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Concentrations of metals in water, sediments and aquatic macrophytes in a river located in a region with a hot semi-arid climate

Concentrações de metais na água, sedimentos e macrófitas aquáticas em um rio localizado em uma região de clima semiárido quente

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Abstract: Aim: i) is there a difference in the level of contamination in the different parts of the basin in the water, sediment and aquatic macrophytes compartments? and ii) do the three compartments respond similarly to metal contamination? **Methods:** Samples of water, sediment and aquatic macrophytes (*Salvinia auriculata* Aubl., *Pistia stratiotes* L., *Ludwigia helminthorrhiza* (Mart.) H. Hara and *Eichhornia crassipes* (Mart.) Solms) were collected at 10 sampling sites in different stretches of a tropical hydrographic basin. We determined the metal concentrations of Fe, Pb, Ni, Zn, Mn, Cr, Cu and Cd, and to the results we applied Principal Component Analysis (PCA), separately for each compartment, to order the sampling sites. **Results:** Fe and Mn had higher concentrations than other metals in plants and sediment. With the exception of Mn, the order of metals was similar between water and sediment. However, the PCAs ordered the sampling sites differently. Our results demonstrated that the ordering of sampling sites by metal concentrations differs among water, sediment and macrophytes. **Conclusions:** We conclude that to evaluate the contamination of aquatic environments by metals and the effects of contamination on the food chain, it is not enough to evaluate them only in water or sediment, but also in an aquatic community.

Keywords: metallic contaminants; water pollution; fluvial ecosystem; aquatic macrophytes.

Resumo: Objetivo: i) existe diferença no grau de contaminação nas diferentes partes da bacia nos compartimentos água, sedimento e macrófitas aquáticas? e ii) os três compartimentos respondem de forma semelhante à contaminação por metais? **Metódos:** Amostras de água, sedimento e macrófitas aquáticas (*Salvinia auriculata* Aubl., *Pistia stratiotes* L., *Ludwigia helminthorrhiza* (Mart.) H. Hara e

Eichhornia crassipes (Mart.) Solms) foram coletadas em 10 locais de amostragem em diferentes trechos de uma bacia hidrográfica tropical. Foram determinadas as concentrações de Fe, Pb, Ni, Zn, Mn, Cr, Cu e Cd e aos resultados nós aplicamos uma Análise de Componentes Principais (ACP), separadamente para cada compartimento, para ordenar os locais de coleta. **Resultados:** Fe e Mn mostraram maiores concentrações do que os outros metais nas plantas e no sedimento. Com exceção do Mn, a ordem dos metais foi similar na água e no sedimento. No entanto, a ACP ordenou os locais de coleta de forma diferente. Nossos resultados demonstraram que a ordenação dos locais de amostragem por concentração de metais difere entre água, sedimento e macrófitas. **Conclusão:** Nós concluímos que avaliar a contaminação de ambientes aquáticos por metais e os efeitos da contaminação na cadeia alimentar, não basta avalia-los apenas na água e sedimento, mas também em alguma comunidade aquática.

Palavras-chave: contaminantes metálicos; poluição da água; ecossistema fluvial; macrófitas aquáticas.

1. Introduction

Metals are natural elements of the earth's crust, however, due to anthropic activities, the concentration of these elements in the most diverse ecosystems has been increasing. Thus, the pollution of aquatic environments by metals has attracted worldwide attention, as they persist in nature, as they are not destroyed (Chopra et al., 2009), originate from different sources (Guo et al., 2012; Yu et al., 2014) and accumulate in aquatic organisms, which can be magnified in the food web (Aydin-Önen & Öztürk, 2017; Loureiro & Hepp, 2020). Metals have high toxicity, being harmful to most aquatic organisms and can cause harm to human health (Chowdhury et al., 2016; Ali et al., 2016; Antoniadis et al., 2017).

Many studies analyze the concentration of metals in aquatic environments, however, most studies determine the concentration of metals only in water and sediment (Torregroza-Espinosa et al., 2018; Hossain et al., 2020; Zhao et al., 2020). Furhtermore, it is essential to understand whether different compartments of the aquatic ecosystem behave the same way in relation to contamination by metals. Thus, it is necessary to analyze the concentrations of metals in water, sediment and in aquatic organisms, since the metals have the capacity to be transferred constantly from one compartment to another. Therefore, analysis of water, sediment and aquatic communities, such as aquatic macrophytes, should be performed to assess general metal pollution and the impact of these contaminants on aquatic ecosystems (Li et al., 2019).

The metals released into rivers and lakes can become deposited in the sediments and, later, be released again to the water column (Huang et al., 2012) to later be absorbed and accumulated in the tissues of the organisms in the trophic web (Said et al., 2009; Fazio et al., 2014; Krishnamurti et al., 2015; Shakouri & Gheytasi, 2018). Thus, monitoring of metal pollutants only in the water column is insufficient to assess the contamination of aquatic environments by metals, since sediments can cause secondary pollution to the aquatic environment (Xu et al., 2017). Therefore, sediment is an important compartment (Wan et al., 2016; Yang et al., 2016) to be studied, as well as the aquatic organisms that are at the base of the trophic web and absorb metallic contaminants.

