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Bioavailability of metals in sediments and fish in agricultural and urban areas of the Pirapó river: potential toxicity and environmental monitoring

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ABSTRACT

The level of anthropogenic interference in aquatic environments, based on the unbridled use of resources and actions incompatible with the balance in the various types of ecosystems, has triggered important research. Studies have shown that fish and sediments can be used as a tool for biomonitoring, as they demonstrate the ability to accumulate metals. Thus, to investigate the level of ecological disturbance due to contamination by metals, mainly heavy metals in the Pirapó River Basin in Paraná state (PR), the quantification of the elements Al, As, Hg, Zn, Pb, Cd, Ni, Co, Mn, Fe, Cr and Cu was carried out by optical emission spectrophotometry using Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES). Samples (sediment and fish) were collected from the Pirapó River at three different points (P1: near the source; P2: intermediate, close to the water collection point for public supply in the city of Maringá; P3: downstream from Maringá). The results showed concentration levels higher than the Maximum Residue Limit (MRL) for nine (9) of the twelve (12) elements in the sediment samples, including elements known for their high toxicity (Cr, Ni and Pb), in addition to those considered essential (Cu, Fe and Zn). For the fish samples, four (4) elements (Al, Cu, Hg and Zn) showed concentrations higher than the MRL. These results point to a high level of anthropogenic interference in these environments, configuring potential toxicity to the ichthyofauna of the Pirapó River and to the population supplied by the water of this river or that consumes fish.

KEYWORDS: Extraction of metals. Biomonitoring. ICP OES

1 INTRODUCTION

Over time, population increase and economic growth exponentially boost the acquisition of consumer goods and, with this, lead to an increase in waste generation (ALCÂNTARA et al., 2020; VIEIRA et al., 2016). There has been indiscriminate growth in industrialization and urbanization, to meet the needs of society, with a culture focused on the consumption and production of goods (DE AMORIM et al., 2019). This has promoted degradation and environmental impacts in aquatic environments through the inappropriate disposal of waste (AMÉRICO-PINHEIRO et al., 2021; VIEIRA, 2020; CAMPOS, 2012; GOUVEIA, 2012).

Tropical aquatic ecosystems are one of the most vulnerable environments on earth, facing rising pressures from increasingly significant anthropogenic activities, which result in pollution and environmental degradation, especially of water resources (ADAMOVIC et al., 2022; ORTEGA et al., 2022; PRIYADARSHINI et al., 2022; RAO et al., 2022; LIZAMA et al., 2013). The health of the ecological system can be indicated by its degree of biological diversity, which demonstrates that any disturbance that occurs in the habitat causes changes in the diversity of the environment in question. Changes in the environment cause reactions in both biotic communities and abiotic components.

There are several elements that can be used as an object of study to investigate water quality and ecosystem well-being, and one of these tools is the study of aquatic communities (AHMED et al., 2021; OVASKAINEN et al., 2019; SIDDIG et al., 2016; RAPPORT & HILDÉN, 2013). Within this type of study, the use of fish as bioindicators of water quality can help in the production of environmental sensitivity maps, risk assessment, and pollutant contingency plans, among others (FAKHRADINI et al., 2021; GARNERO et al., 2018; JAYAPRAKASH et al., 2015).

Studies carried out to investigate the response to various pollutants (agrochemicals, heavy metals, domestic and industrial effluents) have observed enzymatic changes in the liver and gills of fish, with significant histopathological changes being observed as a result of the

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presence of heavy metals, which can be lethal to these animals (MODEL et al., 2018; NIMET et al. 2017; VIEIRA et al.; 2016; FERNANDES et al., 2013; LIZAMA et al., 2013).

