for the total data investigated as PCs. The results obtained with the principal component analysis were also used to construct the distribution maps of metals along the São Raimundo Basin. All the statistical analyses and graph construction were performed in the RStudio environment using the statistical software R (Version 4.3.1) with the packages ggplot, vegan, tidyverse, readr and patchwork (R Core Team, 2020).

3. RESULTS AND DISCUSSION

The Brazilian legislation related to the water quality parameters of freshwater rivers is established by the National Environment Council (Conselho Nacional do Meio Ambiente - CONAMA). In 2005, the agency in question published a resolution establishing, among other parameters, the parameters of some of the metals that were identified in the São Raimundo Basin (Figure 2).

Among the parameters established by CONAMA resolution 357/2005 for Class 4 rivers, the category in which the São Raimundo Basin is inserted, The metallic element aluminum (Al) was the only one to present an average concentration outside the limit established by the CONAMA resolution. This result was observed only in October 2021. All the other elements either were not outside the established range or did not have a concentration range established by the aforementioned environmental agency in its resolution.

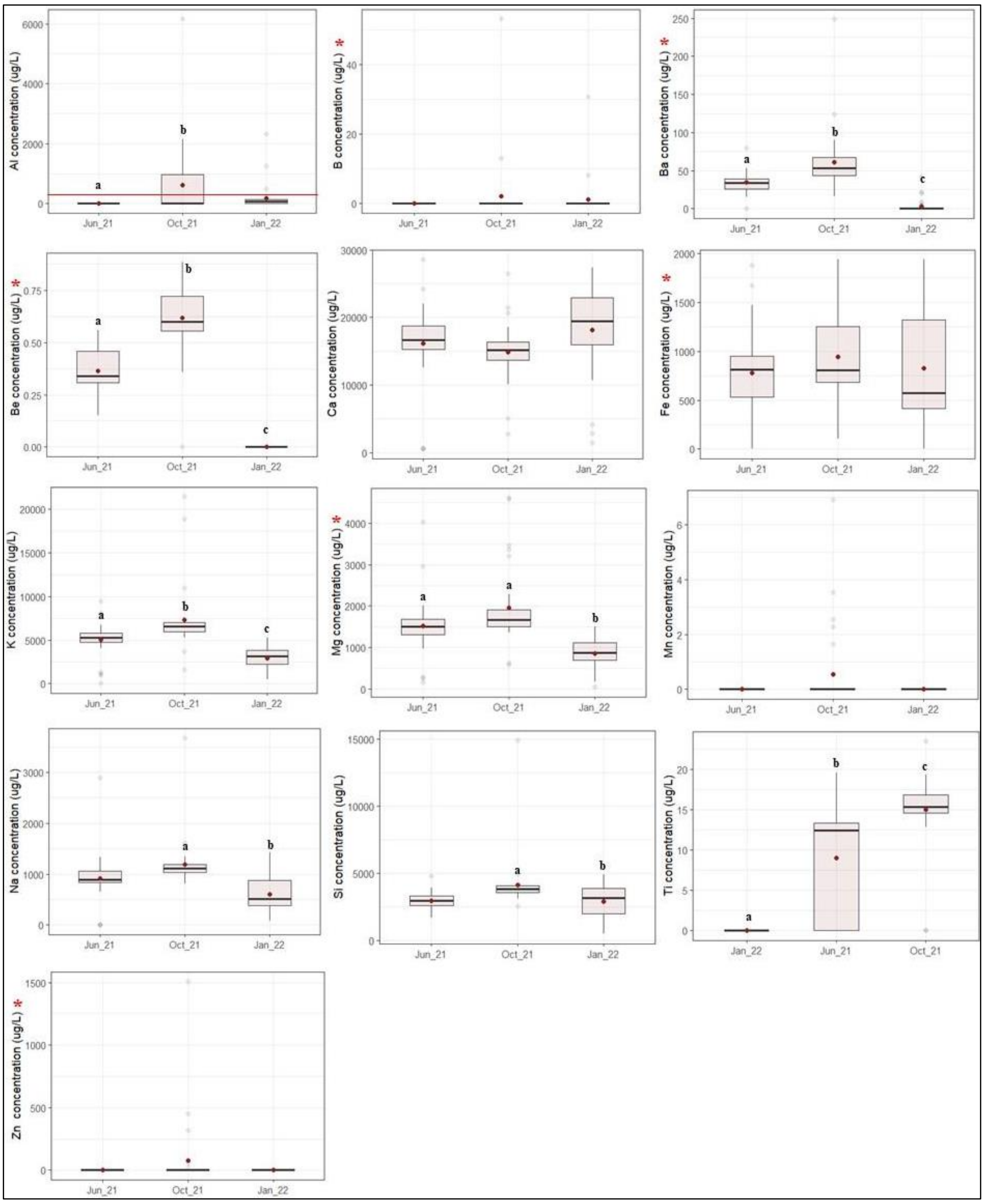


Figure 2. ANOVA results for metal concentrations in each analyzed month (boxplot). Al – aluminum, B – boron, Ba – barium, Be – beryllium, Ca – calcium, Fe – iron, K – potassium, Mg – magnesium, Mn – manganese, Na – sodium, Si – silicon, Ti – titanium, Zn – zinc. Boxplot with the same letters indicate no significant difference in the ANOVA test. * - Indicates that the concentration of the element is below that established by CONAMA, Resolution 345/2005 for freshwater classified as Class 4. The red dashed line indicates the concentration established by CONAMA.

