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Environment

Contamination by potentially toxic metals from urban rivers located in an area covered by the Guarani Aquifer in Southern Brazil

Contaminação por metais potencialmente tóxicos de rios urbanos localizados em uma área abrangida pelo Aquífero Guarani no Sul do Brasil

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ABSTRACT

The present study aimed to evaluate the concentration of heavy metals considered globally alarming, such as cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), and zinc (Zn), in the surface water and in the sediment of urban rivers located in an area covered by the Guarani Aquifer in Lages, southern Brazil. The water and sediment samples were collected in September and October 2016 in three urban rivers. The quantification of the metals was performed through an atomic absorption spectrometer. The levels of Cd, Cr, Cu, Pb and Zn in the control points (P1 and P7) presented a concentration below the level I proposed by Brazilian legislation 344/2004 of the National Environment Council (CONAMA), while the other points presented concentrations higher and above level I, evidencing an increase of metals in the rivers from upstream to downstream of the urban area of Lages. Cr concentrations above level II proposed by Brazilian legislation at the mouth of the Carahá River were also found, and this value may have adverse effects on aquatic biota. The results show that urban rivers in the area covered by the Guarani Aquifer in Lages have been contaminated by toxic elements associated with anthropogenic activities.

Keywords: Guarani Aquifer; Emerging contaminants; Toxic metals; Urban rivers

RESUMO

O presente estudo teve como objetivo avaliar a concentração de metais pesados considerados globalmente alarmantes, como cádmio (Cd), cromo (Cr), cobre (Cu), chumbo (Pb) e zinco (Zn) nas águas superficiais e no sedimento de rios urbanos localizados em uma área de abrangência do Aquífero

Guarani, em Lages, sul do Brasil. As amostras de água e sedimento foram coletadas em setembro e outubro de 2016 em três rios urbanos. A quantificação dos metais foi realizada através de um espectrômetro de absorção atômica. Os teores de Cd, Cr, Cu, Pb e Zn nos pontos de controle (P1 e P7) apresentaram concentração abaixo do nível I proposto pela legislação brasileira 344/2004 do Conselho Nacional do Meio Ambiente (CONAMA), enquanto os demais pontos apresentaram concentrações mais alto e acima do nível I, evidenciando um aumento de metais nos rios da montante para jusante da área urbana de Lages. Concentrações de Cr acima do nível II proposto pela legislação brasileira na foz do rio Carahá também foram encontradas, e esse valor pode ter efeitos adversos na biota aquática. Os resultados mostram que os rios urbanos da área de abrangência do Aquífero Guarani em Lages têm sido contaminados por elementos tóxicos associados as atividades antrópicas.

Palavras-chave: Aquífero Guarani; Contaminantes emergentes; Metais tóxicos; Rios urbanos

1 INTRODUCTION

The unplanned urbanization process in Brazilian cities has been causing contamination of aquatic systems and causing damage to the biological, physical and chemical processes of natural systems (Nascimento et al., 2015). Large amounts of environmental contaminants, especially heavy metals, have been released into urban rivers in various parts of the world associated with rapid population growth, land use and occupation. Toxic metals are not biodegradable, which triggers a high potential for bioaccumulation (Wu et al., 2017).

The indiscriminate use of fertilizers and pesticides, mining, lack of basic sanitation, urban and industrial liquid waste, particles resulting from tire wear, residues from fuels, oils and greases and the accumulated waste in the streets are the main sources of contamination of soil and of water by toxic metals (Augusto et al., 2014; Brandelero et al., 2017; Nascimento et al., 2015; Volpato; et al., 2017). The concern with this type of contamination is associated with the capacity of retention (accumulation) and mobility of these metals in the soil and the possibility of contaminating the water table, surface water and groundwater. Toxic metals can be absorbed by plants and accumulated in plant tissues and thus enter the aquatic food chain (Augusto et al., 2014; Lima et al., 2015; Soleimani et al., 2023).

Metals such as Cd, Cr, Cu, Pb and Zn are considered potentially toxic, they tend to accumulate in living organisms, affecting soil and water quality and are associated with disturbances and diseases in the population when ingested. These contaminants have been used to characterize and to evaluate the contamination of water and soils in urban areas (Trindade, Ribeiro, 2012; Augusto et al., 2014; Lima et al., 2015; Nascimento et al., 2015; Uwizeyimana et al., 2017; Tahervand; Jalali, 2017).

Rivers are important routes for transportation and transformation of toxic elements in urban centers (Wu et al., 2017). The sediment deposited in the bed of rivers and streams adsorbs organic and inorganic particles by means of physical and chemical mechanisms. The metals may be in the bioavailable form making the contamination persistent (Tao et al., 2023). The analysis of metals in sediments is an important tool for monitoring the quality of aquatic ecosystems, as these may accumulate toxic metal concentrations higher than in the water column.

Physicochemical properties of rivers such as potential hydrogen (pH), dissolved oxygen (DO) and temperature are factors that influence the mobility and consequently the toxic potential of metallic elements, whereas factors such as precipitation, cation exchange and complexation with organic molecules are important mechanisms that regulate the availability of these metallic elements in aquatic environments (Lima et al., 2015; Wu et al., 2017). When the concentration of a substance in water, air or soil is above the defined legal value, it is treated as a contaminant (Horta et al., 2015).

