

# Factors influencing the contamination of urban sediments in the Barigüi River, southern Brazil

Fatores que influenciam a contaminação de sedimentos urbanos no rio Barigüi, sul do Brasil

Paulo Roberto Bairros da Silva<sup>1</sup> , Cleyton Nascimento Makara<sup>2</sup> ,  
Ana Paula Munaro<sup>3</sup> , Lurian Aparecida Domingos da Cruz<sup>3</sup> ,  
Arci Dirceu Wastowski<sup>1</sup> , Danielle Caroline Schnitzler<sup>3</sup> 

<sup>1</sup>Universidade Federal de Santa Maria – UFSM, Santa Maria, RS, Brasil. E-mails: paulo.bairros-silva@ufsm.br, wastowski@ufsm.br

<sup>2</sup>Universidade de São Paulo – USP, São Carlos, SP, Brasil. E-mail: cleyton186@hotmail.com

<sup>3</sup>Universidade Tecnológica Federal do Paraná – UTFPR, Curitiba, PR, Brasil. E-mails: anapaulamunaro@hotmail.com, lurian.2016@alunos.utfpr.edu.br, daniellec@utfpr.edu.br

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**ABSTRACT:** Due to their storage characteristics and the distribution of chemical elements, sediments can influence the dynamics of aquatic ecosystems, exchange species with the water column, and affect water quality. Assessing the behavior of sediments in relation to potential environmental stressors is essential for the management of urban water systems. In this study, we analyzed sediments from the Barigüi River, which flows through the third-largest industrial region in Brazil to assess its quality by identifying and differentiating contamination by chemical elements of anthropogenic origin. We determined trace concentrations of Cu (47.3 to 55.7 mg·kg<sup>-1</sup>), Zn (60.6 to 92.0 mg·kg<sup>-1</sup>), Mn (195.6 to 538.1 mg·kg<sup>-1</sup>), and Zr (414.0 to 958.1 mg·kg<sup>-1</sup>), as well as major mineral oxide concentrations of Al<sub>2</sub>O<sub>3</sub> (3.6 to 4.4%), Fe<sub>2</sub>O<sub>3</sub> (1.3 to 3.2%), TiO<sub>2</sub> (0.2 to 28.5%), K<sub>2</sub>O (0.5 to 0.8%), and CaO (0.4 to 0.8%) in the fine fractions (< 63 µm) of bottom sediment samples. Analyses were conducted using the Energy Dispersive X-Ray Fluorescence Spectrometry (ED-XRF) technique. We also characterized environmental quality indexes, including the Contamination Factor, Pollution Load Index, Enrichment Factor, and Geo-accumulation Index. These indexes suggest possible sediment contamination, particularly by TiO<sub>2</sub> and K<sub>2</sub>O. Spatial variations in sediment quality along the Barigüi River were evident, indicating that the presence of these elements may contribute to episodic toxicity and deleterious effects on the ecosystem.

**Keywords:** Sediment Quality; Geochemical Quality Index; ED-XRF.

**RESUMO:** Devido às suas características de armazenamento e distribuição de elementos químicos, os sedimentos podem influenciar a dinâmica dos ecossistemas aquáticos, promover a troca de espécies com a coluna d'água e afetar a qualidade da água. Avaliar o comportamento dos sedimentos em relação a seu potencial estressores ambiental é essencial para a gestão de sistemas hídricos urbanos. Neste estudo, analisamos sedimentos do rio Barigüi, que atravessa a terceira maior região industrial do Brasil, para avaliar sua qualidade por meio da identificação e diferenciação da contaminação por elementos químicos de origem antropogênica. Determinamos concentrações residuais de Cu (47,3 a 55,7 mg·kg<sup>-1</sup>), Zn (60,6 a 92,0 mg·kg<sup>-1</sup>), Mn (195,6 a 538,1 mg·kg<sup>-1</sup>) e Zr (414,0 a 958,1 mg·kg<sup>-1</sup>), bem como concentrações de óxidos minerais principais de Al<sub>2</sub>O<sub>3</sub> (3,6 a 4,4%), Fe<sub>2</sub>O<sub>3</sub> (1,3 a 3,2%), TiO<sub>2</sub> (0,2 a 28,5%), K<sub>2</sub>O (0,5 a 0,8%) e CaO (0,4 a 0,8%) nas frações finas (< 63 µm) de amostras de sedimentos de fundo. As análises foram realizadas utilizando a técnica de Espectrometria de Fluorescência de Raios X por Dispersão de Energia (ED-XRF). Também caracterizamos índices de qualidade ambiental, incluindo o Fator de Contaminação, o Índice de Carga Poluente, o Fator de Enriquecimento e o Índice de Geoacumulação. Esses índices sugerem possível contaminação dos sedimentos, particularmente por TiO<sub>2</sub> e K<sub>2</sub>O. Variações espaciais na qualidade dos sedimentos ao longo do rio Barigüi foram evidentes, indicando que a presença desses elementos pode contribuir para toxicidade episódica e efeitos deletérios no ecossistema.