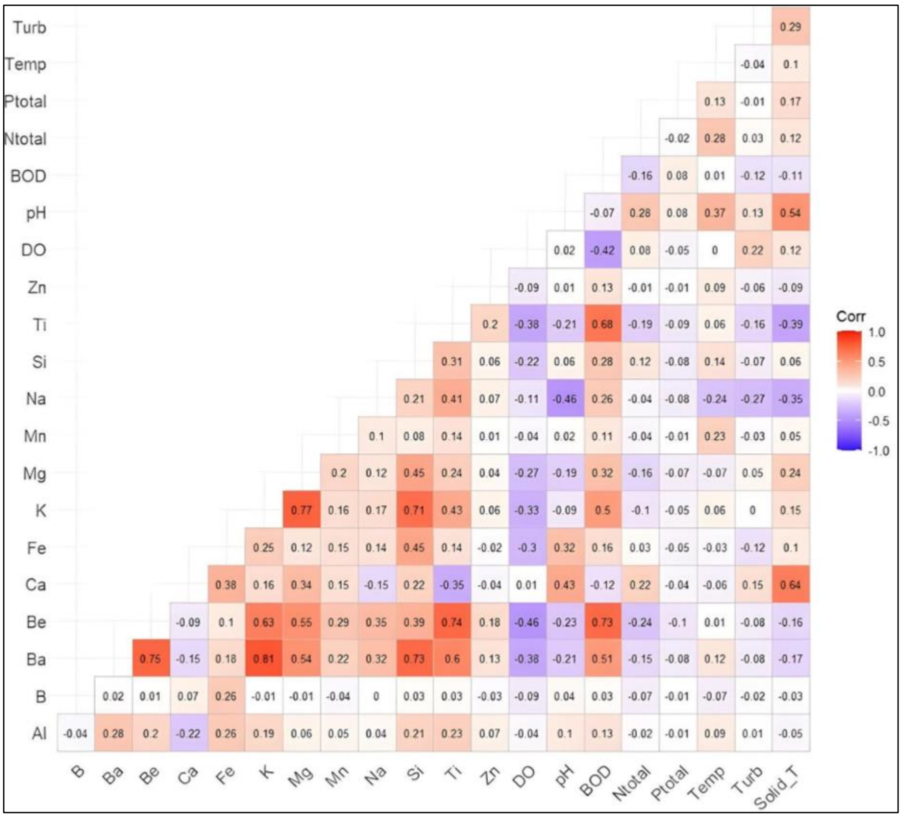
It was possible to observe the influence of seasonality on metal concentrations, resulting in modifications across the evaluated sampling periods. Thus, the elements Al, Ba, Be, K, Mg, Na, Si, and Ti showed statistically significant inferences ($p \leq 0.05$) in their concentrations, as determined by the ANOVA test.

The results of the ANOVA showed the significant role of seasonality in the concentrations of most of the metals evaluated. For some of the metallic elements, the changes are significant in the three periods investigated, as in the cases of barium (Ba), beryllium (Be), potassium (K) and titanium (Ti). This information indicates that these elements are the most sensitive to the environmental changes promoted by seasonal periods and are thus probably the most suitable for mapping the metallic elements in the São Raimundo Basin.

Among the outstanding metallic elements, aluminum (Al) was the only one that was higher than recommended by the CONAMA resolution. The element Al, although found naturally as one of the most abundant elements in the Earth's crust, can be a cause of toxicity and morbidity in aquatic animals (Borrell *et al.*, 2023). A factor that needs to be taken into account in relation to the toxicity of Al is the pH of the water, which is a physicochemical parameter that increases Al toxicity when it is between values of 6.0 and 6.5 (Rahman *et al.*, 2018; Saalidong *et al.*, 2022). The waters of the São Raimundo Basin have pH values that are between 6.0 and 7.0, which gives them high potential for increased toxicity with respect to the element Al.