Aquatic macrophytes underlie the trophic web, playing an important role in nutrient cycling through active and passive transport of elements (Azaizeh et al., 2006; Yoon et al., 2006). These plants absorb nutrients and other ions from water and/or sediment, and can be used in the treatment of effluents, due to their ability to accumulate contaminants and store them in biomass (Henry-Silva & Camargo, 2006; Mishra & Tripathi, 2008; Hassan et al., 2010; Jutsz & Gnida, 2015; Ugya, 2015; Kumar et al., 2017; Mishra & Maiti, 2017). In addition, aquatic macrophytes can be used to assess metal contamination in aquatic ecosystems (Griboff et al., 2017; Sijakova-Ivanova et al., 2017; Hesami et al., 2018; Zhang et al., 2018).

The Apodi-Mossoró river basin located in a semi-arid region has great socioeconomic importance, however, the water bodies have many environmental impacts (Medeiros et al, 2023). The water resources of the river basin are used in the most diverse human activities, among them, the watering of animals and for human consumption after treatment. Araújo & Pinto Filho (2010) identified several polluting sources of heavy metals in the soils of the Apodi-Mossoró river basin. Paula Filho et al. (2021) evaluated metal concentrations in the sediment of the Parnaíba river estuary (Brazilian semi-arid region) and Campagna-Fernandes et al. (2022) developed ecotoxicological studies on water and sediment samples from the Apodi-Mossoró river. Furhtermore, studies on metal concentrations in water, sediments and aquatic organisms have not been carried out in the region. In this context, we evaluated the concentrations of metals (copper, iron, manganese, zinc, nickel, chromium, lead and cadmium) in water, sediment and aquatic macrophytes *S. auriculata*, *P. stratiotes*, *L. helminthorrhiza* and *E. crassipes* in different sites in a hydrographic basin in the semi-arid region of Brazil. Our objectives were to answer the following questions: i) is there a difference in the level of contamination in the different parts of the basin in the water, sediment and aquatic macrophytes compartments? and ii) do the three compartments respond similarly to metal contamination?

2. Methods

2.1. Study area

This study was conducted in aquatic environments of the River Apodi-Mossoró hydrographic basin located in semiarid Brazil (Figure 1). Average precipitation in the hydrographic basin is 700 mm per year (SEMARH, 2017) and the average annual air temperature is 28 ° C, with an average maximum of 36°C and an average minimum of 20°C, while the relative humidity of the air (annual average) is 68%. The climate of the region, according to the Köppen climate classification (Kottek et al., 2006), is type BSwh, that is, very hot and semi-arid climate with the rainy season covering the months of February, March, April and May. The basin occupies an area of 14,276 km^2, and constitutes the main source of surface water for the region (IGARN, 2018). The hydrographic basin has an altitude that varies from 1m to 830 m, and the total length of channels ranging from the first to the seventh order is equivalent to 11,085.87 km (Lira de Carvalho & Henry-Silva, 2022). According to Siqueira et al. (2022), the Apodi-Mossoró River has stretches with eutrophic and hypereutrophic waters, in addition to a large amount of fecal coliforms, especially in the stretches where it crosses urban areas. In other stretches it was classified, by these authors, as mesotrophic, in addition the trophic state indices are higher in periods of drought. For more information about the basin see Henry-Silva & Camargo (2022).

The municipalities located in the hydrographic basin with the highest population densities according to the IBGE estimate for the year 2020 are Mossoró with an estimated 300,618 inhabitants, Pau dos Ferros with 30,600 and Apodi with 35,874 inhabitants (IBGE, 2010). The activities developed in the hydrographic basin, such as oil extraction, sea salt production, irrigated fruit production, extensive livestock, limestone mining, agriculture and livestock are sources of pollutants for water. The basin has an area of crystalline geological formation, consisting of igneous and metamorphic rocks and another area of sedimentary formation, formed by sandy-clay and limestone rocks. The first area is approximately 6,500 km^2 and the second, 4,500 km^2 (Justo et al., 2016).

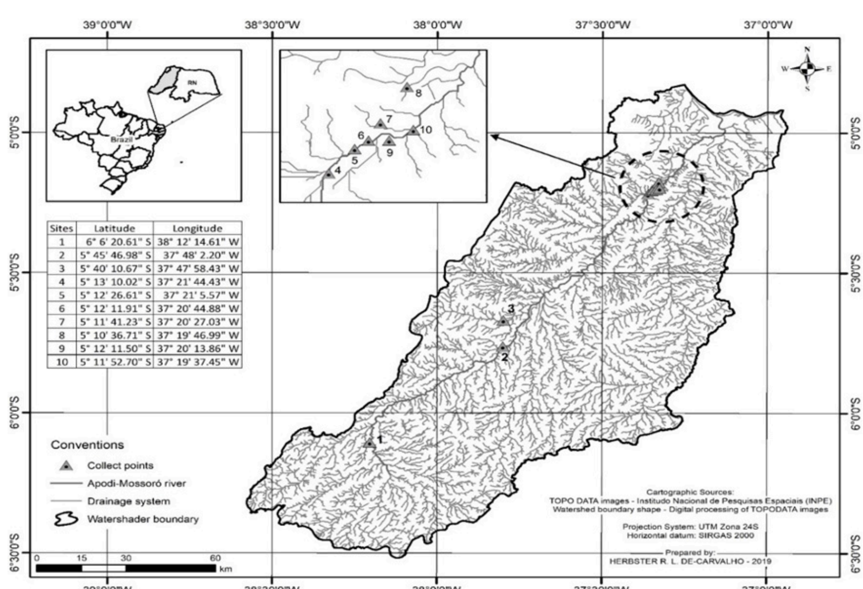

Figure 1. Location of the study area. The numbers indicate the sampling sites in the Apodi-Mossoró river basin, state of Rio Grande do Norte, Northeastern Brazil. Caption: Water flows from site 1 to 10. Sites 3, 7 and 8 are tributaries and the rest are mains streams.