The Guarani Aquifer is considered the second largest transboundary groundwater reservoir in the world, both in territorial extent and in volume of water. It is located in the Paraná sedimentary basin, covering Brazil, Paraguay, Argentina and Uruguay, and approximately 70% is in the Brazilian territory, occurring in eight states (Curtarelli et al., 2010; Carasek et al.,2020), among them, Santa Catarina, located in southern Brazil. The area of this study is located in the hydrographic basin of the Caveiras river in the city of Lages, region of the Santa Catarina plateau.

The Caveiras river basin is influenced by different sources of contamination associated with the type of land use and occupation that contribute to the accumulation of toxic metals in aquatic ecosystems. It should be noted that the urban area of Lages is located on a strip of outcrop of the Guarani Aquifer, which makes the risk of environmental contamination even more worrying, since there are numerous sandstone outcrops along the water basin where there may be infiltration of contaminated water. With the above in mind, this study aimed to determine the concentration of Cd, Cr, Cu, Pb and Zn in the water and sediments of rivers of the Caveiras river basin, located in an urban area in the city of Lages and in the area covered by the Guarani Aquifer.

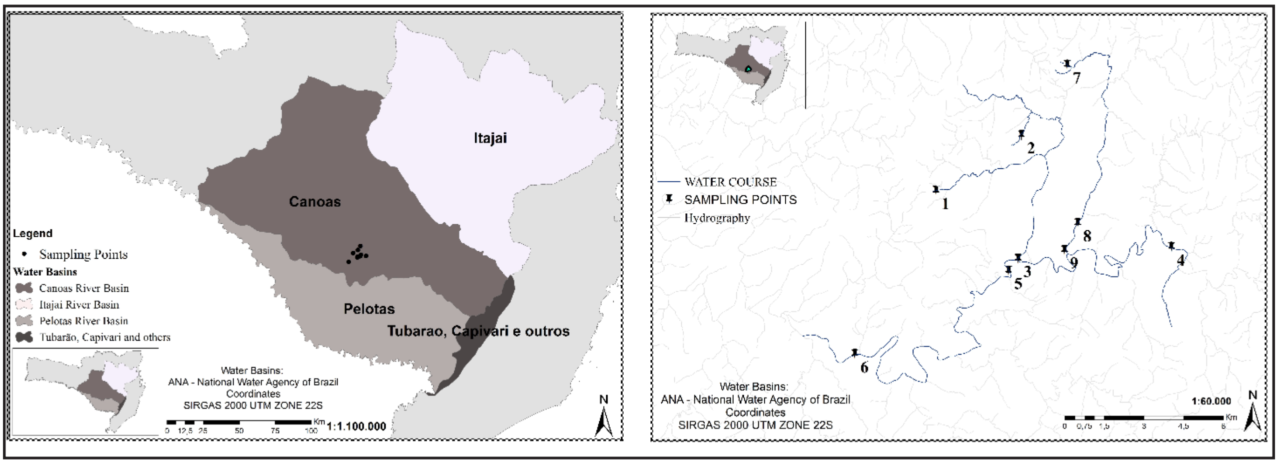
2 MATERIALS AND METHODS

2.1 Characterization of the study area

The study site is located in the Caveiras river water basin, in the section that runs through the city of Lages (latitude: –27º48'58"S, longitude: – 50º19'34"W, altitude: 916 m), situated in the State of Santa Catarina, southern Brazil (Figure 1). The municipality of Lages is located on the mountain plateau of Santa Catarina and has approximately 158,000 inhabitants, average annual temperature of 16°C and average annual precipitation of 1236.2 mm, well distributed throughout the year. In the section where it passes through the urban area of Lages, the Caveiras River receives urban effluents (industrial and domiciliary) and the water contribution of two main tributaries, the Ponte Grande and Carahá rivers with 24 and 30 km^2 of extension, respectively. The rivers Carahá and Ponte Grande are born and run through the urban area of the city of Lages and flow into the Caveiras River, and because they are exclusively urban, they receive a high load of waste. In addition, in the study site, outcrop areas occur with direct recharge of the Guarani Aquifer, considered a strategic reserve for the water supply to the population of the State. Scheibe; Hirata (2008) highlight the occurrence of indented outcrops of the sandstones of the Botucatu Formation (Guarani Aquifer

Matrix) caused by the over-elevation of the Lages Dome, to the west of the municipality of Lages volcanic rocks of Serra Geral cover Botucatu.

Figure 1 – Location of the sampling points (P1 to P9) located in urban rivers of the city of Lages, state of Santa Catarina, southern Brazil



Source: Authors

In the present study, nine sampling points located in the Caveiras river basin were selected, located in areas covered by the Guarani Aquifer. Of these, three points (P1, P2 and P3) were sampled in the Carahá River, a river whose extension is predominantly urban, being respectively a point near the headstream (upstream), one in the central section and the other at the mouth (downstream of the urban area). Similarly, three points (P4, P5 and P6) were sampled in the Caveiras river, a point upstream of the city of Lages, one point after receiving the contribution of the Carahá river (center) and another one downstream of the city of Lages. The points (P7, P8 and P9) correspond to the samples collected in the Ponte Grande river (upstream, center and downstream), whose springs are located in the rural area, however, its largest extension runs through the urban area. The points P1 and P7 are located in a permanent preservation area and were used as environmental control.