The element Ba, in addition to its presence in nature as barium sulfate and barium carbonate, is also an element used in various industrial products such as paints, tiles, glass and rubber (Kresse *et al.*, 2007). Thus, it is expected to find this element in industrial waste such as that which occurs in the city of Manaus, which has several industrial areas scattered throughout the basin. However, it is essential to understand how this element is related to the aquatic environment and what is the result of its relationship with the other physicochemical parameters of the water.

The environmental modifications promoted by seasonality have a direct influence on the physicochemical parameters of the water, and these are parameters that can be decisive for a higher or lower concentration of metals in the basin's waters. Pearson's correlation analysis allows us to understand, though partially, how the metallic elements identified in the São Raimundo Basin are related to these parameters (Figure 3). In addition, it can also contribute to a greater understanding of how different metals correlate with each other.



	B	Ba	Be	Ca	Fe	K	Mg	Mn	Na	Si	Ti	Zn	DO	pH	BOD	Ntotal	Ptotal	Temp	Turb	Solid_T
Turb																				0.29
Temp																			-0.04	0.1
Ptotal																		0.13	-0.01	0.17
Ntotal																	-0.02	0.28	0.03	0.12
BOD																-0.16	0.08	0.01	-0.12	-0.11
pH															-0.07	0.28	0.08	0.37	0.13	0.54
DO														0.02	-0.42	0.08	-0.05	0	0.22	0.12
Zn													-0.09	0.01	0.13	-0.01	-0.01	0.09	-0.06	-0.09
Ti												0.2	-0.38	-0.21	0.68	-0.19	-0.09	0.06	-0.16	-0.39
Si											0.31	0.06	-0.22	0.06	0.28	0.12	-0.08	0.14	-0.07	0.06
Na										0.21	0.41	0.07	-0.11	-0.46	0.26	-0.04	-0.08	-0.24	-0.27	-0.35
Mn									0.1	0.08	0.14	0.01	-0.04	0.02	0.11	-0.04	-0.01	0.23	-0.03	0.05
Mg								0.2	0.12	0.45	0.24	0.04	-0.27	-0.19	0.32	-0.16	-0.07	-0.07	0.05	0.24
K							0.77	0.16	0.17	0.71	0.43	0.06	-0.33	-0.09	0.5	-0.1	-0.05	0.06	0	0.15
Fe						0.25	0.12	0.15	0.14	0.45	0.14	-0.02	-0.3	0.32	0.16	0.03	-0.05	-0.03	-0.12	0.1
Ca					0.38	0.16	0.34	0.15	-0.15	0.22	-0.35	-0.04	0.01	0.43	-0.12	0.22	-0.04	-0.06	0.15	0.64
Be				-0.09	0.1	0.63	0.55	0.29	0.35	0.39	0.74	0.18	-0.46	-0.23	0.73	-0.24	-0.1	0.01	-0.08	-0.16
Ba			0.75	-0.15	0.18	0.81	0.54	0.22	0.32	0.73	0.6	0.13	-0.38	-0.21	0.51	-0.15	-0.08	0.12	-0.08	-0.17
B		0.02	0.01	0.07	0.26	-0.01	-0.01	-0.04	0	0.03	0.03	-0.03	-0.09	0.04	0.03	-0.07	-0.01	-0.07	-0.02	-0.03
Al	-0.04	0.28	0.2	-0.22	0.26	0.19	0.06	0.05	0.04	0.21	0.23	0.07	-0.04	0.1	0.13	-0.02	-0.01	0.09	0.01	-0.05

Figure 3. Pearson's correlation matrix between physicochemical parameters and metal concentrations in the São Raimundo Basin in Manaus. Cophenetic correlation coefficient with a value of 0.796, which was obtained in the Pearson's correlation.

Pearson’s correlation analysis revealed that biochemical oxygen demand (BOD) is one of the physicochemical parameters that is most related to the presence of metals in the basin’s waters, considering the correlation analysis values with the metals Be (0.73), Ti (0.68), Ba (0.51) and K (0.50). In addition to this parameter, the analysis also revealed the relatively high correlation between total solids (Solid_T) and the element calcium (Ca), with a value of 0.64.

As expected, the metals had a higher level of correlation between them when compared with those obtained between the metals and the physicochemical parameters. It is also possible to point out the high correlations of the elements K and Ba and Be. A strong correlation between Si and K and Ba was also observed, as well as a correlation between the elements Ti and Ba and Be. Despite this, it was not possible to observe a significant correlation between K and Ti (0.43).