**Palavras-chave:** Qualidade dos Sedimentos; Índice de Qualidade Geoquímica; ED-XRF.

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## INTRODUCTION

The sediments are environmental matrices with a porous structure, polygranular composition (formed by organic and inorganic fractions), and complex multi-elemental characteristics, resulting from various interactions occurring within aquatic ecosystems (Wang et al., 2023; Silva et al., 2019; Martínez et al., 2016). The sediments play a crucial role in the storage and dispersion of compounds and in the functioning of water systems, while also potentially acting as environmental stressors for ecosystems (Silva et al., 2019, 2023; Ali et al., 2022; Wang et al., 2021).

The contamination of sediments by inorganic chemical elements (metals, nonmetals, semimetals) can cause deleterious effects on aquatic ecosystems due to their toxicity, persistence, and bioavailability (Silva et al., 2025; Jia et al., 2023; Mizel et al., 2020). As an active environmental compartment, sediments are capable of accumulating and resuspending metals, nutrients, pharmaceuticals, pesticides, and emerging contaminants, among others, affecting the quality of the water column (Silva et al., 2023; Vergilio et al., 2020; Fagnani et al., 2011).

In urban watersheds, the concentrations of chemical elements accumulated in sediments are generally higher than natural geological background levels and may pose significant risks to ecosystems, as sediments tend to exchange contaminants with the water column, thereby affecting water quality (Wang et al., 2022, 2023). Strategies for assessing sediment quality in relation to the presence of chemical elements have advanced over the past decade, employing various methodological approaches (Silva et al., 2023; Tiwari et al., 2020; Martínez et al., 2016).

In Brazil, the assessment of water resource quality remains primarily focused on physical, chemical, and microbiological parameters of the water column, as established by the National Environmental Council (CONAMA) through Resolutions 357/2005 and 430/2011 (Brasil, 2012). Although CONAMA Resolution 454/2012 (Brasil, 2012) provides general guidelines and procedures for sediment assessment, its application is mainly restricted to dredged materials from water systems. Consequently, Brazil lacks standardized reference values for sediment quality assessments, limiting the ability to comprehensively evaluate the effects of contamination on aquatic ecosystems (Cervi et al., 2021; Fagnani et al., 2011; Silva et al., 2017, 2019, 2023).

In southern Brazil, the metropolitan region of Curitiba has a population exceeding 3.5 million inhabitants and comprises 29 municipalities, making it one of the largest urban areas in the country (Agência de Assuntos Metropolitanos do Paraná, 2024; Curitiba, 2018). In this region, urban rivers such as the Barigüi River serve as conduits for effluents from densely industrialized areas and irregularly populated regions that lack basic sanitation infrastructure (Instituto Brasileiro de Geografia e Estatística, 2024; Leithold et al., 2020; Curitiba, 2019).

In the absence of established reference values, sediment quality is commonly assessed using environmental indexes, employing background concentrations of chemical elements in situ as a decision-making tool for water resource management (Ali et al., 2022; Silva et al., 2023; Vergilio et al., 2020; Wang et al., 2022).

This study innovates by characterizing and quantifying major mineral oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{K}_2\text{O}$  and  $\text{CaO}$ ) and chemical elements (Zr, Mn, Zn and Cu) in fine fractions of sediment samples from the Barigüi River using the instrumental analysis technique Energy Dispersive X-ray Spectrometry (ED-XRF), which has not yet been established in previous studies (Melquiades et al., 2024; Santos et al., 2024). Recent advancements in ED-XRF technology, particularly with the new generation of compact silicon drift detectors (SDDs), have improved the signal-to-noise ratio and instrumental detection limits, allowing for the determination of toxic element concentrations even at trace levels in environmental samples (Tiwari et al., 2020; Silva et al., 2019).