2.2 Collection and extraction of metals

Water and sediment samples were collected between May and October 2016 (in a period without rainfall for at least five days prior to collection). At each point, 0.5L of water was collected in backwater sections, using a polyethylene bottle containing 1ml of nitric acid (65%) to preserve the sample. Sediment samples were also collected with the help of a stainless-steel dredge, at a depth of 0-0.1 m. In each river, three sediment samples distant from each other about 50 m were collected, and they were mixed, homogenized and placed in polypropylene bags. After the collection, the water and sediment samples were transported to the laboratory in an ice box, preserving the samples at low temperature. Two water samples and two sediment samples were collected at each point between September and October 2016, each of which was analyzed individually.

A 100 mL aliquot of water from each previously homogenized collected water sample was acidified with 2 μL of HNO_3 (65%). Afterwards, they were placed in 100 mL containers and analyzed by atomic absorption.

The sediment samples were prepared through acid digestion in a microwave oven (Provecto Analítica/model DGT 100). Three hundred mg of sample were weighed in the digester block and two mL of HF, three mL of HNO_3 and two mL of HCl were added. After the addition of the reactants, the digester blocks were closed and placed in the microwave oven applying the digestion schedule of table I.

Table I – Schedule used in the microwave oven for digestion of sediment samples

Step	Time	Power
1	5 minutes	180 W
2	5 minutes	000W
3	5 minutes	340 W
4	5 minutes	000W
5	6 minutes	250 W

Source: Authors

At the end of the digestion, with the samples at room temperature, 5 mL of saturated boric acid solution were added to each block. Subsequently, the samples were transferred to 250 ml volumetric flasks and swollen with ultrapure water. The prepared samples were stored in 250 mL flasks and sent for analysis by atomic absorption.

2.3 Determination of metals and statistical analysis of data

To perform the zinc analysis, a flame Atomic Absorption Spectrophotometer was used (Agilent, Model AA 200, with Auto Sampler and SIPS – Sample Introduction Pump System). For the analysis of Cd, Pb, Cu and Cr, a Graphite Furnace Atomic Absorption Spectrophotometer (Varian, Model Spectr AA Zeeman 220, with auto Sampler) was used.

The limit of quantification of the analytical method (LQAM) was determined according to the equation $LQMA = 10.\ sd$, in which sd is the standard deviation of the reading of 10 blank samples. After the determination of the absorbances by the equation, the obtained values were converted to concentration through calibration curves.

In order to evaluate the quantification of the metals in the sediment and in the water, the reference samples NIST San Joaquin Soil SRM 2709 and reference sample Padrão®1640a were used respectively for trace elements in water. The certified values in the reference samples were compared with the determined values.

In the statistical analysis, the mean of the data collected in September and October 2016 was used. A graphic analysis was performed to evaluate the concentration of the metals at the points from upstream to downstream of the city of Lages. In order to evaluate the distribution of the toxic metal concentration between the sediment and water samples and among the points sampled along the environmental contamination gradient, a similarity analysis was performed using Euclidean distance, and the matrix was represented by grouping by unweighted arithmetic means (UPGMA – Unweighted Pair Group Method with Arithmetic Mean). The UPGMA algorithm constructs a rooted tree (dendrogram) that reflects the structure present in a pairwise similarity matrix. The statistical significance of the formed groups in similarity analysis was tested using similarity profile tests (SIMPROF). Principal component analysis (PCA) was used to test the relationship between the sampled points and the values of measured toxic metals. The PCA cluster the sampled points according to the variation in the concentrations of the measured metals. For all analyses, the metal concentration values matrix was transformed by log (x+1) and the analyses were performed in the Primer-E Software (Clarke; Gorley, 2006).

2.4 Reference values

Resolution No. 344/2004 of the National Environment Council (CONAMA) (Brasil, 2004) establishes the general guidelines and minimum procedures for the evaluation of the material to be dredged in Brazilian jurisdictional waters. In order to classify the material to be dredged, two levels of organic and inorganic parameters are established. At level 1 are contained the parameters with threshold below which one predicts a low probability of adverse effects to biota. On the other hand, at level 2 are contained the parameters with threshold above which one predicts a probable adverse effect to biota. These levels were used as an indicator of quality and parameter of comparison with the concentrations obtained in this study (Brasil, 2004; Table II).

Table II – Concentration levels in freshwater sediment established by CONAMA's legislation No. 344/2004 in Brazil for the elements evaluated in this study [mg kg^{-1}]

Element	Level 1	Level 2
Cd	0.6	3.5
Cr	37.3	90
Cu	35.7	197
Pb	35	91.3
Zn	123	315

Source: Brasil, 2004

CONAMA's Resolution No. 357/2005, applied in Brazil, provides for the classification of water bodies and environmental guidelines for their classification, as well as establishing the conditions and standards for the discharge of effluents. According to this resolution, the following classes of freshwater are established: special class for public distribution and preservation of aquatic environments, class I intended for human distribution after the simplified treatment, protection of aquatic communities, recreation of primary contact and irrigation of vegetables, class II intended for human distribution after conventional treatment, protection of aquatic communities, recreation of primary contact, irrigation of vegetables, agriculture and fishing, class III intended for human distribution after conventional or advanced treatment, irrigation of tree crops, amateur fishing, recreation of secondary contact and water for animals, in class IV is water intended for navigation and landscape harmony (Brasil, 2005). Several organic and inorganic parameters are established for the classification of water bodies in one of the classes. Table III presents the water classes of this resolution based on the parameters evaluated in this study, using them to compare the obtained results.