In addition to the aquatic community, sediment is extremely relevant in the functioning of water bodies. It is in the sediment that the decomposition of organic matter and the accumulation of various compounds occurs. As sediment is an active material, it not only accumulates material from the water column but also reprocesses this material, which can make it available again in solution (AHMED et al., 2021; FERREIRA et al., 2021; PANDIYAN et al., 2021). Thus, the toxic contaminants present in the sediment are potentially harmful, and they can continue to affect environmental degradation even when present at low levels in the water column and even after the discharge of pollutants into the receiving water body has ceased (PRIYADARSHINI et al., 2022; AHMED et al., 2021; USEPA 2005).

The importance of assessing the level of contamination of sediments lies not only in their ability to accumulate pollutants but also because they harbor some contaminating species, which are generally released from the sediment due to changes in the environment. Such species then promote changes in environmental and physicochemical conditions (pH, redox potential, microbial action, among others). These changes can contaminate water and biota, which can lead to increased concentration due to processes such as bioaccumulation and biomagnification by transfer of these contaminants into the food chain (NGO-MASSOU et al., 2022; FERREIRA et al., 2021).

Among the classes of contaminants, metals, and especially heavy metals, merit greater concern, due to their high toxicity, even at low concentrations (ARISEKAR et al., 2022). These metals have accumulative and biomagnification properties, as they do not degrade into less toxic compounds, and they remain for long periods in the environment, especially in sediment (NGO-MASSOU et al., 2022; PANDIYAN et al., 2021; POMPÊO et al., 2013).

2 OBJECTIVES

Given the importance of knowing and measuring the damage caused by urbanization and anthropogenic actions in a rural-urban river, the objective of this work was to detect the levels of metals and semimetals in fish and sediments to determine their bioavailability in the basin of the Pirapó River, Paraná state (PR), in southern Brazil. The study also aimed to assess the potential risk to the health of the fauna of the region, as well as to the population in the northwestern region of the state of Paraná that is supplied by this river.

3 METHODOLOGY

3.1 Study area

The Pirapó watershed comprises a drainage area of 5,067 km2, located on the third plateau of Paraná state. The Pirapó River rises in the municipality of Apucarana, Paraná state (PR), in southern Brazil. (23º 33' 05" S and 51º 27' 47" W) at an altitude of 863 meters, and flows northwards, covering a length of 168 km to its mouth and flowing into the Paranapanema River in the municipality of Jardim Olinda (22° 33' 42'' S and 52° 02' 46'' W) at an altitude of 321 meters (DA GRAÇA & SILVEIRA, 2020). Its coverage area is 33 municipalities that together have a population of approximately 950,000 inhabitants.

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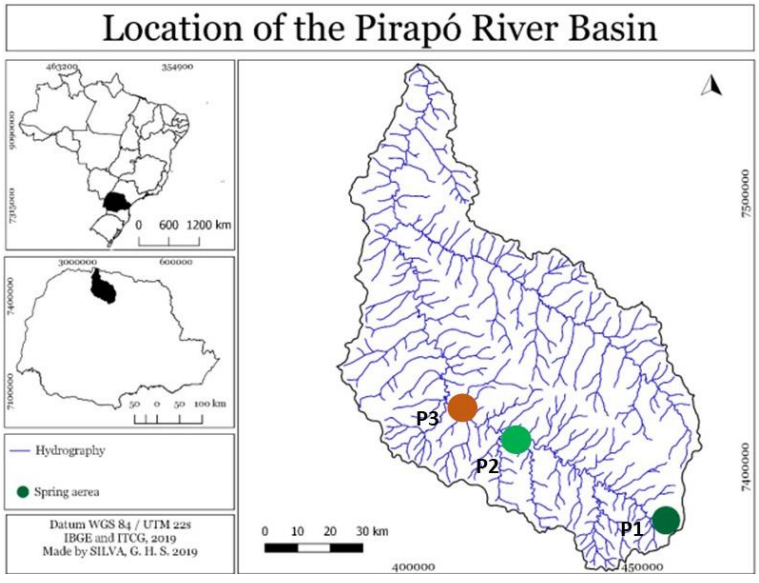
The Pirapó River falls under the classification of Class II freshwater bodies, according to the parameters evaluated by indicators established in CONAMA Resolution No. 357, of 03/17/2005 (CONAMA, 2005), since its waters can be destined: (i) to supplying human consumption, after conventional or advanced treatment; (ii) to the irrigation of arboreal, cereal and forage crops; (iii) to amateur fishing; (iv) to secondary-contact recreation; and to supplying drinking water for animals.