2.2. Sampling procedure

We sampled 10 sites in the River Apodi-Mossoró hydrographic basin (Figure 1) in stretches that cross urban center in October 2017, in the dry season. This study was carried out in the dry season because at this time there is less dilution and, consequently, higher concentrations of substances and chemical elements in the water. Generally higher concentrations of metals in water are detected in water bodies during the dry season (Kamari et al., 2017). In these places we collected water, sediment and *S. auriculata*, *P. stratiotes*, *L. helminthorrhiza* and *E.crassipes*. A sample was collected at each of the sites.

The sampling sites were selected according to the occurrence of the studied aquatic macrophytes and also aiming to contemplate stretches of the river that cross the cities with the highest population density, with seven of the sampling sites (4 to 10) being located in the city with the largest number of habitats and greater occurrence of aquatic macrophytes in the river. In the hydrographic basin of the River Apodi-Mossoró, several species of aquatic macrophytes occur, with the lowest richness observed in the estuarine region and the highest in the upper part of the hydrographic basin. The most frequent free-floating species in the basin are *E. crassipes*, *P. stratiotes*, and *S. auriculata*, which occur predominantly in stretches surrounded by urban centers and the most frequent rooted floating-leaf species is *L. helminthorrhiza* (Henry-Silva et al., 2010).

Direct measurements and water samples were performed at approximately 50 cm deep near the margin at each sampling sites. Total dissolved solids (TDS) and pH were obtained with Horiba U10 equipment. Water samples of 150 ml were collected in pre-sterilized bottles washed with nitric acid (HNO_3), to which 2 ml of HNO_3 (concentrate) was added for preservation. Samples of surface sediment (approximately 1 kg) were collected and stored in plastic bags for transport to the laboratory. The species of aquatic macrophytes were collected at the sampling sites where they occurred (Table 1) in sufficient quantity for subsequent determination of metals. We tried to sample species with similar characteristics, that is, green leaves and a healthy appearance.

2.3. Laboratory procedure

The sediment samples were dried in an oven at 60°C until constant mass, and were subsequently incinerated in a muffle furnace, according to the method described by Goldin (1987), to determine organic matter (OM). The samples of aquatic macrophytes (leaf, rhizomes and root) were washed first with running water and then with distilled water, then dried in an oven at 60°C, ground in a Willey mill and stored in labeled plastic pots. Next, 2.0 g of macrophyte samples and 0.400 g of crushed sediment samples were placed in a crucible and baked in a muffle furnace for two hours at a temperature of 560°C to remove organic matter. Subsequently, 10 ml of hydrochloric acid (concentrate) and 3 ml of nitric acid (concentrate) were added and the macrophyte samples were heated to 300°C in a block heater. After cooling, the samples were transferred to 100 ml volumetric flasks and the volume completed with deionized water. The acids used to analyze metals in water, sediment and macrophytes were used in the same proportion to compose the blanks used in the analyses. All determinations were carried out in accordance with quality control. For quality assurance we use standard reagents analysis of certified reference (Table 2). The precision of analysis for heavy metals was validated through Standard Reference Material sample – SRM 928 NIST (US National Institute of Standards and Technology) (NIST, 2016). Standard curves were constructed using standard solutions with known con-centrations to calculate sample concentrations. All metal analyzes were performed in duplicate.

Metal analysis of the water used the 3015a method (C.A.S. Element, 2007) while of the sediment was performed by the 3050b method (A. M. Arsenic, 1996). Determination of metals in macrophytes followed an adaptation of the 3050b method (A. M. Arsenic, 1996). The metals

Table 1. Occurrence of the four studied species of aquatic macrophytes among sampling sites of River Apodi-Mossoró, state of Rio Grande do Norte, Northeast Brazil.

Species	Biological form	Sampling sites
L. helminthorrhiza	Rooted with floating leaves	2, 3, 5, 9
S. auriculata	Free floating	2, 3, 9
P. stratiotes	Free floating	3, 5, 9, 10
E. crassipes	Free floating	1, 4, 5, 6, 7, 8, 9, 10

analyzed in the three compartments were copper (Cu), iron (Fe), manganese (Mn), zinc (Zn), nickel (Ni), chromium (Cr), lead (Pb) and cadmium (Cd). All analyses were performed using a Varian model AA240FS atomic absorption spectrophotometer.

2.4. Statistical analysis

For the values of concentration of metals in water, sediment and aquatic macrophytes, we applied Principal Component Analysis (PCA) separately for each compartment. The purpose of applying the PCAs was to verify whether the three compartments respond equally to metal concentrations, that is, the ordering of sites would be similar or different for the three compartments. Before applying the PCA, the values were standardized to minimize the influence arising from the difference in metal concentration in the sampled locations (Singh et al., 2005; Zhou et al., 2007). Correlation tests ($p<0,05$) were applied between the concentrations of metals in water and in of macrophyte *E. crassipes*. We applied correlations only to *E. crassipes*, as the other species occurred in few sites. Statistical analysis was performed in the free software R Core Team (2018) using the Vegan package.