In the case of Ba, through Pearson’s correlation analysis, it was possible to observe its relationship with biochemical oxygen demand (BOD). The direct relationship between Ba and BOD must be related to the cation exchanges that the metallic element exerts in the aquatic environment, which are enhanced by the complexation with organic matter and thus reduce the availability of oxygen in the environment (Lu *et al.*, 2018). Such factors together increase oxygen demand and establish the direct relationship between these factors.

As with Ba, Be is also naturally part of the Earth’s crust, and is identified in several minerals such as beryl, bromelite and chrysoberyl, among others (Lyalina *et al.*, 2018). It is utilized in electronic, computer, telecommunication and mechanical industries due to its chemical properties (Bolan *et al.*, 2023).

Some characteristics of Be may explain its high correlation with BOD observed in Pearson’s correlation analysis. First, Be can be complex, intermixing with organic compounds, such as humic and fulvic substances, and accumulates in these environments and provides a reduction in oxygen availability, thus increasing BOD. In addition, the high pH of the water observed in the São Raimundo Basin increases the solubility and mobility of beryllium with the formation of complexes with hydroxide ions, as observed in the works of Boschi and Willenbring (2016).

Furthermore, in the results of Pearson’s correlation analysis, BOD showed a high and direct correlation with the element Ti. The element in question is a component of a wide list of products in the plastics, paper, paint, medicines, cosmetics and other industries, which places it at the top of the list of metallic elements that deserve monitoring with regard to their effects on the environment and human health (Wang *et al.*, 2016).

Titanium, in the form of TiO_2, a nanoparticle often used in industry, is generally discarded in the aquatic environment via various routes, such as the washing of surfaces where it was applied, discarded as sewage, in urine and feces (Bevacqua *et al.*, 2023). Its correlation with BOD is explained by the adsorption of TiO_2 molecules by natural compounds such as humic and fulvic acids, resulting in the stabilization of the aqueous solution and also increasing the migration mobility of titanium in the aqueous medium (Erhayem and Sohn, 2014). These characteristics of titanium also seem to have influenced the results of Pearson's correlation analysis, which showed this element to have a significant correlation with the elements Ba and Be, which seems to have something to do with the characteristics of oxy-reduction in these elements in relation to the TiO_2.

The correlation analysis showed some metals to be quite correlated, as expected. The correlation between Ba, Be and Mg must be the result of their similar chemical characteristics, such as having only two electrons in their valence shell and thus presenting a +2 oxidation state. Such characteristics make it possible for these elements to react quite similarly in the environment. The significant correlation between Ba and Be seems to involve the role of the element Si in soil formation in the region. Thus, when Si is leached from the soil to the basin through rainwater, it establishes a direct relationship with these other metallic elements.

Bartlett's sphericity test showed a p-value <0.005, thus rejecting the null hypothesis, and showed that the variables are correlated and that the PCA can be applied to this data set (Neves *et al.*, 2021). Similarly, the KMO test presented a value of 0.68, therefore over 0.50, and may be considered satisfactory, indicating the possibility of using the PCA (Manly and Navarro Alberto, 2016).

The number of metals and physicochemical parameters evaluated makes the investigation a challenge, mainly due to the large amount of data obtained and the possible relationships between them. Thus, PCA is the analysis of choice since it reduces data with a minimal loss of information. For the data from the São Raimundo Basin, we even considered the principal component 6 (PC6), reaching a percentage of explanation of over 60%, which is quite significant for aquatic environments (Table 2).

Table 2. Principal Component Analysis (PCA) of metal concentrations in the São Raimundo Basin in Manaus.

Variables	Principal Components of the São Raimundo Basin					
	PC1	PC2	PC3	PC4	PC5	PC6
Al	0.41	0.06	0.56	0.00	-0.25	**-0.89**
B	0.06	0.09	-0.05	**-0.78**	0.43	-0.27
Ba	**1.29**	0.08	0.04	0.19	-0.23	-0.15
Be	**1.27**	-0.08	-0.04	0.24	0.20	0.07
Ca	-0.13	**1.14**	-0.47	-0.30	0.00	0.37
Fe	0.44	0.64	0.23	**-0.97**	0.00	-0.18
K	**1.16**	0.51	-0.27	0.24	-0.13	-0.10
Mg	**0.91**	0.52	-0.68	0.29	-0.01	0.10
Mn	0.36	0.27	0.14	0.20	-0.09	0.61
Na	0.65	-0.56	-0.20	-0.44	-0.40	0.37
Si	**0.93**	0.59	0.05	-0.19	-0.53	-0.13
Ti	**1.11**	-0.42	0.34	0.03	0.14	-0.05
Zn	0.26	-0.09	0.37	0.15	0.04	0.15
DO	**-0.76**	-0.05	-0.18	0.34	-0.58	0.20
pH	-0.37	**1.00**	0.64	-0.10	0.23	-0.13
BOD	**1.04**	-0.08	0.18	0.10	0.51	0.06
Ntotal	-0.31	0.43	0.50	-0.09	-0.66	0.38
Ptotal	-0.13	0.10	0.29	0.27	0.75	0.17
Temp	0.02	0.40	**1.00**	0.50	-0.13	0.27
Turb	-0.27	0.39	-0.36	0.59	0.00	-0.64
Solid_T	-0.30	**1.14**	-0.26	0.27	0.26	0.00
Eigenvalue	5.13	2.91	1.67	1.48	1.26	1.15
% of variance	0.24	0.13	0.07	0.07	0.06	0.05
Cumulative %	0.24	0.38	0.46	0.53	0.59	0.64