The water demand of the basin is approximately 3,000 L/s, of which 75% comes from surface springs and 25% from underground springs. Regarding the user sectors, 38% goes to public supply, 43% to industrial use, 10% to the agricultural sector, 9% to the livestock sector and 1% to the mineral sector. Much of the basin is occupied by intensive agriculture. In the northern and central regions, there are areas of artificial pastures and natural grasslands. To the south, there is the mixed-use class, where there is an urban and industrial concentration in the region of Maringá (SEMA, 2010).

Even though it is of paramount importance for the region, the Pirapó River has serious problems such as degradation of riparian forests, drying up of springs, pressure for urban growth, construction works in the area, intensive use of pesticides with application and disposal of packaging carried out irregularly (SANTOS et al., 2019). Thus, it is essential to carry out environmental monitoring and preservation actions, aiming at solutions for the proper use and management of water.

The sampling points were selected and distributed along the Pirapó River according to the level of anthropogenic interference (Figure 1).

Figure 1: Map of the location of the Pirapó River basin/PR and sampling points.



Source: LIMA & SILVA (2019), adapted by the authors.

The upstream point (P1) is located at the headwaters of the Pirapó River, in the city of Apucarana, and is the most preserved place, with established riparian forest and vegetation cover. The intermediate point (P2), located in Maringá, before the extraction of water for public supply, presents intensive agriculture and industrial activity in the vicinity of the banks (very

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degraded riparian forest). The downstream point (P3) has less dense forest on the banks, intensive agriculture, and the influence of effluent discharges from the municipal sewage treatment plant and nearby industries.

3.2 Fish and Sediment Sampling Methodology

The fish and sediment samples were obtained at the pre-established points of the Pirapó River basin from August 2020 to March 2021. After collection, the samples were sent to the LIABQ (Interdisciplinary Laboratory of Biological and Chemical Analysis), and then they were frozen so as not to undergo degradation until the moment of extraction and analysis.

The fish species analyzed were determined according to the frequency of capture and their economic importance, following the methodology proposed by Leite et al. (2019). Simple nets of different mesh sizes were used to collect fish. The captured fish were anesthetized, euthanized, and preserved in ice, where they were later identified, measured (total and standard length), weighed (total weight), and necropsied for tissue collection (muscle and gill) and sex identification. The samples were collected under SISBIO authorization No. 51570-4 of the Chico Mendes Institute for Biodiversity Conservation and using the euthanasia methodology authorized by the Ethics Committee on the Use of Animals (No. 003/2018-2) of Cesumar University (Unicesumar) and through the guidelines suggested by the National Council for the Control of Animal Experimentation (CONCEA).

Sediment samples were collected in the first 10 cm of the sedimentary column, since at this depth it is believed that, if there is contamination, it is relatively recent and corresponds to the history of occupation of the area.

Sediment collection was performed manually at the respective collection points, following the methodology described by Pompêo et al. (2013). After collection, the samples were kept on ice and transported to the Interdisciplinary Laboratory of Biological and Chemical Analysis – LIABQ/Unicesumar, to be stored in a freezer for further extraction and analysis.

3.3 Methodology for sample preparation and treatment

The sediment samples were homogenized and dried in an oven with an average temperature of 40 °C until a constant mass was generated, after this process the samples were pulverized with the use of a porcelain pestle and mortar. Subsequently, they were screened with the use of an electromagnetic sieve agitator and a 62 µm mesh particle size screen, where the phases of greater granulometry such as gravel and sand were discarded. The samples with sieved sediment were packed in plastic bags until the moment of metal extraction.