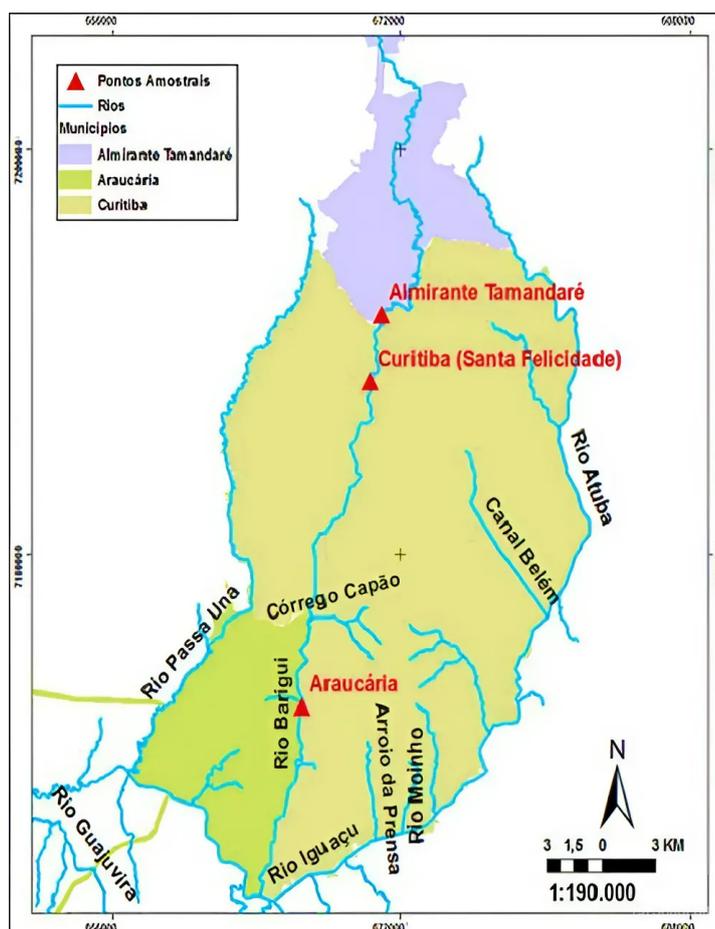
Accordingly, this study aimed to evaluate the quality of sediments from the Barigüi River using environmental quality indexes namely the Contamination Factor, Pollution Load Index, Enrichment Factor, and Geo-accumulation Index by quantifying major chemical elements through Energy Dispersive X-Ray Fluorescence Spectrometry (ED-XRF) differentiating contamination by chemical elements of anthropogenic origin. Additionally, these results can be integrated into statistical models to identify significant relationships between chemical elements and spatially differentiate their average concentrations at sampling points.

## EXPERIMENTAL

### Study area

The Barigüi River is located in the metropolitan region of Curitiba, in the state of Paraná, southern Brazil. It has an area of 267 km<sup>2</sup>, a length of 66 km, and an average flow rate of 4.8 m<sup>3</sup>.s<sup>-1</sup>, crossing the

municipal boundaries of Almirante Tamandaré (AT), where its headwaters are located; Curitiba, in the district of Santa Felicidade (SF); and the municipality of Araucária, which houses one of the largest industrial districts in the state of Paraná (Leithold et al., 2020; Machado et al., 2020; Curitiba, 2018; Silva et al., 2017; Froehner & Martins, 2008). The upstream region of the river, in the municipality of Almirante Tamandaré ( $25^{\circ}22'49.5''$  S and  $49^{\circ}18'3.7''$  W), is predominantly rural, with small scattered urban areas. The central portion of the river, in the municipality of Curitiba, located in the district of Santa Felicidade ( $25^{\circ}24'37.4''$  S and  $49^{\circ}18'24.7''$  W), was chosen due to its high urban density, with numerous commercial establishments and services. The Figure 1 shows the Barigüi River - PR and the location of the surface sediment sampling stations.



**Figure 1.** Geographical location of the sampling points in the municipality of Araucária (A); municipality of Curitiba, district of Santa Felicidade (SF); municipality of Almirante Tamandaré (AT) and limits of study area of the Barigüi River (Adapted: Silva et al., 2017).

The downstream region, in the municipality of Araucária ( $25^{\circ}33'20.56''$  S and  $49^{\circ}20'32.70''$  W), is predominantly industrial and includes the Curitiba Industrial City (CIC), part of the Araucária Industrial City (ICAR), and the Petrobras Refinery (REPAR). Additionally, the industrial zones have attracted various regular and irregular occupations, small metallurgical industries, and service providers (Leithold et al., 2020; Curitiba, 2018; Silva et al., 2016; Froehner & Martins, 2008).

This water system originates in a region with small rural properties, crosses the western zone of the city of Curitiba, where it encounters greater urbanization, and drains densely populated areas with intense industrial activity. This makes the choice of sampling points representative of areas with different land uses and occupations, with different degrees of urbanization and under different anthropogenic pressures (Silva et al., 2017, 2023; Vergilio et al., 2020).

Currently, 766 industries are installed in the ICAR, with a strong presence of the oil and gas sector, as well as large companies manufacturing wooden panels for the furniture industry, plastic, metalworking, rolling mills, enzyme production, transport companies, and other industrial sectors. In 2023, ICAR was recognized as the largest industrial hub in the state of Paraná, generating R\$ 36.6 billion in state taxes, surpassing the capital, Curitiba, which collected R\$ 16.1 billion (Popular do Paraná, 2023; Silva, 2006).

The watershed is part of the Curitiba Sedimentary Basin Geological Formation (composed of gneiss, quartzite, quartzite-schist, mica-schist, amphibolite, gneiss-granite, and granulite), with a relatively flat relief compared to the surrounding areas (Serra do Mar and the dissected zone of the Açungui Group). The Barigüi River exhibits a sub dendritic drainage pattern, embedded in NW-SE fractures, with asymmetric valleys, eroded fault scarps, and gentle slopes (Salamuni et al., 2013).