Table III – Freshwater classes established by CONAMA's Resolution No. 357/2005 applied in Brazil for the evaluated parameters – [mg L^{-1}]

Element	Class I	Class II	Class III	Class IV
Cd	0.001	0.001	0.01	>0.01
Cr	0.05	0.05	0.05	>0.05
Dissolved Cu	0.009	0.009	0.013	>0.013
Pd	0.01	0.01	0.033	>0.033
Zn	0.18	0.18	5	>5

Values for a possible classification of the metals evaluated among the classes established by CONAMA's Resolution No. 357/05
Source: Brasil, 2005

3 RESULTS AND DISCUSSION

Certified values and reading results obtained by analyzing the reference sample San Joaquin Soil SRM 2709 NIST for sediment and reference sample Padrão®1640ª for trace elements in natural water are presented in tables IV and V. When comparing the certified values with the values obtained in the reading, it is possible to observe that the determined concentration was extremely precise, guaranteeing reliability in the reading of the samples.

Table IV – Determined and certified contents of the elements analyzed for reference sample Nist San Joaquin Soil SRM 2709[a] and LQAM – [mg kg^{-1}]

Metals	Result ± standard deviation	Certified Values ± Standard deviation	LQAM
Cd	0.37±0.02	0.38±0.01	0.1
Cr	114.32±3.82	130±4	1.5
Cu	32.59±0.92	34.6±0.7	2
Pb	16.78±1.42	18.9±0.5	3
Zn	95.17±0.61	106±3	3

Source: Authors

Table V – Determined and certified contents of the elements analyzed for reference sample Padrão®1640[a] – Trace Elements in Natural Water and LQAM – [µg L^{-1}]

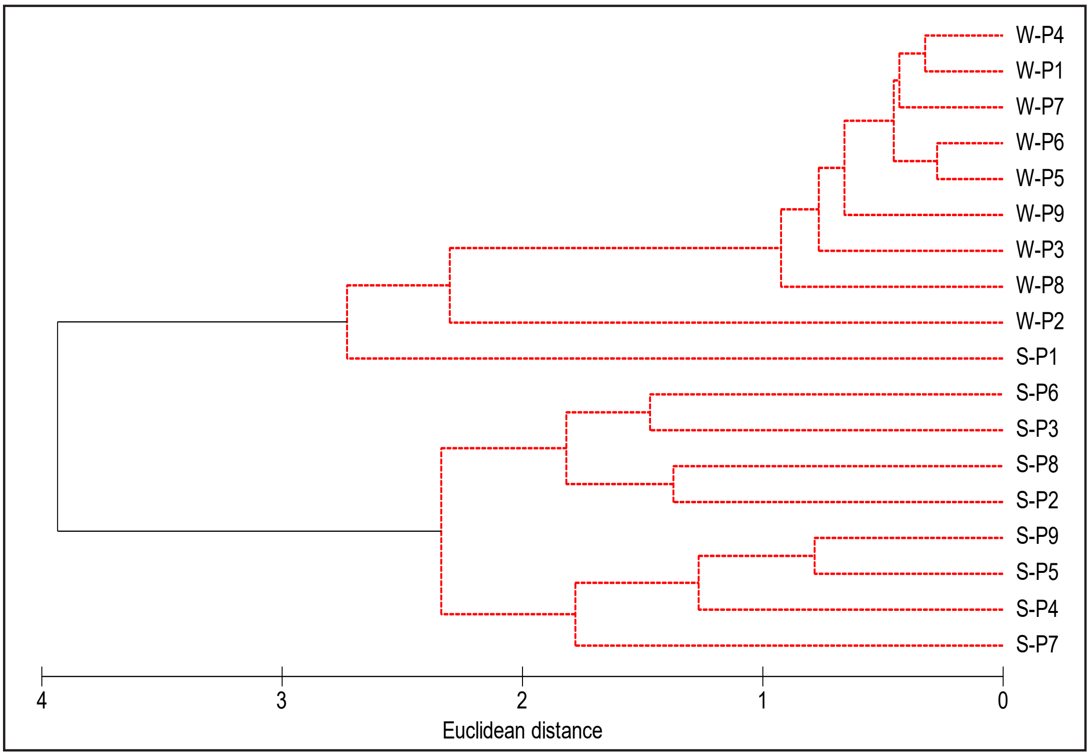
Metals	Result ± standard deviation	Certified Values ± Standard deviation	LQAM
Cd	3.51±0.03	3.99±0.07	0.1
Cr	40.69±0.35	40.54±0.30	0.1
Cu	85.79±0.43	85.75±0.51	1.0
Pb	12.66±0.08	12.10±0.05	0.5
Zn	55.90±0.31	55.64±0.35	6.0