The results obtained for PCA revealed that principal component 1 (PC1) included the elements Ba, Be, K, Mg, Si and Ti and the parameters dissolved oxygen (DO) and biochemical oxygen demand (BOD) as the most relevant factors for the formation of the component that was responsible for 24% of the total variation of the data. The second component (PC2) includes the metallic element Ca and the parameters pH and total solids (Solid_T) as the most relevant factors for the formation of this component, with eigenvalues ≤1.0. PC2 was responsible for 13% of the total variance and, when added to the PC, reached a percentage of 38% of explanation of the total variation of the data.

The PCA generated a PC1 with eigenvalues with strong positive loadings (≥1.00), as is the case of Ba, Be, K, Ti and BOD, others with eigenvalues with moderate positive loadings (≥0.75), as in Mg, Si and DO (Finkler *et al.*, 2015). The strong positive loadings corroborate part of the information obtained via Pearson's correlation analysis and related to the BOD parameter, and its response as a function of the metals Ba, Be and Ti.

The set of elements that make up PC1, which brings together elements that occur naturally, such as Ba and Be, to others that are usually components of human actions, such as Ti and K, and all this added to the levels of eigenvalues found, indicate that the sources of contamination by these metallic elements are both natural and of anthropogenic origin (Hammoumi *et al.*, 2024).

The PC2 formed in the analysis generated eigenvalues with strong positive loadings (>1.00) for Ca, pH, and total solids (Solid_T), indicating that the PC2 was formed mainly due to environmental parameters. The relationship between Ca and total solids was also observed in the correlation analysis and should be linked to the fact that the increase in Ca concentration in surface waters generates an increase in the total solids parameter (Rafiqul Islam, 2016). The pH in turn is a factor that plays a role in the solubility and mobility of Ca generated by increasing the pH to around 6.0 to 6.5. This fact explains the relationship between these parameters, which defined the composition of the PC2 in the analysis.

With regard to Figure 4, we can highlight the results of the eigenvalues of the metals Ti, Be and Ba, which are directly related to BOD, a fact that was observed in the results of Pearson's correlation analysis. This information confirms the interrelation between these factors; in addition, it places these elements as the main metallic contaminants of the São Raimundo Basin.

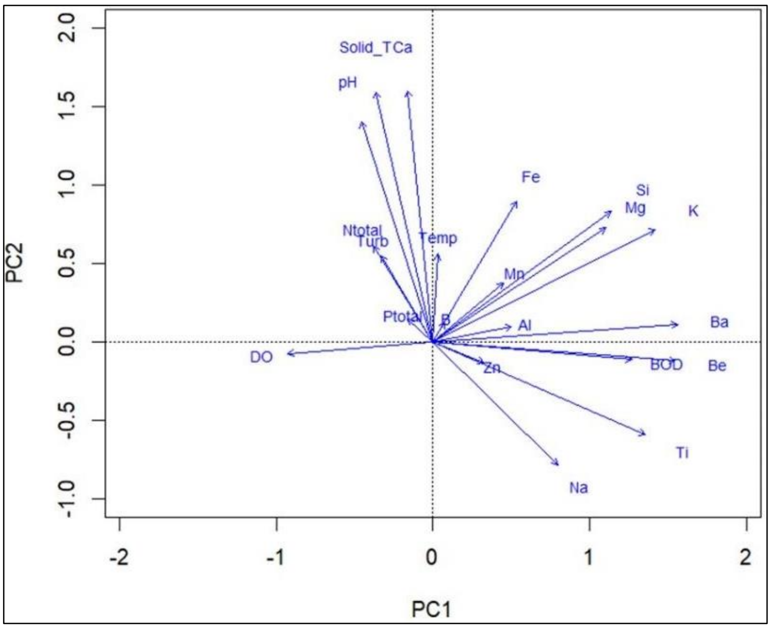


Figure 4. Graphic analysis of the principal components of metal concentrations identified in the São Raimundo Basin in Manaus. Eigenvalues of the variables PC1 and PC2.