The region's subtropical climate (hot summers and cold winters, with well-distributed rainfall throughout the year) has an average annual temperature of approximately 17 °C and a rainfall index of 1,200 mm/year (Curitiba, 2007). Using satellite images and geoprocessing techniques, Leithold et al. (2020) identified the loss of wetland areas, reduction of vegetation and forests, as well as urban expansion and increased soil impermeabilization in the Barigüi River Basin between 1999 and 2019.

### Sample collection and handling

All collection, storage, and handling containers were cleaned following a rigorous protocol, including a 24-hour soak in 10% detergent, followed by three washes with distilled water. Subsequently, they were immersed in a 10% nitric acid bath for 24 hours, followed by five washes with ultrapure water and air drying at room temperature. All reagents and standards used in the chemical analyses were of analytical grade, and the solutions were prepared with ultrapure water from a Direct-K 8UV system (Millipore brand).

Surface sediment samples (2 kg) were collected following technical cleaning protocols using a Petersen grab sampler. They were stored in double polypropylene bags, labeled, and kept in a refrigerated cooler until arrival at the laboratory (Agência Nacional de Águas, 2024). The sampling procedure ensured representativity of the region, with samples taken from the river's cross-section (banks and center), resulting in a total of 15 sediment samples from the three collection points (Figure 1, points in red).

The samples were homogenized in polypropylene trays using plastic spatulas and dried in circulation ovens at 50 °C for 48 hours. Subsequently, they were disaggregated in a mortar and separated by granulometry using magnetic sieves, with the fine fraction (< 63 µm) designated for analysis by ED-XRF.

### Instrumental analysis

Energy Dispersive X-ray Fluorescence Spectrometry (ED-XRF) allows for the quantification of major inorganic species in solid environmental samples, such as soil and sediments, eliminating the need for sample digestion (Agbogun et al., 2024; Tiwari et al., 2020; Silva et al., 2019). The sediment samples were placed in a support covered with a thin Mylar® film and analyzed using a Shimadzu EDX-720 instrument (irradiation time of 200 s, air atmosphere, rhodium (Rh) source with voltage up to 50 keV, Si (Li) semiconductor detector, 10 mm collimator).

The analyses aimed to establish a multi-elemental profile of the main chemical constituents in the fine fraction (< 63 µm), comparing them to a certified reference material (Supplementary Figure S1).

### Environmental quality indices

To improve the assessment of chemical element levels in aquatic system sediments in regions without established guidelines, it is essential to use local background values (Silva et al., 2019, 2023). The use of these average values allows for the calculation of environmental quality indices, which are widely used in sediment quality assessments (Ali et al., 2022; Wang et al., 2021; Silva et al., 2019).

In this study, background values were obtained from the Geochemical Atlas of the Curitiba Sheet, provided by the public company Minerais do Paraná S.A. (Curitiba, 2001). The indices analyzed include:

#### Contamination factor

The Contamination Factor (FC) is a geochemical tool that allows evaluating individually the contamination of sediments to some given chemical elements (Ali et al., 2022; Silva et al., 2019; Martínez et al., 2016). The (FC) is the concentration of each chemical elements in the sediment divided by the value of the bottom sediments (background) not contaminated, according to Equation 1.

$$FC = \frac{C_{Sediment}}{C_{Background}} \quad (1)$$

The scores generated in the FC were suggested by Hakanson (1980). In this study, background values were obtained from the Geochemical Atlas of the Curitiba Sheet, provided by the public company Minerais do Paraná S.A. (Curitiba, 2001). The Table 1 presents the weights of the Contamination Factor.

**Table 1.** Rating and scores of Contamination Factor (FC).

Scores	Rating
FC < 1	low contamination
1 < FC < 3	moderately contaminated
3 < FC < 6	considerable contamination
FC ≥ 6	very high contaminations

### Pollution load index

The Pollution Load Index (PLI) refers to the number of times that the concentration of chemical elements in the sediment exceeds the background concentration. The PLI provides a general indication of the general level of toxicity in a particular sample (Ali et al., 2022; Martínez et al., 2016). The PLI is defined according to Equation 2.

$$PLI = (FC_1 \times FC_2 \times FC_3 \times \dots \times FC_n)^{\frac{1}{n}} \quad (2)$$

where FC is the contamination factor, n is the used number of chemical elements. This empirical index provides a simple comparison to assess the level of pollution by chemical elements. When  $PLI \geq 1$ , there is pollution; otherwise, if  $PLI < 1$ , there is no pollution by a specific element.