Source: Authors

When comparing the concentration of metals found in the sediment and water samples, the similarity analysis with subsequent grouping showed the formation of two significantly different groups, one formed by the water samples and another group by the sediment samples from the urban rivers (Figure 2), indicating that the concentrations of heavy metals are different among the environmental matrices of the aquatic systems, with higher concentration in the sediment. These results were confirmed by principal component analysis (PCA) (Figure 3). PCA axes I and II explained

89.6% of the accumulated variation of the data. The first axis explained 74.5% of the data variability and was associated with the highest concentrations of Cd, Cr, Cu and Pb found in P2, P4, P5 and P9 of the sediment. Axis 2 explained 15.1% of the data variation and was related to the highest Zn values of the P3, P6 and P8 Points of the sediment. In other words, higher concentration values of heavy metals were found in the sediment, except in points 1 and 7, while low values were obtained in water samples collected at the same sampling points (Figure 4).

Figure 2 – Analysis of groupings for the parameters Cd, Cr, Cr, Pb and Zn measured in nine points sampled in water (W) and sediment (S), in urban rivers of Lages, SC, mean from two collection periods



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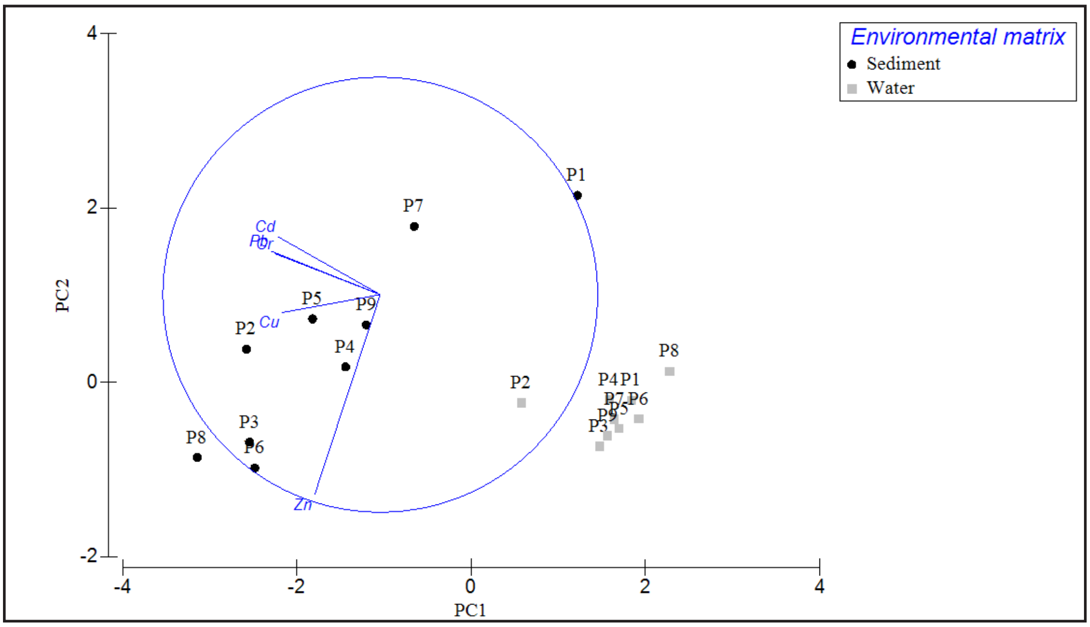
In general, sediment deposited in riverbeds are important sinks of pollutants and suspended particles in the water column, such as heavy metals, which have high toxicity, difficult degradation and easy accumulation (Lundy et al., 2017; Yang et al., 2012). However, when substrate revolving or changes in environmental conditions and/ or anthropogenic disturbances that interfere with chemical and biological processes occur, sediment becomes a source of heavy metals and other pollutants emissions to the water column and downstream sections (Lundy et al., 2017; Soleimani et al., 2023). Unfortunately, due attention is not given by much of the water quality monitoring in rivers to sediments that are in constant interaction with the aquatic system, which is also habitat for many benthic organisms (Duncan et al., 2018).

Figure 3 – Principal component analysis for the parameters Cd, Cr, Cu, Pb and Zn in the nine points evaluated in water and sediment in urban rivers of Lages, SC. Mean from two collection periods