The graph further illustrates the direct relationship between the element Ca and the parameters pH and total solids. Another observation is the close relationship between the data of Si, K and Mg, which, despite being part of Component 1, when evaluated graphically they stand out by forming a subgroup with relative distance from the other groups.

Graphic analysis of Components 1 and 2 with their eigenvalues shows the formation of groups between variables, and the proximity of the lines between these variables indicates the strength of their mutual correlations. The first case involves the upper left quadrant, which is formed by the eigenvalues of Ca, pH, Solid_T, Turb, N_total, P_total. This quadrant confirms that the analysis basically gathered the physicochemical parameters related to water quality, in addition to the element Ca. Despite this being a result that is considered normal, the almost absence of other metallic elements besides Ca was not expected, considering that factors such as pH and N_total are parameters that exert a strong influence on the mobility and solubility of some metallic elements (Frémion *et al.*, 2017).

The right upper quadrant basically gathered metallic elements; K, Mg, Si, Ba, Al, Fe, Mn, B, in addition to temperature, which shows their relationship proximity levels. Due to the characteristics of the metallic elements that clustered in this quadrant, we can corroborate the information previously described that the São Raimundo Basin has been suffering a process of contamination by metallic elements that have multiple origins, i.e., coming from households, but also from industry, and possibly agricultural fertilizers, in addition to natural sources. This information can be reinforced by evaluating the lower right quadrant of the figure, which brings together Be, Ti, Zn, Na, in addition to the BOD parameter.

Regarding the mapping of the metals Ba, Be and Ti, these were considered the main metallic contaminants identified in the São Raimundo Basin. The maps formed showed that the month of January 2022 was the month in which the concentrations of the three metals were at their lowest levels, a fact already observed in the data from the ANOVA. However, in this other approach, it is possible to observe that the low concentrations of these elements were found at all the sampling points, which confirms that the most relevant factor for this result is the seasonality of this period, which influences the basin as a whole, and considerably increases the volume of water in January due to increased rainfall, diluting all the identified metallic elements.

The information obtained in the work allowed the construction of Figures 5, 6 and 7, which illustrate the mapping of the metals barium, beryllium and titanium in the São Raimundo Basin in the months of June, October 2021 and January 2022. In the maps, it is possible to observe not only the differences in the concentration of the metals in each month, but also what the concentrations of the metal were like at each sampling point, which is important information for the identification of possible points with critical levels and of possible regions of the city where the sources of contamination are located.

The map constructed from the data on Ba concentrations indicated that January was the month with the lowest concentrations of the metal, with most of the sampling points presenting concentrations close to zero (0). Quite differently, the months of June and October presented most of the points with levels above 50 mg/L, with few points close to 100 mg/L, as observed in the month of October 2021 in sampling points 3, 9, and 31.

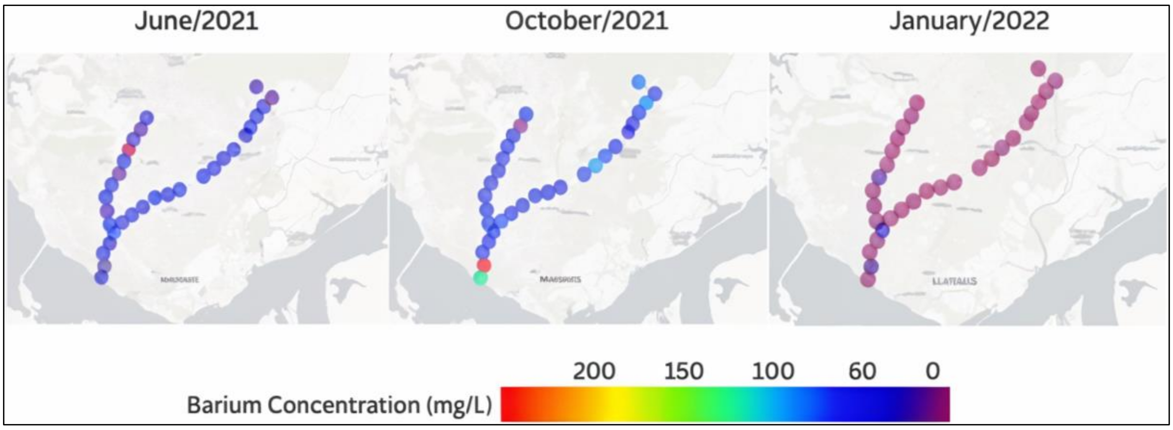


Figure 5. Mapping of the concentrations of Ba in the surface waters of the São Raimundo Basin in Manaus.