Table 2. Values of certified reference standard reagents.

Heavy metal	Certified values (mg kg^{-1})
Cu	0.978 ± 0.004
Fe	0.977 ± 0.053
Mn	0.979 ± 0.005
Zn	0.979 ± 0.004
Cr	9.545 ± 0.044
Cd	9.597 ± 0.039
Ni	0.977 ± 0.005
Pb	9.619 ± 0.039

3. Results

3.1. Physical and chemical variables

Physical and chemical analyses of water found the pH to range from 6.9 at sampling site 1 to 8.6 at site 2 and was alkaline at all the other sampling sites. Total dissolved solids (TDS) ranged from 0.23 g.L at site 2 to 1.70 g.L at site 8. Percentage OM of sediment ranged from 0.4% at site 3 to 26% at site 1 (Table 3).

3.2. Metals in water and sediment

The analysis of metals from sediment samples revealed that the metal with the highest concentration was Fe, with a value of 16,244.91 mg.kg^{-1} at sampling site 10, whereas Cd had the lowest value, with a minimum of 1.73 mg.kg^{-1} at site 6. The highest concentrations of metals in water samples occurred at site 5, with 0.049 mg.L^{-1} of Cu; 1.143 mg.L^{-1} of Zn; 0.066 mg.L^{-1} of Cr; 0.486 mg.L^{-1} of Ni; 0.025 mg.L^{-1} of Cd and 0.485 mg.L^{-1} of Pb. Site 4 had the highest concentration of Fe (1.386 mg.L^{-1}) and site 6 had the highest concentration of Mn (0.242 mg.L^{-1}) (Figure 2).

3.3. Metals in aquatic macrophytes

Metals with the highest concentrations in macrophyte plant tissues were Fe and Mn, while the lowest concentrations were for Cd and Cr. The highest concentration of Cu was 31.35 mg.kg^{-1} for *S. auriculata* at site 3, while the highest concentration of Mn was 17,827.31 mg.kg^{-1} for *L. helminthorrhiza* at site 2. The highest concentrations of Fe, Zn and Cr were 10,909.53 mg.kg^{-1}, 219.82 mg.kg^{-1} and 10.17 mg.kg^{-1}, respectively, for *P. stratiotes* at site 3. The highest concentrations of Pb and Cd were both for *P. stratiotes*, with 73.13 mg.kg^{-1} at site 9 and 1.45 mg.kg^{-1} at site 10, respectively. The species

Table 3. Values for hydrogen potential (pH) and total dissolved solids (TDS) in water and organic matter (OM) in sediment of sampling sites of a river located in a semiarid climate region.

Sampling Site	pH	TDS (g.L)	OM (%)
1	6.9	0.91	26
2	8.6	0.23	1
3	8.4	0.60	0.4
4	8.4	1.41	5
5	7.7	1.68	13
6	7.9	1.64	1
7	7.7	1.24	6
8	7.8	1.70	2
9	8.5	1.38	7
10	8.4	1.66	16