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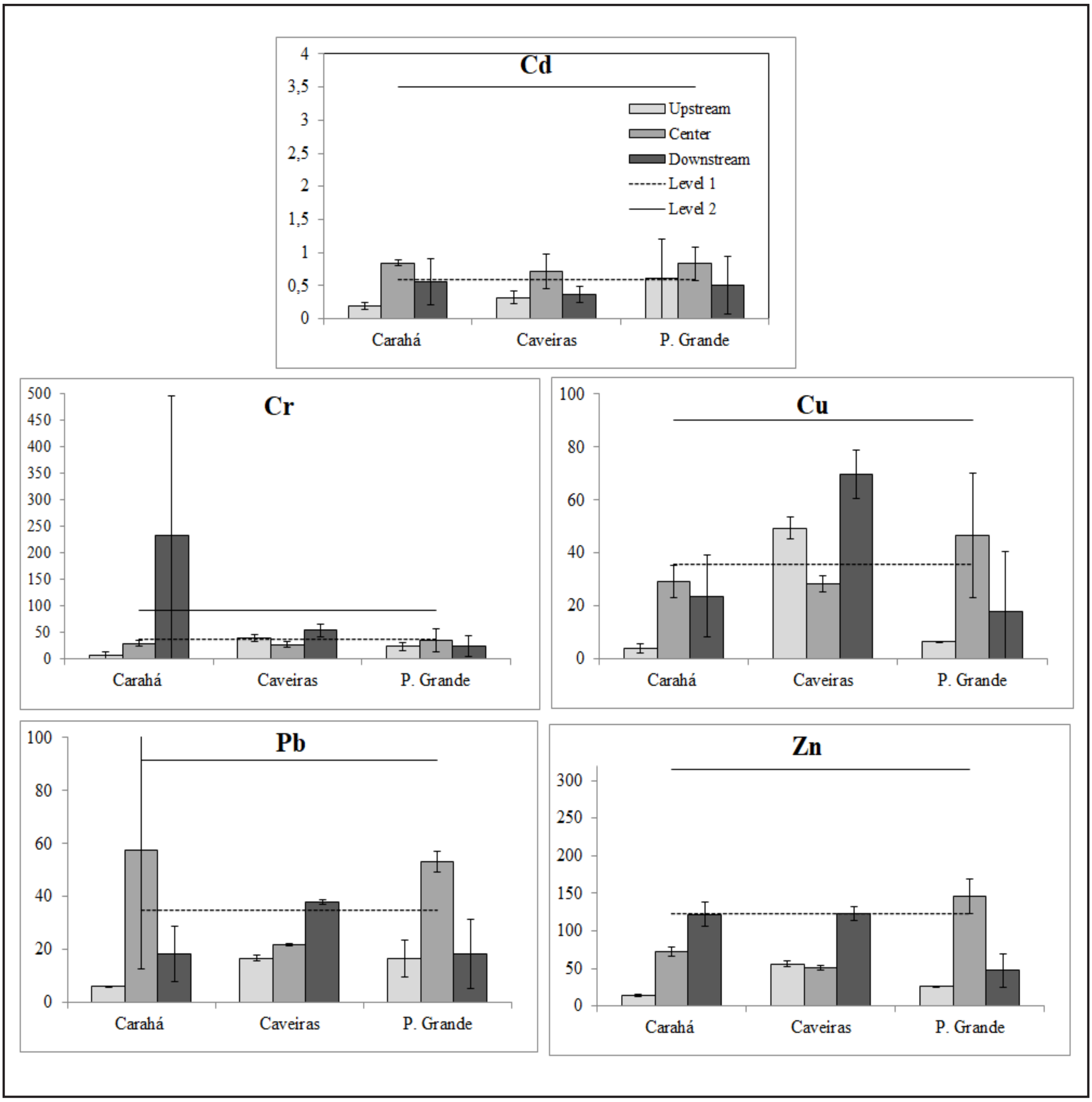
In addition, sediments represent a more stable means of tracking metal sources when compared to water (Yang et al., 2022). While a water sample provides data of metal concentrations over a relatively short time scale that does not exceed the hours due to the constant flow of lotic systems, the sediments deposited in the bed may be more representative regarding the pollutant loads of the environment (Owens et al., 2001; Yang et al., 2022). For this reason, bed sediments have been increasingly used in evaluating the contamination of river systems in urban and suburban areas under different environmental conditions (Lundy et al., 2017).

3.1 Metals in the Sediment of the Rivers

The Figure 4 shows the mean concentrations of Cd, Cr, Cu, Pb and Zn at the points sampled for the sediments collected in the urban rivers of Lages. A gradient of increasing concentration (spring of the rivers to mouth) was obtained for Cr and Zn in the Carahá river and Pb in the Caveiras river, from upstream to downstream of Lages. The levels of Cd, Cr, Cu, Pb and Zn in the sampling points used as control P1 (spring of Carahá) and P7 (spring of Ponte Grande), presented concentration below the level I predicted by the Brazilian legislation of CONAMA (table II) and lower than all of the other sampled points, evidencing an increase in the contamination from upstream to downstream. Wu et al. (2017) when investigating the spatial distribution of toxic elements in the Qinhuai River sediments in eastern China, following a gradient of urbanization, showed that points sampled downstream of urban centers had concentrations 1.9 times higher than upstream sites, in rural areas, indicating more severe pollution in terms of toxic metals downstream of cities.

We have registered concentrations above level 1 proposed by the CONAMA's legislation No. 344/2004 (table II) of Cd in the central section of the rivers Carahá (P2), Caveiras (P5) and Ponte Grande (P8), of Cr at the mouth of the Carahá river (P3) and downstream of the Caveiras river (P6), of Cu upstream and downstream of the Caveiras river (P4 and P6) and in the central section of the Ponte Grande river (P8), of Pb in the central section of the Carahá river (P2), downstream of the Caveiras river (P6) and central section of the Ponte Grande river (P8) and of Zn in the central section of the Ponte Grande river (P8). Cr concentrations above level II (table II) were also found in the mouth of Carahá, and this value may cause adverse effects on aquatic biota, as well as possible source of contamination to the Guarani Aquifer that has several areas of outcrop of the Botucatu sandstone along the water basin, a place susceptible to discharge and recharge of water.