For metal analysis, acid digestion was performed, starting from 10 g of sample, digested with 30 mL of aqua regia (3:1 HCl/HNO_3); after evaporation, 10 mL of NaOH was added for basic digestion, followed by resuspension in deionized water and filtration in a 100 mL flask, where the volume was completed with distilled water.

The recovery of metals in fish (gill and muscle) was carried out using the methodology of Leite et al (2017), with modifications. The extraction started with 1 g of fish tissue being digested with 3 mL of aqua regia, followed by basic digestion with 1 mL of NaOH, resuspension with ultrapurified water and filtration in a 10 mL flask.

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3.4 Solvents, Standards & Analysis

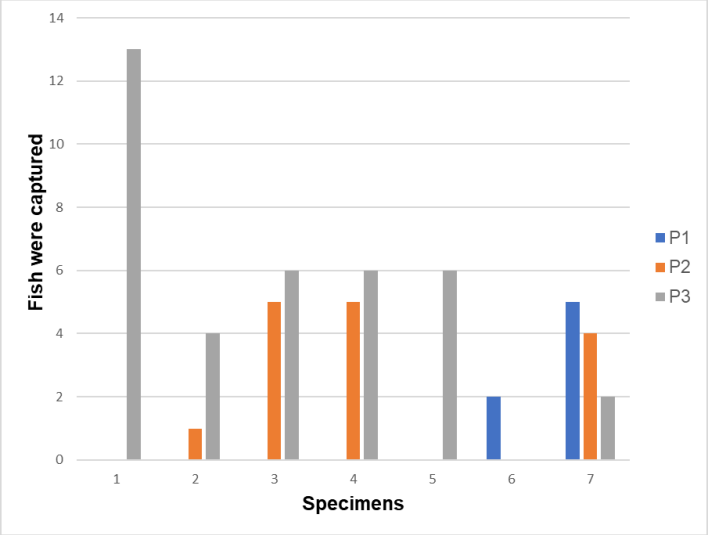
All standards, solvents and reagents used in the study were of analytical grade or appropriate to the spectrophotometric method. All aqueous solutions used in this study were prepared with ultra-purified water obtained from the Satorius Arium® Mini Ultrapure Water System.

Readings of the concentrations of the elements were performed in the Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) iCAP PRO XP, Thermo Fisher. For the analysis, a calibration curve was prepared at the following concentrations: 0.01 mg L^{-1}, 0.05 mg L^{-1}, 0.5 mg L^{-1}, 0.8 mg L^{-1} and 1 mg L^{-1} from a pure standard of each metal analyzed. To eliminate the matrix effect, an aqueous solution with 5 % nitric acid was used as the blank control.

4 RESULTS AND DISCUSSIONS

For the present study, 59 specimens of fish were captured, of seven (7) different species: *Hypostomus strigaticeps* (Regan, 1908), *H. ancistroides* (Ihering, 1911), *H. plecostomus* (Linnaeus, 1758), *H. paulinus* (Ihering, 1905), *Hoplias malabaricus* (Bloch, 1794), *Geophagus* spp and *Astyanax* spp, along the three collection points in the Pirapó River (Figure 2).

Figure 2: Number of fish captured in the sampling points by species. *H. ancistroides* (1), *H. strigaticeps* (2), *H. paulinus* (3), *H. plecostomus* (4), *Hoplias malabaricus* (5), *Geophagus* spp (6) and *Astyanax* spp (7).



Source: Prepared by the authors based on Levin, Fox and Forde, 2012.

Table 1 shows the biometric data from the fish collected at different points (P1, P2, and P3). In this analysis, 38 species of the 59 captured were used, and the specimens of fish that presented some type of alteration in their physical structure were discarded.