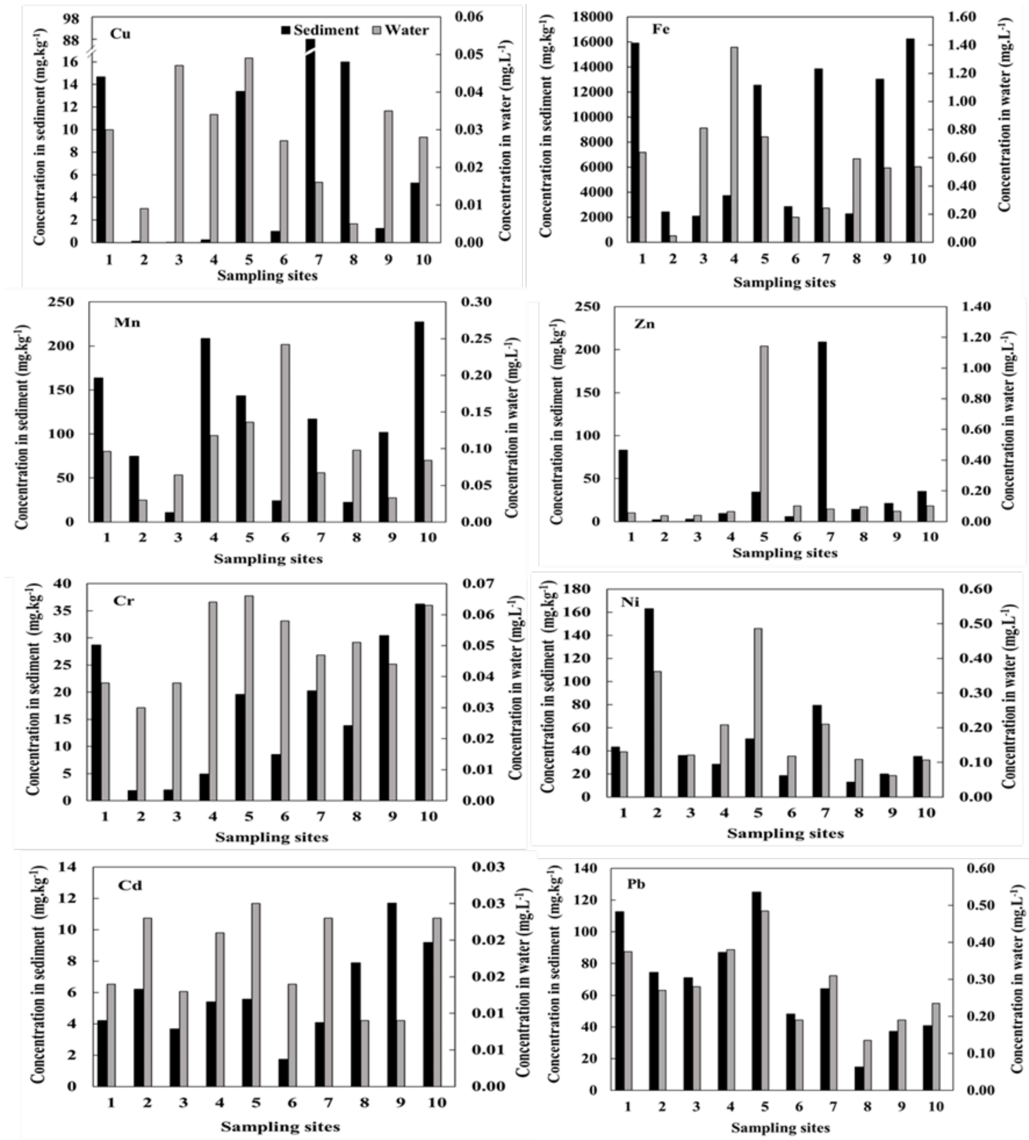

Figure 2. Metal concentration of surface sediment (mg.kg^{-1}) and water (mg.L^{-1}) in sampling sites of the Apodi-Mossoró river basin.

E. crassipes had the highest concentration of Ni with 18.80 mg.kg^{-1} at site 8 (Table 4).

The first two axes of the Principal Component Analysis explained 65.64% of the data for metal in water samples, 66.16% for sediments and 58.36% for the metal data in the macrophytes (Figure 3 and Table 5). In the water PCA, all metals are negatively correlated with axis 1. Thus, sites 5 and 4 are the ones with the highest concentrations of metals, especially Zn, Ni and Pb, which are the ones with the highest correlation with axis 1. In the sediment PCA most metals are positively correlated with axis 1 and the metals with the highest correlation are Fe, Zn and Cr. In the PCA of macrophytes, some metals are positively correlated and others are negatively correlated. The ones with the highest positive correlation are Cu and Ni and with the highest correlation which is negative Pb. In addition, in the PCA applied to aquatic macrophytes *P. stratiotes* has more Pb in site 9, while in site 3, *P. stratiotes* and *S. auriculata* have higher concentrations of Cr and Fe.

Significant correlations were found between the concentrations of Mn, Fe and Cr in the sediment and the percentage of organic matter in the sediments (Figure 4).

No significant correlation was found between the concentrations of metals in the water and in the macrophyte *E. crassipes* present in eight sampling sites. In the other species of aquatic macrophytes, *L. helminthorrhiza*, *S. auriculata* and *P. stratiotes*, correlation tests were not carried out due to the small number of samples.

Table 4. Metal concentrations (mg.kg^{-1}) in aquatic macrophytes collected from sampling sites of a river located in a semiarid climate region.

Species	Site	Cu	Mn	Fe	Zn	Cr	Ni	Cd	Pb
L. helminthorrhiza	2	4.47	17,827.31	3,188.30	15.47	1.39	5.82	0.55	12.73
	3	22.28	1,357.17	2,593.96	31.91	3.74	9.75	0.42	10.73
	5	27.30	840.83	1,081.76	36.93	1.80	8.31	0.85	18.97
	9	1.67	445.53	502.86	32.29	0.90	2.07	1.27	19.91
S. auriculata	2	6.94	2,715.18	945.57	14.96	0.99	3.60	0.75	11.74
	3	31.35	3,158.55	9,155.04	35.35	6.64	8.74	0.72	11.74
	9	5.29	484.47	2,144.20	34.04	4.62	4.19	1.17	16.47
P. stratiotes	3	15.15	3,813.17	10,909.53	55.12	10.17	14.60	1.12	18.94
	5	4.09	1,390.33	912.46	27.80	2.22	7.53	1.27	19.95
	9	1.58	692.24	1,282.48	219.82	1.91	1.36	1.08	73.13
	10	4.24	2,269.26	2,272.07	25.51	4.12	3.44	1.45	18.47
E. crassipes	1	6.79	260.37	834.98	20.13	1.60	9.55	0.39	8.60
	4	7.27	2,564.08	1,204.89	17.54	1.50	6.44	0.69	15.92
	5	18.23	987.32	1,772.13	34.05	4.68	12.27	1.16	24.32
	6	4.95	700.02	324.13	8.79	1.22	11.76	1.43	14.28
	7	22.43	508.82	310.32	9.91	1.51	12.93	0.90	15.01
	8	5.41	627.79	1,348.95	15.91	2.81	18.80	1.06	17.15
	9	20.65	1,015.28	2,077.21	33.52	4.20	5.28	1.10	21.31
	10	1.02	326.66	340.05	12.47	0.96	11.24	0.39	10.79

Cu = copper; Mn = manganese; Fe = iron; Zn = zinc; Cr = chromium; Ni = nickel; Cd = cadmium; Pb = lead.