Figure 4 – Mean concentration of Cd, Cr, Cu, Pb and Zn in the sediment for the sampled points with their respective standard deviation (SD) and level of probability of adverse



Source: Authors

The mean concentration of Cr in sediment at the mouth of the Carahá River was above the level 2 proposed by Law 344/2005 of CONAMA (table II). The Carahá river is characterized as an urban river for having its route totally in urban area. In general, it is used as a receiver for all domestic and industrial effluents and for a multitude of debris coming from the surrounding residents along its extension within the city of Lages. In addition, it is worth mentioning that in the city of Lages, only 28.37% of sewage is treated according to the historical series of the National Sanitation Information System (SNIS, 2017), with urban rivers being the main destination of the population's effluents.

The main sources of Cr contamination come from the steel and alloy industries, cement industry, electroplating, tanneries, electronic waste disposal, textile industry, wood treatment, paints, among other sources (Carolin et al., 2017; Kobielska et al., 2018; Magro et al., 2013; Yang et al., 2022). The high standard deviation in Cr values may characterize both point contamination and that it occurs frequently. Therefore, programs of permanent monitoring of water quality and levels of contamination should be developed to avoid possible impacts on the environment and on public health.

Although Cr+3 is an essential micronutrient in human metabolism, the other forms are highly toxic. The Cr+6 form is carcinogenic, being found in the form of chromates, dichromates and chromic acid, and the ingestion of small amounts of these elements can lead to death. Cr+6 is about one hundred times more toxic than Cr+2 (Kobielska et al., 2018; Magro et al., 2013).

Hungen et al. (2013) carried out a study on the concentration of Cu and Zn in a group of 111 samples in different lithologies of the state of Santa Catarina, reaching a mean content of 29 (mg kg^{-1}) of Cu and 39 (mg kg^{-1}) of Zn. The Cu and Zn values for the control points (P1 and P7) were lower than the mean content found by the authors. The points P4 (upstream of the Caveiras river), P6 (center of the Caveiras river) and P8 (center of the Ponte Grande river) presented copper contents and the points P2 (center of the Carahá river), P3 (downstream of the Carahá river), P4 (upstream of the Caveiras river), P5 (center of the Caveiras river), P6 (downstream of the Caveiras river) and P8 (center of the Ponte Grande river) presented contents of Zn above the values found by Hugen et al. (2013).

The mean contents of copper and zinc found above the level 1 of CONAMA's resolution No. 344/04 (figure II) may be associated with the use of pesticides, improperly disposal of kitchen utensils and batteries (Kobielska et al., 2018; Soleimani et al., 2023).

On the other hand, the values of lead above this threshold found in the central section of the Carahá and Ponte Grande rivers and downstream of the Caveiras river may be associated with the disposal of metal alloys, batteries, plastics, glass and inks (Carolin et al., 2017; Kobielska et al., 2018; Haghnazar et al., 2023). Lead has an extremely high toxicity potential, ranking second among the 275 priority pollutants proposed by the Agency for Toxic Substances and Disease Registry (ATSDR, 2013).

The first two axes of the principal component analysis (Figure V) accounted for 74.8% of the variation in the measured environmental data. The first axis explained 54.5% of the data variability and was associated to the indicative variables of the concentrations of metals (Cd, Cu, Pb, Zn), separating the samples collected at the springs (P1 and P7), which have less impact of anthropogenic activities. Axis 2 explained 20.3% of the data variation and was associated with the electrical conductivity and sediment composition (percentage of clay). Points P4 and P6 had a higher proportion of clay and a higher value of electrical conductivity in P9.