### Enrichment factor

The Enrichment Factor (EF), according to Equation 3, was established to indicate the possible anthropogenic contribution of chemical elements in the sediment (Vergilio et al., 2020; Martínez et al., 2016).

$$EF = \frac{[Element\ in\ the\ Sample] / [Al\ in\ the\ Sample]}{[Element\ Background] / [Al\ Background]} \quad (3)$$

It is defined as the ratio between the concentration of elements in the sample and the background concentration of the same element. The reference factor or normalizer is usually the average of aluminum content in the study environment, as well as in the area of natural reference, background (Mizel et al., 2020). In the study, aluminum was adopted as normalizer element, being abundant in the matrix and its relative proportion of concentration is considered constant.

The scores generated in the equation suggest that for  $EF > 1$  there is contribution of chemical elements for the hydrous body (Silva et al., 2023; Martínez et al., 2016). In this study, background values were obtained from the Geochemical Atlas of the Curitiba Sheet, provided by the public company Minerais do Paraná S.A. (Curitiba, 2001).

### Geo-accumulation index

The Geo-accumulation Index ( $I_{Geo}$ ) indicates the level of background contamination by sediment (Muller, 1981) and is expressed according to Equation 4.

$$I_{Geo} = \log_2 \left( \frac{C_n}{1,5 \times B_n} \right) \quad (4)$$

In which:  $C_n$  is the value of concentration, and  $B_n$  is the geochemical background concentration of the kind of the chemical elements of "n". The factor of 1.5 is a constant that helps with the lithological variability (Silva et al., 2023; Vieira et al., 2019; Martínez et al., 2016). The Table 2 defined classes of  $I_{Geo}$ .

In this study, background values were obtained from the Geochemical Atlas of the Curitiba Sheet, provided by the public company Minerais do Paraná S.A. (Curitiba, 2001).

**Table 2.** Class, rating and scores of Geo-accumulation Index.

Class	Scores	Rating
0	$I_{Geo} \leq 0$	virtually pollution-free
1	$0 < I_{Geo} \leq 1$	pollution-free to moderately polluted
2	$1 < I_{Geo} \leq 2$	moderately polluted
3	$2 < I_{Geo} \leq 3$	moderately to heavily polluted
4	$3 < I_{Geo} \leq 4$	heavily polluted
5	$4 < I_{Geo} \leq 5$	heavily polluted to polluted
6	$5 < I_{Geo} \leq 6$	Polluted
	$6 > I_{Geo}$	extremely polluted

### Statistical and graphical methods

The free and open-source software PAST - PALEontological Statistics (Version 4.17), developed by Hammer (2024), was used to perform the Kolmogorov-Smirnov Normality tests (assesses whether data follow a normal Gaussian distribution), Pearson’s correlation (measures the linear relationship between quantitative variables), cluster multivariate analysis (a statistical method used to group objects based on their similarities), cross-dependency tables (analyzes the relationship between two or more categorical variables), and discriminant analysis (separates and classifies objects into predefined groups). The graphs were constructed using SciDAVis software (SourceForge, 2024). Basic statistical values were obtained using Microsoft Excel.

## RESULTS AND DISCUSSION

### Concentrations of chemical elements in the sediments by ED-XRF

Table 3 presents the concentrations of chemical elements in the sediment samples at each sampling point. These results were obtained after the removal of significant outliers ( $p < 0.05$ ) using the Grubbs test (Supplementary Table S1).

**Table 3.** Average concentration of majority chemical elements obtained in thin fractions ( $< 63 \mu\text{m}$ ) by EDXRF.

Mineral oxides (%)	(A)		(SF)		(AT)	
	$\bar{x}$	CV	$\bar{x}$	CV	$\bar{x}$	CV
$\text{Al}_2\text{O}_3$	4.0	5.7	3.6	4.8	4.9	5.0
$\text{Fe}_2\text{O}_3$	3.2	3.8	1.3	1.1	2.5	2.1
$\text{TiO}_2$	1.2	4.4	0.6	1.1	5.2	5.4
$\text{K}_2\text{O}$	0.8	1.9	0.5	1.1	0.6	1.4
$\text{CaO}$	0.4	2.7	0.4	1.2	0.8	1.1
Elements ( $\text{mg kg}^{-1}$ )						
Zr	958.1	10.8	414.7	1.0	420.0	2.4
Mn	538.2	5.3	195.6	2.9	307.1	3.6
Zn	91.0	6.9	92.0	4.0	60.6	1.6
Cu	55.4	4.7	47.3	5.5	55.7	9.6

(A) = Araucária point; (SF) = Santa Felicidade point; (AT) = Almirante Tamandaré point.

Studies have demonstrated the influence of clay minerals, hydroxides, and hydrated oxides of Fe and Mn in controlling the transport and resuspension of trace metals in sediments (Agbogun et al., 2024; Silva et al., 2023; Curitiba, 2001). These minerals may originate from chemical weathering or anthropogenic industrial activities. In these minerals, element adsorption is predominant due to their cation exchange capacity, which is influenced by pH variations (Agbogun et al., 2024; Souza et al., 2015; Curitiba, 2001). In our sediment samples, the average concentrations of iron oxides are higher at the Araucária sampling point (A) compared to other sampling points, reinforcing the idea of external contributions.