Table 1 – Biometry of the specimens and Relative Condition Factor (Kn) for the specimens captured at P1, P2 and P3 of the Pirapó River, 2020 – 2021.

P	Specimens	Biometrics			Length
		Lt (cm)	Ls (cm)	Wt (g)	(cm)
3	*Hypostomus strigaticeps*	24.5	18.4	163.38	14

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2	*Hypostomus strigaticeps*	18.7	11.5	26.17	24.5
3	*Hypostomus strigaticeps*	22.6	16.2	78.25	18.7
3	*Hypostomus strigaticeps*	13.9	10.2	19.97	22.6
3	*Hoplias malabaricus*	18.3	14.1	64.6	13.9
3	*Hoplias malabaricus*	22.9	16.5	106.26	15.1
2	*Hoplias malabaricus*	26.2	19.5	94.93	14.01
2	*Hoplias malabaricus*	25.4	17	157.4	24.2
1	*Hoplias malabaricus*	13.9	9.6	37.75	19.4
1	*Hoplias malabaricus*	10.6	7.1	12.49	22.7
3	*Hypostomus paulinus*	12	8.5	13.87	21
3	*Hypostomus paulinus*	9.2	6.8	8.28	22.1
3	*Hypostomus paulinus*	11	7.5	11.11	14.4
3	*Hypostomus paulinus*	22.5	15.5	87.44	13.1
3	*Hypostomus paulinus*	11.4	8	13.07	14.8
1	*Astyanax* spp	15.5	11.4	74.57	10.6
1	*Astyanax* spp	16	11.8	63.67	11.6
1	*Astyanax spp*	13.2	10.2	33.99	22.7
1	*Astyanax* spp	12.6	10.3	30.78	18.1
2	*Hypostomus plecostomus*	18.1	12.5	46.9	16.6
3	*Hypostomus plecostomus*	16.1	11.1	61.36	16.9
2	*Hypostomus plecostomus*	16.6	11.1	29.15	19.5
2	*Hypostomus plecostomus*	16.9	11.5	30.21	18.1
2	*Hypostomus plecostomus*	19.5	15.2	45.58	16.1
2	*Hypostomus plecostomus*	18.1	12.7	37.66	18.2
3	*Hypostomus plecostomus*	18.2	13.1	41.34	18
3	*Hypostomus plecostomus*	15	11	28.6	15
3	*Hypostomus ancistroides*	24.2	19.2	83.02	15.5
3	*Hypostomus ancistroides*	22.1	17.1	87.29	13
3	*Hypostomus ancistroides*	22.7	15.1	93.84	22.9
3	*Hypostomus ancistroides*	22.7	18.3	90.05	26.2
3	*Hypostomus ancistroides*	14.8	11.4	27.8	25.4
3	*Hypostomus ancistroides*	15.1	11.8	23.08	18.3
3	*Hypostomus ancistroides*	19.4	13.8	52.45	13.9
3	*Hypostomus ancistroides*	21	16.3	79	10.6
3	*Hypostomus ancistroides*	13.1	10.2	21.72	9.2
1	*Geophagus* spp	13.8	12.3	50.46	12
1	*Geophagus* spp	15.4	12.3	55.56	11.4

(P) sampling points; (Ls) standard length; (Lt) total length; (Wt) total weight.
Source: Prepared by the authors based on Levin, et al. (2012).

The weight-length ratio describes the forms of increment in the different stages of the life cycle of fish species, making it a good indicator of feeding and reproductive activities. In addition, this relationship can serve as a basis for comparing the degree of stress or different environmental conditions among fish with a wide geographic distribution (LIMA et al., 2015; PEREIRA et al., 2010; FERNANDES et al. 2008).