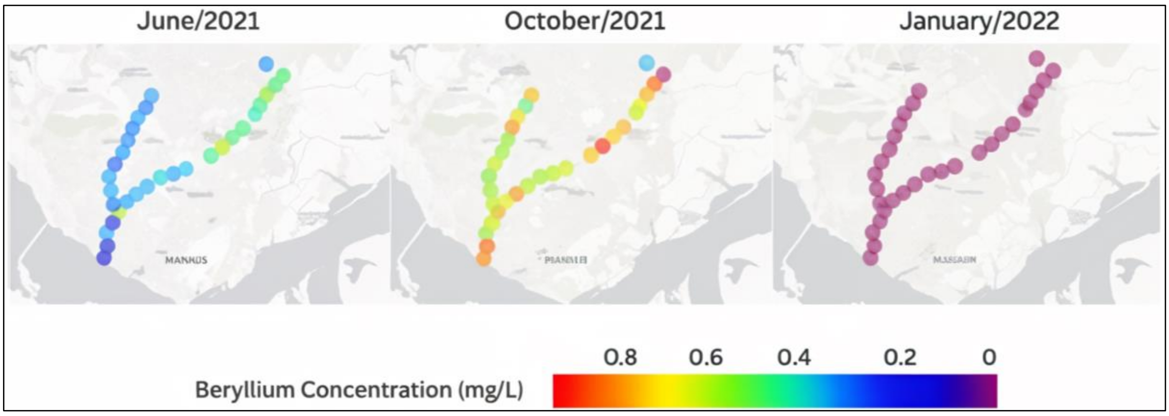


Figure 6. Mapping of the concentrations of Be in the surface waters of the São Raimundo Basin in Manaus.

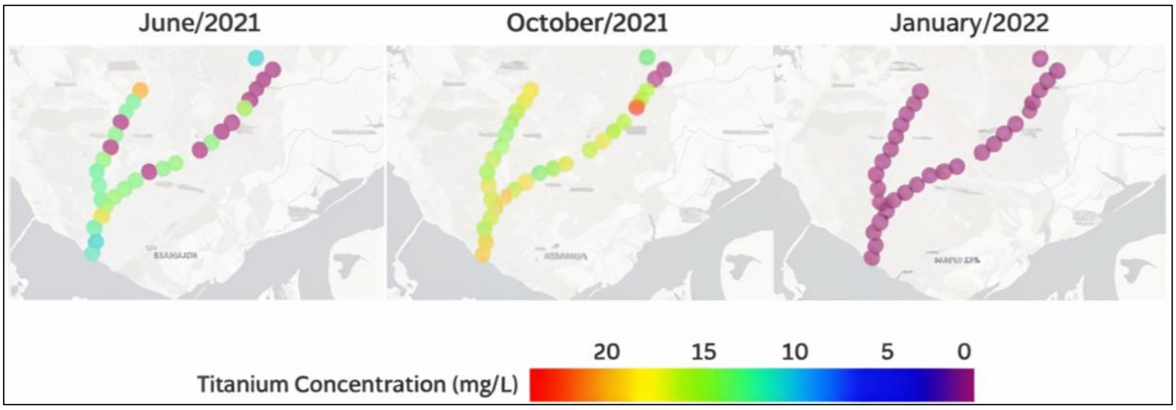


Figure 7. Mapping of concentrations of Ti in the surface waters of the São Raimundo Basin in Manaus.

Similarly, the mapping of the concentrations of Be indicated the month of January 2022 as having concentrations close to zero. In addition, higher concentrations of the metal were observed in the month of October 2021, whereby it was possible to identify values of 0.8 mg/L at points 3, 9, 30, and 31. In the month of June 2021, the values of the metallic element were mostly close to 0.4 mg/L, with the exception of point 9, which presented a value of about 0.6 mg/L.

The results for the element Ti in January 2022 were shown to follow the pattern, with all sampling points presenting values close to zero. In October 2021, the highest values were shown at points 6, 30 and 31, which had concentrations of about 20 mg/L. In June 2021, the titanium concentration at several points was close to zero, with the rest revealing values of about 10 mg/L.

The mapping also allows us to infer about the presence of sources of contamination along the basin, depending on the variation in the concentration of metals at each sampling point. For the elements Ba and Be, it is possible to observe their highest concentrations in the months of October 2021 at sampling points 3, 9, 30 and 31. This information may indicate the existence of sources of contamination in this part of the city, close to the basin. This proximity allows the metallic contaminants produced by these sources to be leached by rainwater, thus reaching the basin bed, increasing the concentration of these metals at these collection points.