The significant influence of  $TiO_2$ ,  $K_2O$ , and Zr, particularly in the Araucária (A) environment, is evident. The results exceed reference values, suggesting that these elements contribute to the water system. The presence of these elements may be related to industrial activities in the region, where  $TiO_2$  is used in white pigment production for paints, paper bleaching, and plastic manufacturing.  $K_2O$  is employed in agricultural fertilizers and toiletries, while Zr is used in refractory materials, ceramics, and glass production. Currently, the Cidade Industrial neighborhood of Curitiba has 18,439 companies and an estimated population of 172,822 inhabitants with a focus on metalworking, textiles, and processed foods (Curitiba, 2024).

At the AT sampling point, the high concentrations of CaO stand out. This compound is abundant in soils from regions with industrial activities linked to lime extraction for agricultural use (Machado et al., 2020; Froehner & Martins, 2008; Curitiba, 2001). These results were evaluated using statistical models and were also used in the generation of environmental indices.

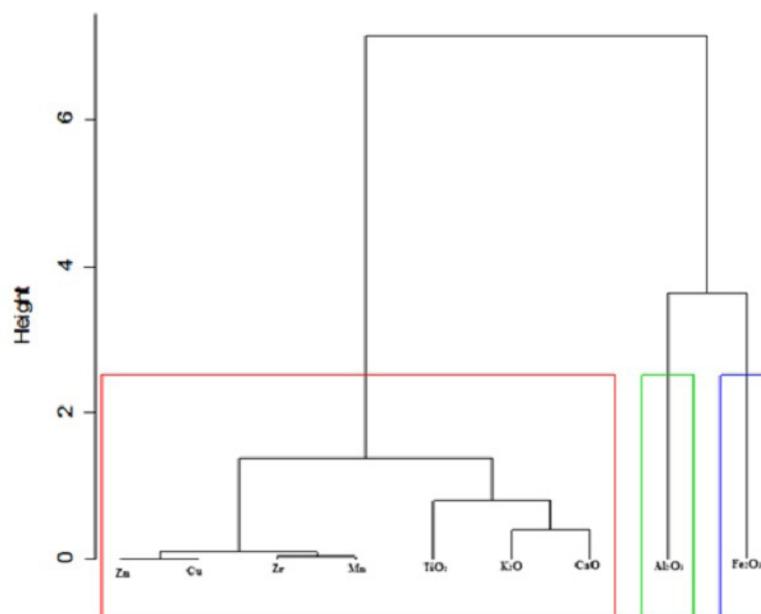
### Statistical models with ED-XRF data

The Kolmogorov-Smirnov normality test was applied to the dataset obtained from the ED-XRF analysis of the fine sediment fractions (Supplementary Table S2). The data distribution follows a Gaussian function, allowing the application of parametric statistical methods such as Pearson's correlation, cluster multivariate analysis, cross-dependency tables, and discriminant analysis. Pearson's correlation analysis was used to identify potential factors controlling the distribution of chemical elements in the sediments. The Pearson correlation matrix is presented in Table 4.

**Table 4.** Pearson's Correlation Matrix test (95% confidence,  $p > 0.05$ ).

	$Al_2O_3$	$Fe_2O_3$	$TiO_2$	$K_2O$	CaO	Zr	Mn	Zn	Cu
$Al_2O_3$	1.0								
$Fe_2O_3$	0.4	1.0							
$TiO_2$	-0.3	0.8	1.0						
$K_2O$	0.3	1.0	0.8	1.0					
CaO	1.0	0.2	-0.5	0.1	1.0				
Zr	-0.2	0.8	1.0	0.9	-0.4	1.0			
Mn	0.1	1.0	0.9	1.0	-0.1	1.0	1.0		
Zn	-1.0	-0.2	0.5	-0.1	-1.0	0.5	0.2	1.0	
Cu	0.8	0.9	0.4	0.9	0.6	0.5	0.8	-0.5	1.0

The correlation matrix highlights strong correlations between  $K_2O$  and  $Fe_2O_3$  ( $r = 1.0$ ),  $K_2O$  and  $TiO_2$  ( $r = 0.8$ ), Ca and  $Al_2O_3$  ( $r = 1.0$ ), Zr and  $Fe_2O_3$  ( $r = 0.8$ ), Zr and  $TiO_2$  ( $r = 1.0$ ), Zr and  $K_2O$  ( $r = 0.9$ ), Mn and  $Fe_2O_3$  ( $r = 1.0$ ), Mn and  $TiO_2$  ( $r = 0.9$ ), Mn and  $K_2O$  ( $r = 1.0$ ), Mn and Zr ( $r = 1.0$ ), Cu and  $Fe_2O_3$  ( $r = 0.9$ ), and Cu and  $K_2O$  ( $r = 0.9$ ), with 95% confidence ( $p > 0.05$ ). The strong correlations between  $Fe_2O_3$ , Mn, and  $TiO_2$ , among themselves and with other metal species, suggest their role in controlling the distribution of chemical elements in these sediments. Cluster multivariable analysis using the hierarchical method was employed to identify groups of samples based on similarities or differences. This method characterizes sediment groups according to their geochemical composition (Silva et al., 2019, 2023; Wang et al., 2021). Figure 2 shows the dendrogram of the clusters.