The readings of the elements recovered from the tissue samples of the specimens of this study (muscle and gill) and sediment at the three sampling points performed by the ICP-OES method can be seen in Table 2. In bold, the concentrations of the elements that presented concentrations higher than the maximum limit allowed by CONAMA Resolution No. 357/2005 for Class II freshwater water bodies are highlighted.

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Table 2: Concentration (mg L^{-1}) of elements detected by ICP OES in fish and sediment at the sampling points of the Pirapó River, 2020-2021.

Elements	Fish						Sediment (mg L^{-1})			MRL (mg L^{-1})*
	Muscle (mg L^{-1})			Gill (mg L^{-1})						
	P1	P2	P3	P1	P2	P3	P1	P2	P3	
Al	**3.43**	**2.39**	**1.86**	**1.22**	**6.20**	**1.04**	**2.44**	**2.48**	**1.79**	0.2
As	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.033
Hg	**0.003**	**0.005**	0.002	**0.003**	0.001	0.001	ND	ND	ND	0.002
Zn	**0.600**	**0.257**	**0.432**	**0.513**	**0.151**	**0.773**	**1.59**	**1.33**	**0.464**	0.025
Pb	0.015	0.013	0.014	0.013	0.002	0.007	**0.661**	**0.623**	0.009	0.033
Cd	0.001	0.001	0.001	0.0008	0.0003	0.0008	ND	ND	ND	0.01
Ni	0.009	0.007	0.008	0.0148	0.016	0.010	**2.924**	**2.487**	0.013	0.025
Co	ND	ND	ND	ND	ND	ND	**1.261**	**1.163**	ND	0.2
Mn	0.076	0.081	0.095	0.26	0.08	0.60	**6.8**	**6.5**	0.5	0.5
Fe	1.368	1.179	1.6605	**6.23**	2.22	**9.29**	**49.51**	**49.64**	**15.4**	5.0
Cr	0.024	0.007	0.018	0.02	0.003	0.01	**1.65**	**1.77**	0.03	0.05
Cu	**0.129**	0.008	**0.029**	**0.08**	**0.03**	**0.03**	**1.91**	**1.98**	**0.040**	0.013

*CONAMA Resolution No. 357/2005; ND = Not detected; P = sampling points; MRL = Maximum residue limit. In bold, concentrations above the MRLs.

From the results indicated by the analysis of the concentration of metals, it is possible to assess that there is a strong variation in the concentration between the different elements, highlighting concentrations higher than the MRL for five elements in the fish tissue (Al, Hg, Zn, Fe and Cu) and nine of the 12 elements recorded in the sediment (Al, Zn, Pb, Ni, Co, Mn, Fe, Cr and Cu), and Al, Zn, Fe and Cu, found in both fish and sediment tissues. This fact raises concerns about the level of bioavailability of these elements in the water body, since the dynamics of divalent metal sequestration is mediated by Partition Equilibrium (EqP).

In fish tissues, concentrations for Al were found to be 5.2 to 31 times higher than the MRL, and the essential elements, Fe (1.3 – 1.7), Zn (6 – 31) and Cu (2.3 – 6.8), were also higher when compared to the MRL. For the sediment, the concentrations of heavy metals stand out, namely Pb (20 times), Ni (116 times) and Cr (35 times) higher than the MRL, while for the essential elements, higher values were observed, from 3 – 9.8 for Fe, 18.6 – 63.6 for Zn and 3 – 152 for Cu.

Although Cu and Zn are essential elements for organisms and are easily metabolized (Leite et al., 2017; Sures et al., 2017; PEREIRA et al., 2010), their values were found to be above what is allowed (Table 2), in all collection sites; these values may be related to the sediment constitution itself. However, the non-essential elements related to the heavy metals Cr, Ni and Pb, although not detected in high concentrations in the fish tissues, showed high values in the sediment. These elements are extremely toxic and can be found in organic matter (OM). The fact that this element is in lower concentrations than that allowed by Brazilian legislation (CONAMA, 2005) demonstrates low availability in the water body for the species analyzed.