Table 5. Factorial coordinates of the parameters, based on correlations from the Principal Component Analysis.

Parameters	PCA Water		PCA Sediment		PCA Macrophytes	
	Axis 1	Axis 2	Axis 1	Axis 2	Axis 1	Axis 2
Cu	-0.60	-0.44	0.63	0.61	0.62	-0.29
Mn	-0.29	-0.52	0.69	-0.18	0.19	0.07
Fe	-0.42	-0.59	0.95	-0.15	0.62	-0.68
Zn	-0.85	0.07	0.74	0.53	-0.62	0.68
Cr	-0.59	-0.52	0.82	-0.48	0.57	-0.75
Ni	-0.75	0.57	-0.02	0.54	0.61	0.06
Cd	-0.66	0.53	0.26	-0.79	-0.30	-0.37
Pb	-0.86	0.16	0.22	0.49	-0.73	-0.61

4. Discussion

Our results showed that the concentrations of metals in water, sediments and aquatic macrophytes do not have the same pattern. The PCAs order the sampling sites very differently, and the correlations of metals with the axes are also quite different. These differences were probably due to the characteristics of each compartment, such as the granulometric texture of sediment, which influences metal distribution (Sun et al., 2018). The concentration of metals in the different compartments of the sampling sites depends on opposing processes, such as resuspension and sedimentation and the physiology of macrophytes in absorbing or excreting metals (Xia et al., 2018). Moreover, urbanization also influences metal concentrations, as can be observed in locations 2 and 3, which are less urbanized areas and have the lowest concentrations of metals in water and sediments.

The different concentrations of metals in the sediment can be explained by the characteristics of this compartment. For example, sediments with higher organic matter content tend to accumulate more metals (Martins et al., 2021). The reduced amounts of organic matter preclude the formation of stable complexes between metals and humic substances present in organic matter (Clemente et al., 2006). Sites 2 and 3, for example, had a small percentage of organic matter, with 1% and 0.4%, respectively, so probably, metals did not accumulate in the sediment, as observed by the lower concentrations for Cu, Mn, Fe and Cr in the sediment of these sites. It was possible to observe a

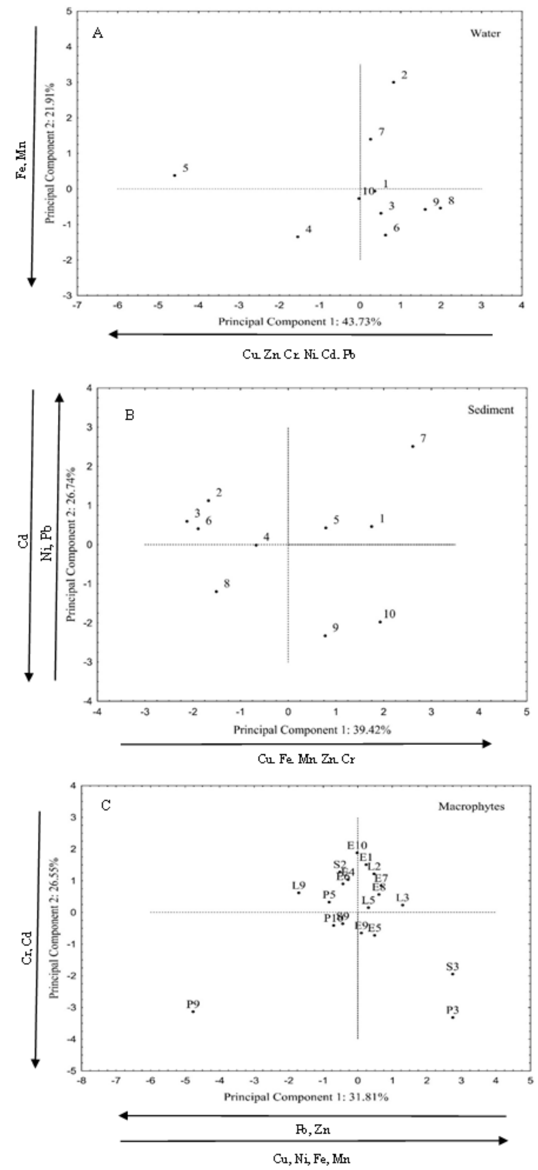

Figure 3. Principal Component Analysis of metals contained in (A) water, (B) sediment and (C) aquatic macrophytes and their respective correlation values between variables and principal components 1 and 2. Numbers correspond to sampling sites along of a river located in a semiarid climate region. L = *L. helminthorrhiza*; S = *S. auriculata*; P = *P. stratiotes*; E = *E. crassipes.*

significant correlation between the organic matter present in the sediments and the metals Mn, Fe and Cr.

Metal concentrations in water also differed among sampling sites. Low concentrations in water may be the result of absorption by free floating aquatic macrophytes or sediment retention. At site 10, for example, Mn and Fe concentrations were high in the sediment that containing high percentages of organic matter and in the biomass of *P. stratiotes*. In fact, organic matter influences the distribution and dispersion of metals through chelation and cation exchange mechanisms (El-Badry & El-Kammar, 2018), while metals present in the water column are largely absorbed by macrophytes (Ergönül et al., 2019).