**Figure 2.** Clustered multivariable analysis by hierarchical method and similarity of Euclidian distances.

The clusters were generated using the “Complete with Euclidean distances” method, forming two distinct groups based on similarity. This suggests that the chemical elements within each group have similar geochemical characteristics.

Dissolved Fe can precipitate due to variations in pH and/or Eh, leading to hydrated oxide coatings (goethite, limonite, and alumina) on mineral and rock fragments in bottom sediments. Aluminum oxides (present in feldspar and mafic minerals) are susceptible to weathering, forming residual sediments that become adsorbed onto clay minerals (Silva et al., 2023; Santos, 2013; Curitiba, 2001).

These findings align with the Pearson correlation results for Mn and Zr, TiO<sub>2</sub> and K<sub>2</sub>O, Zr and TiO<sub>2</sub>, Zr and K<sub>2</sub>O, Mn and TiO<sub>2</sub>, Mn and K<sub>2</sub>O, Mn and Zr, and Cu and K<sub>2</sub>O. The statistical analyses indicate that Fe and Mn play a crucial role in controlling the distribution of inorganic chemical elements in the sediments of the Barigüi River.

### Environmental Quality Index of the Sediments

The results of the FC and IGEO indices for the different sampling points of the Barigüi River are presented in Table 5, background in the Supplementary Table S3.

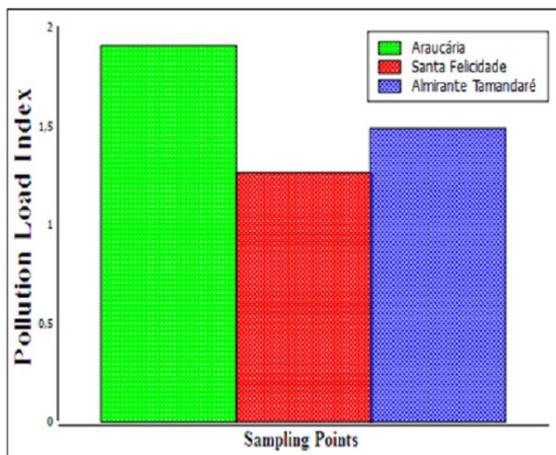
**Table 5.** Environmental quality index for the sediments of the Barigüi River.

Mineral oxides (%)	Background	(A)		(SF)		(AT)	
	$\bar{x}$	FC	I <sub>TGO</sub>	FC	I <sub>TGO</sub>	FC	I <sub>TGO</sub>
Al <sub>2</sub> O <sub>3</sub>	1.7	2.3	0.6	2.1	0.5	2.8	0.9
Fe <sub>2</sub> O <sub>3</sub>	0.9	3.5	1.2	1.5	0.0	2.7	0.8
TiO <sub>2</sub>	0.2	61.6	5.2	28.5	4.2	26.4	4.2
K <sub>2</sub> O	0.1	8.0	5.7	4.6	1.6	6.3	2.1
CaO	1.6	0.3	-2.6	0.2	-2.7	0.5	-1.6
<b>Elements (mg kg<sup>-1</sup>)</b>							
Zr	1143.0	0.8	-0.8	0.4	-2.0	0.4	-2.0
Mn	550.0	1.0	-0.6	0.4	-2.1	0.6	-1.4
Zn	158.0	0.6	-1.4	0.6	-1.4	0.4	-2.0
Cu	35.0	1.6	0.1	1.4	-0.1	1.6	0.1

Background (Curitiba, 2001), (A) = Araucária; (SF) = Santa Felicidade; (AT) = Almirante Tamandaré.

The FC results (Figure 5) indicate intense contamination by  $TiO_2$  and  $K_2O$  at all collection points, considerable pollution by  $Al_2O_3$  and  $Fe_2O_3$ , and moderate contamination by Cu. The IGeo values reveal moderate pollution by Fe and heavy pollution by  $TiO_2$  and  $K_2O$  in Araucária. The sediments in Santa Felicidade show heavy to very heavy pollution by  $TiO_2$  and moderate pollution by  $K_2O$ . In Almirante Tamandaré, the sediments exhibit heavy to very heavy pollution by  $TiO_2$  and moderate to heavy pollution by  $K_2O$ .