Numerous field studies have been carried out to determine concentrations of elements, mainly heavy metals, and to assess the bioaccumulative potential in fish tissues, parasites, sediment, and water (Leite et al., 2021a; Leite et al., 2021b; Leite et al., 2017; Sures et al., 2017; Pompêo et al., 2013). In this study, however, it was not possible to show a pattern in the distribution of the concentrations of the elements in fish tissues and sediments or in the

bioconcentration factors among the different fish species. The absence of distribution patterns of the concentrations of the recovered elements in the tissues of fish and sediments points to the existence of anthropogenic influences interfering in the environment.

High concentrations of inorganic contaminants found in fish tissues (gill and muscle) and sediment may be associated with intense agricultural activities carried out at point P1 (source) and the fact that this area has lower water flow, with a predominance of sedimentation processes and small particles that have more adsorption sites for metals (ADAMOVIC et al., 2022; AKSHITHA et al., 2022; NGO-MASSOU et al., 2022; AHMED et al., 2021). For points P2 and P3 it may be related to the proximity to the largest urban center, affected by intense industrial and agricultural activities. By comparing the concentrations of metals higher than the MRL with the type of increment in the fish analyzed, it is not possible to draw a correlation, which demonstrates that the level of anthropogenic interference at the collection points is not only due to the high presence of metals, but also due to other types of contaminants, such as agrochemicals and/or sewage discharge.

In aquatic organisms, the accumulation of these metals occurs by the dissolved phase and by food ingestion (LEITE et al., 2021b; POMPÊO et al., 2013), i.e., trophic webs play an important role in the bioaccumulation and loading of these metals, since several benthic organisms feed on other organisms present in these sediments and, in turn, are later consumed by larger organisms such as fish and those at higher trophic levels (BOTTÉ et al., 2010). In both sediment and fish, the detection of these metals is used to assess the quality of the aquatic ecosystem, as they are difficult to remove, even in the process of water self-purification (MAKHAYA et al., 2022; NIMET et al., 2017).

The abundant presence of inorganic contaminants, mainly metals, in aquatic environments leads to environmental imbalance in several aspects, affecting not only the environment but also human health. Essential metals (Fe, Cu, and Zn) are important for maintaining human health, but their excesses can cause diseases such as cancer, infertility, diseases of the nervous and skeletal systems, among others (AKSHITHA et al., 2022; FRANCISCO et al., 2019). The presence of toxic metals, especially heavy metals, causes a high level of toxicity and, in large concentrations, these can cause numerous diseases, including death.

Although the results presented here are significant and answer important questions regarding contamination levels and bioavailability of contaminants, we also recommend toxicity analyses, albeit not essential. This is because the bioavailability of metals is not necessarily indicative of toxicity, as ecological and physiological conditions can modify the extent to which organisms are exposed to metals (XU et al., 2022; AUTHMAN, et al., 2015; JAYAPRAKASH et al., 2015).

5 CONCLUSION

The data obtained reveal the presence of contaminants both in the sediment and in the tissues of the different species captured, originating from anthropic action, agriculture, and the urbanization process. There is a need for constant and in-depth studies regarding the bioavailability of inorganic contaminants, especially heavy metals, in the Pirapó River basin,

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Paraná state, to monitor the level of anthropogenic interference in this important biogeographic region. These studies can then enable the development of public policies aimed at avoiding environmental contamination by persistent inorganic pollutants, degradation of the aquatic community and a reduction in the quality of the water used for consumption.

The results suggest potential toxicity of these contaminants due to the high concentrations found in fish tissue (muscle and gills) and in sediment, much higher than the maximum residue limit for class II water bodies, according to CONAMA resolution 357/2005, both for metals considered essential (Fe, Cu and Zn) and for those considered toxic (Pb, Ni and Cr). Thus, it represents an important tool for the monitoring of water bodies.

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