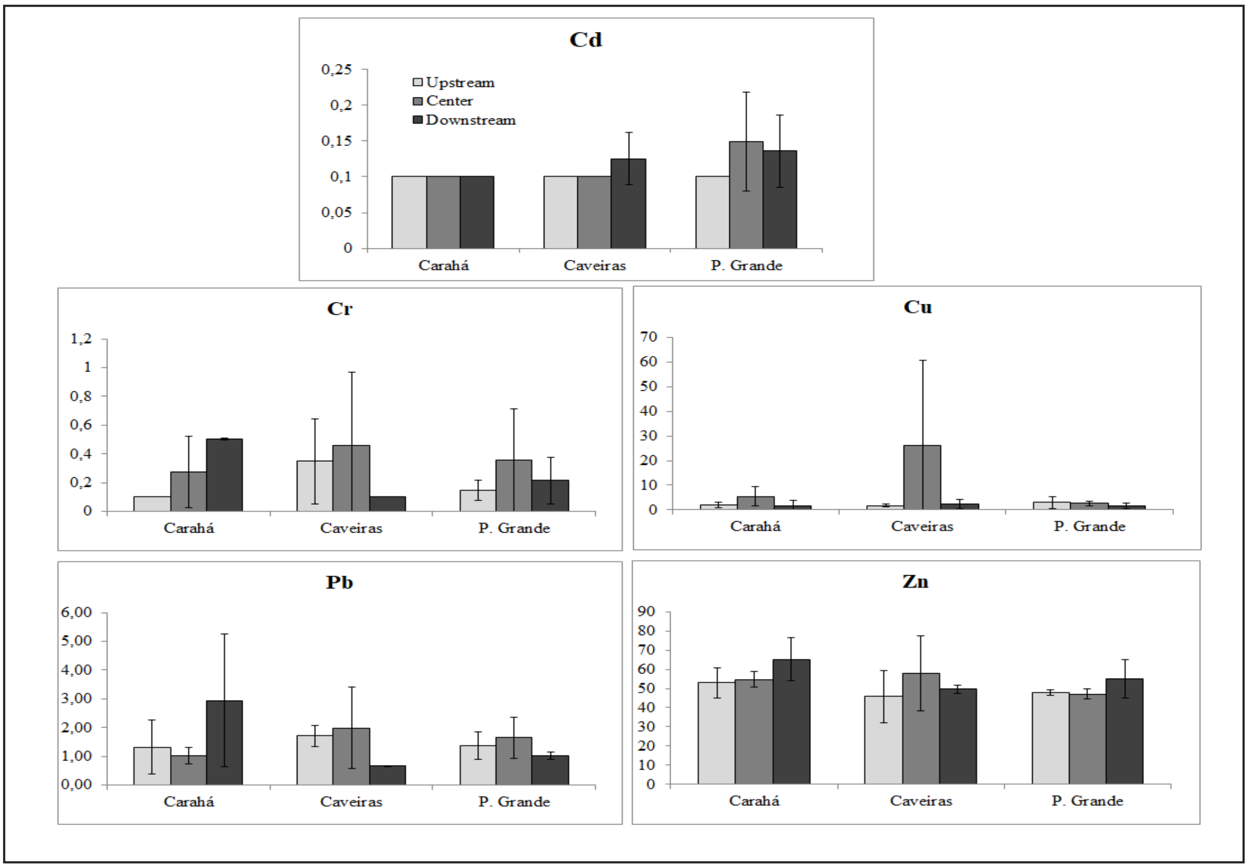
3.2 Metals in the water

In the samples of water, the mean concentrations of Cd, Cr, Cu, Pb and Zn (Figure 5) classified the rivers as class I for the evaluated parameters according to CONAMA's resolution nº. 357 (table III). The concentrations of metals found in the water were very low and were not correlated with the concentration of metals in the sediment for this study, probably due to the effects of natural filtration, dilution and transport of contaminants in the water.

The low concentration can also be explained by the natural filtration process of the water when passing through the layers of soil and rock, the sustainable minerals and metals in the water can be retained and filtered by these statements, sincerely their concentration. Carasek et al. (2020) when analyzing water from wells in the region covered by the Guarani aquifer in southern Brazil, also found low concentration values of Cd, Cu, Pb and Zn.

Another factor that may contribute to the low concentration of metals in water is bioaccumulation. The bioaccumulation of metals is a complex phenomenon that occurs when metallic substances accumulate in the tissues of living organisms. This accumulation can result in adverse effects for both organisms and the environment in general. Haghnazar et al. (2023) evaluated the bioaccumulation of metals in rice crops in northern basins in Iran and reports the absorption of metals such as Cu, Cr, Zn and Pb in rice crops, highlighting the reduced availability of these elements in the environment.

Figure 5 – Mean concentration of Cd, Cr, Cu, Pb and Zn in the water of the sampled points with their respective standard deviation (SD) – [μmg L^{-1}]



Source: Authors

As in the sediment, there was an increase in the concentration of chromium in the Carahá river from upstream to downstream in the water. Nevertheless, the similarity analysis with subsequent grouping for the parameters evaluated in the water did not show significant differences among the sampled points, however, with a concentration below the threshold established in class I of CONAMA's resolution nº. 357 (Figure 5), while for the sediment a concentration above the threshold established by Level II of CONAMA's resolution No. 344 was recorded (Figure 4) (Brasil, 2005).

Sediments may accumulate higher toxic metal concentrations than in the water column. The sediment particles adsorb organic and inorganic substances by means of physical and chemical factors, reducing their mobility and the effects of dilution and transport and making contamination persistent (Tao et al., 2023; Soleimani et al., 2023). The differences in the concentration of the evaluated parameters in water and sediment show that sediment analysis is a more accurate aquatic evaluation tool than the evaluation of metals in water. This highlights the importance of sediment monitoring for evaluating the quality of aquatic ecosystems.

4 CONCLUSIONS

The use of sediment as an environmental matrix for evaluating the enrichment of potentially toxic metals proved to be much more efficient due to the effects of natural filtration, dilution and transport of contaminants in the water. The principal component analysis showed the separation of the sediment samples in two groups, the points used as control (P1 and P7) and the points (P2, P3, P4, P5, P6, P8 and P9) that presented higher concentrations, indicating that the concentrations of such metals accumulate according to a gradient of contamination of the water basins (from upstream to downstream of the urban area). A concentration of Cr above the level II proposed by the Brazilian legislation (344/2004 of CONAMA) was found in the mouth of Carahá, and this value may bring adverse effects to the aquatic biota, which suggests future ecotoxicological studies for the concentration of chromium and monitoring of heavy metals, especially in sections downstream from urban centers.

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