In this study, the metals that showed the highest concentrations in water and sediments were Fe and Mn. However, de Paula Filho et al. (2021) observed in sediments from the estuary of the Parnaíba River (semiarid northeast of Brazil) the following ranking: Al > Fe > Mn > Zn > Cr > Ni > Cu > Pb > Cd, which with the exception of Al followed the same pattern that we observed. We highlight that this study has a geochemical bias and metals were not evaluated in any aquatic community. Hossain et al. (2020) in a study on metals in the Kutubdia Channel near Matarbari, Cox's Bazar, Bangladesh, identified that the contaminants with the highest concentrations in water and sediments were Fe and Mn and associated this result with the origin of these contaminants. The presence of these pollutants in aquatic ecosystems is associated with processes of natural origin and also human intervention in the biogeochemistry of the metal cycle (Saleem et al., 2015). The anthropic sources of these metals are domestic and industrial effluents, agricultural fertilizers, vehicle exhaust particles emission, tire wear particles, worn pavement surface particles (Duong & Lee 2011; Mohiuddin et al., 2011; Adamiec et al., 2016; Belkhiri et al., 2017) among other sources. In fact, the source of metals at sampling site 2 was possibly from agricultural fertilizers, as it has close agricultural areas. The anthropic sources of metals in the other sampling sites were possibly originated from domestic effluents that are discharged along the river, and from particles from vehicle exhaust, from tire wear and from worn pavement surfaces, considering that these sampling sites are located in urban areas. In fact, Campagna-Fernandes et al. (2022) carried out ecotoxicological studies of water and sediment samples from urban areas of the Apodi-Mossoró basin and observed moderate toxic effects on some organisms.

Metal concentrations in biomass were very different among the different aquatic macrophyte species, in which metals also accumulate differently. Concentrations of Fe, Mn and Zn in the four macrophyte species were higher than the other metals studied. This result is probably related to the fact that these elements are essential micronutrients for

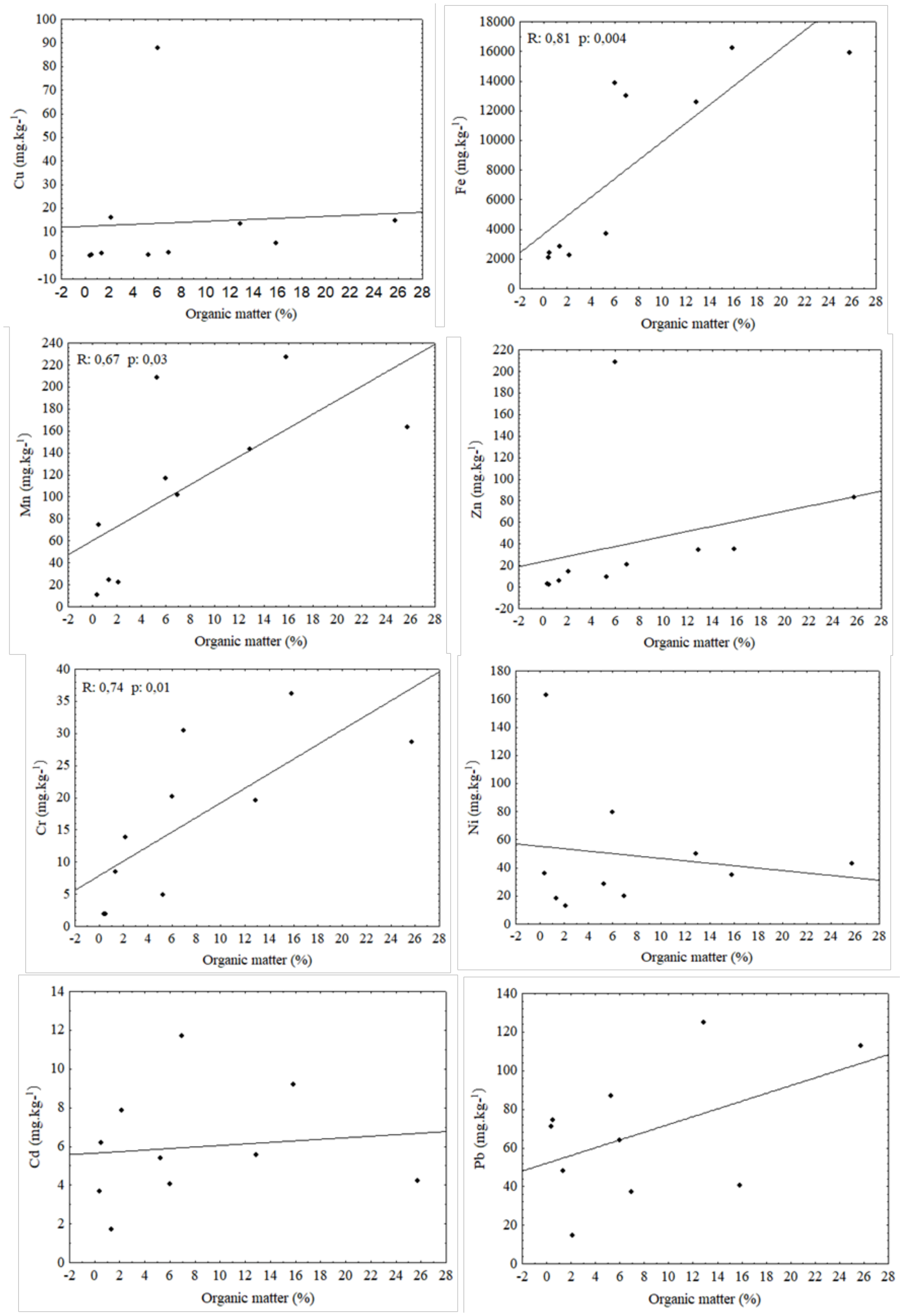

Figure 4. Correlation graph between metal concentrations and percentage of organic matter in the sediment.