The São Raimundo Basin crosses the urban part of the city of Manaus and, therefore, is subject to the most diverse types of contaminants, including metallic ones. Sampling points 3 and 9 are part of a region of the city where many households are located, as well as part of the industrial area of the city.

Sampling points 30 and 31 are located at the mouth of the São Raimundo Basin, in the port of the city of Manaus, on the Negro River. As in points 3 and 9, the results of the concentration of Ba and Be may indicate the presence of discharges contaminated with these elements in this region of the basin. However, as it is the part where the basin issues its waters, it is possible that the results are related to the transport of these metals along the basin and that they accumulate at its mouth.

The idea mentioned above is strengthened when we evaluate the results of the mapping for the element titanium (Ti) that presented, in addition to at sampling point 6, one of the highest concentrations, also points 30 and 31 were among those that presented the highest concentrations of titanium in the evaluated period. In any case, it is necessary to continue monitoring work in the basin as a way of producing data that enable the development of management and decontamination projects for this type of pollutant.

4. CONCLUSION

The São Raimundo Basin, in the city of Manaus, was evaluated for its concentrations of metals. Located in the urban part of the city, its waters are under constant environmental threat for this type of contamination. However, there is little information on the presence and concentration of metallic elements in these waters, nor information on the role of seasonality in the behavior of this type of pollutant.

The study revealed that the element aluminum (Al) was the only one that presented an average concentration above that recommended in the CONAMA resolution, and all the others are below or do not have an established minimum concentration. The ANOVA indicated the month of January 2022 as having the lowest concentrations of the metals. The data reveal that most metals are strongly influenced by seasonality, with the increase in the volume of rainwater being the main factor for reducing the concentrations of the metals.

Pearson's correlation revealed that, among the physicochemical parameters, only biochemical oxygen demand (BOD) established a significant correlation with barium, beryllium, titanium and potassium. This was probably influenced by the interactions of these metals in their ionized form with organic compounds present in the waters of the basin, which has resulted in the reduction of oxygen available in the environment. Also influenced by changes in environmental water quality parameters caused by urban pollution in the basin.

The PCA revealed that the São Raimundo Basin suffers from the contamination of its waters by metallic elements from both natural and anthropogenic sources. The results of the PCA also corroborate the idea that physicochemical parameters do not have a relevant role in the concentration of metals. In addition, the analysis revealed that barium, beryllium and titanium are the main polluting metallic elements in the basin.

The mapping of the elements barium, beryllium and titanium corroborated the information that, in the period of rising river levels, the metallic elements are diluted and have the lowest concentrations, as happened in January 2022. This approach also revealed sampling points 3, 6, 9, 30 and 31 to be the points of highest concentrations of these metals. This information can contribute both to the identification of possible sources of contamination and to the development of environmental management plans that contribute to the reduction of these metals in the waters of the basin.

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Supplementary Material 1. ICP-OES operating conditions for metal analysis.

Radio frequency power	1.20 kW
Plasma Gas	10.00 L/min
Auxiliary Gas	0.60 L/min
Carrier Gas	0.70 L/min
Exposure time	30 seconds
View direction	Axial

Supplementary Material 2. Elements, the wavelengths, the points of the analytical curve, the correlation coefficient (R^2), and their respective limits of detection (LoD) and quantification (LoQ) to ICP-OES for metal analysis in São Raimundo basin.

Element	λ (nm)	Curva (μg L^{-1})	R^2	LD (μg L^{-1})	LQ (μg L^{-1})
Al	396,153	0-1000-4000-5500-7000	0,99995	3,211262	10,70421
B	249,773	0-250-400-550-700-850	0,99951	0,8325570	2,775190
Ba	455,403	0-40-60-80-100-250	0,99989	0,0448887	0,1496289
Be	313,042	0-20-40-60-100	0,99998	0,0099957	0,0333189
Ca	317,933	0-4000-7000-10000-20000-30000	0,99927	1,071238	3,570792
Fe	238,204	0-1000-2500-4000-5500-7000	0,99973	1,132814	3,776048
K	769,896	0-2500-5500-7000-10000	0,99849	3,626050	12,08683
Mg	285,213	0-2500-4000-5500-7000-10000	0,99955	0,2518320	0,8394398
Mn	257,610	0-20-40-60-100	0,99995	0,0203195	0,0677329
Na	330,232	0-2500-4000-5500-7000-8500	0,99986	3,008867	10,02956
P	213,618	0-1000-2500-4000-5500	0,99985	6,529416	21,76472
Si	288,158	0-4000-1000-20000-30000	0,99942	5,516702	18,38901
Ti	334,941	0-100-250-400-550	0,99995	0,2451275	0,8170916
Zn	202,548	0-100-250-400-550-700	0,99973	0,1465372	0,4884575