plants. The four macrophyte species accumulated, in most places, lower concentrations of Cr and Cd, because in addition to these metals being in low concentrations in water and sediment, this result was probably also due to the high toxicity of these metals even in small amounts as demonstrated by other authors (Zayed & Terry, 2003; Bonanno & Giudice, 2010; Alfadul & Al-Fredan, 2013; Gómez-

Bernal et al., 2017). Although Ni is an essential micronutrient for plants, only small concentrations of this element were observed in the studied species, probably because high concentrations of Zn and Fe inhibit Ni uptake because they are competing metals (IPNI, 2016), while lower Cu concentrations in plants may be due to small amounts of this metal in water.

The accumulation of metals in the plant biomass of aquatic macrophytes can also be influenced by pH. Vanhoudt et al. (2018) identified a higher absorption capacity for cobalt metal by four macrophyte species at pH of 5 to 7 and lower absorption starting at pH 9, while the high pH (> 8.0) does not seem to stimulate the bioaccumulation of the metals (Lin et al., 2020). However, although the pH of the sampled sites varied between 6.9 and 8.6, the macrophytes were able to bioaccumulate the metals, demonstrating that other factors have a greater influence on their absorption and accumulation of metals, such as temperature (Balle et al., 2021).

The presence of total dissolved solids (TDS) is another factor that can affect the absorption of metals by aquatic plants since they can be composed of dissolved substances such as chlorides, sulfates and bicarbonates (Miranda & Krishnakumar, 2015) that can bind to metals and prevent them from being absorbed by macrophytes. The species *L.helminthorrhiza* and *S. auriculata* in site 2, presented higher concentrations of metals than those same species located in site 9. In site 2 the dissolved solids values are 6 times smaller than the values in site 9. Which can explain our results. On the other hand, other factors such as the concentration of metals in the abiotic compartments and also the toxicity of each metal presented by macrophytes also interfere in the accumulation of these contaminants in plant biomass. Thus, the influence of pH and total dissolved solids cannot be considered single in a natural aquatic environment.

Similar to Cd and Cr, Pb is a toxic metal, however, it accumulated in higher concentrations in the biomass of the four aquatic macrophyte species analyzed when compared to the accumulation of Cd and Cr metals by the same species. Li et al. (2019) in a study about the concentrations of metals in the biomass of *Potamogeton crispus* Linn. and *Salvinia natans* L. in a river in China, identified that *P. crispus* accumulated higher levels of Cr, Ni, Cu and Zn, while *S. natans* showed high efficiency to accumulate Pb and Zn. Napaldet & Buot Junior (2020) and Malik et al. (2010) indicated that *Eleusine indica* is a good phytoaccumulator of Pb, however, this same species is inefficient for removing other metals, such as Cu, Cd, Cr and Co (Garba et al., 2012). Thus, it is evident that the concentration of Pb in the biomass of aquatic macrophytes is also related to the concentrations of this metal in water and sediments that were higher than those presented by Cd and Cr, and the influence of environmental conditions, also depends on the ability that each species of macrophyte presents to accumulate this metal.

No relationship was observed between the concentration of metals in water and in *E. crassipes*. This result shows that the concentration of metals in plant biomass does not only depend on the concentration in water, since the absorption of metals by plants is influenced by the bioavailability of metals and the absorption capacity of each plant species (Gupta & Sinha, 2007; Núñez et al., 2011; Borisova et al., 2014, 2016). In addition, plant defense mechanisms reduce metal absorption (Bonanno, 2011; Vymazal, 2011). Another point to note is that the metal absorption capacity of *E. crassipes* is more efficient in places with reduced metal concentrations (Das et al., 2016). This result indicates that, despite absorbing the metals contained in aquatic ecosystems, caution is necessary when stating that *E. crassipes* is a good indicator of contamination, since it is necessary to consider the response of the species to each metal, due to their toxicity, and the physical and chemical conditions of the aquatic environment that can interfere with metal absorption.

5. Conclusions

We conclude that the assessment of metal concentrations in water or sediment is not sufficient to indicate contamination in aquatic biota. Higher concentrations in these compartments do not necessarily indicate higher concentrations in any aquatic community, such as macrophytes. Thus, for the monitoring of metal contamination of an aquatic environment, it is necessary that research address metal concentrations in water, sediment and some aquatic organism.

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Data availability

All research data analyzed in the research is available in the Dataverse of Acta Limnologica Brasiliensia in SciELO Data. Access is free. It can be accessed in https://data.scielo.org/dataset.xhtml?persistentId=doi:10.48331/scielodata.AJDWFE

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