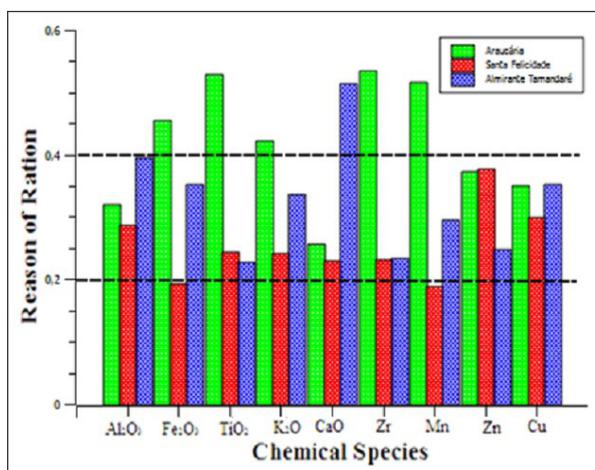
Iron and titanium oxides may be linked to industrial activities, as they are characteristic waste products of metallurgical, textile, pulp, and paper industries (Wang et al., 2022; Machado et al., 2020; Froehner & Martins, 2008; Curitiba, 2001). Titanium naturally occurs in oxide forms, often with oxygen and iron in minerals such as ilmenite, rutile, anatase, and leucoxene. Titanium dioxide ( $TiO_2$ ), abundant in the Earth's crust, is widely used in industrial applications for producing pigments in paints, paper, plastics, rubber, fibers, and varnishes (Agbogun et al., 2024; Silva et al., 2016; Curitiba, 2001).



**Figure 3.** Graph of the pollution load index established for the sampling points of Araucária (A); Santa Felicidade (SF); Almirante Tamandaré (AT).

The Pollution Load Index (PLI) was calculated to evaluate contamination levels at different points of interest. The results, shown in Figure 3, indicate  $PLI > 1$  at all points, confirming water system pollution, with significant contamination at the Araucária sampling point. The Enrichment Factor (EF) was used to identify potential anthropogenic contributions (Vergilio et al., 2020; Silva et al., 2019). The geochemical standardization process correlates chemical element concentrations with a reference element such as  $Al_2O_3$ ,  $Fe_2O_3$ , Li or Sc. These elements are considered geochemical markers due to their relative stability and minimal anthropogenic influence.

Figure 4 presents the cross-table dependency test, demonstrating uniform distribution of  $Al_2O_3$ , Zn, and Cu, while confirming concentration discrepancies for  $Fe_2O_3$ ,  $TiO_2$ , Zr, and Mn at the Araucária sampling point and CaO at Almirante Tamandaré.



**Figure 4.** Graph of the cross-table (dependency) established for the sampling points of Araucária (A); Santa Felicidade (SF); Almirante Tamandaré (AT).

Silva et al. (2019) applied the geochemical indices contamination factor (FC), enrichment factor (FE), and geoaccumulation index (IGeo) to assess the sediment quality of the Várzea River in northwestern Rio Grande do Sul state. The study demonstrated the input and moderate contamination of the sediments with Cu, Ba, Zn, and TiO<sub>2</sub>. Santos et al. (2024) applied the geochemical indices enrichment factor (FE) and geoaccumulation index (IGeo) to evaluate the sediment quality of the Turvo State Park in Rio Grande do Sul. The study demonstrated the natural input of sediments from areas outside the park.

The discriminant analysis, presented in Figure 6, grouped elements into distinct categories corresponding to different sampling locations.

The results highlight the importance of investigating not only trace elements in fine fractions but also major mineral oxides (Table 6).

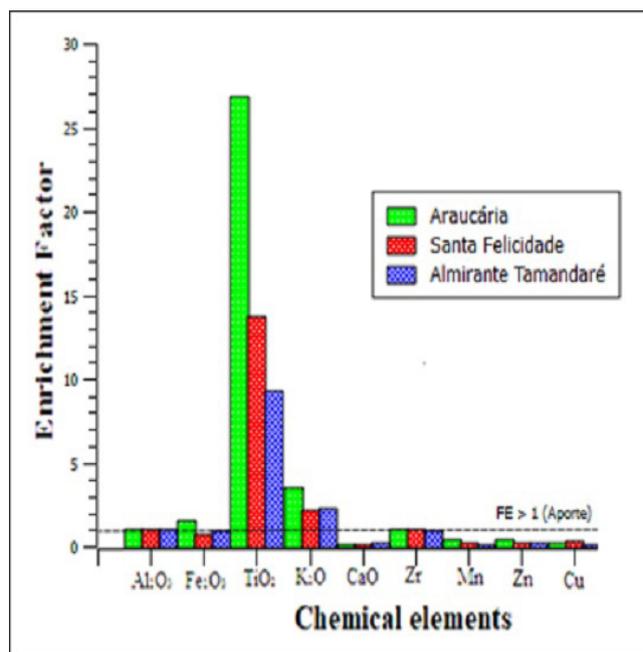


Figure 5. Graph of the enrichment factor established for the sampling points of Araucária (A); Santa Felicidade (SF); Almirante Tamandaré (AT).

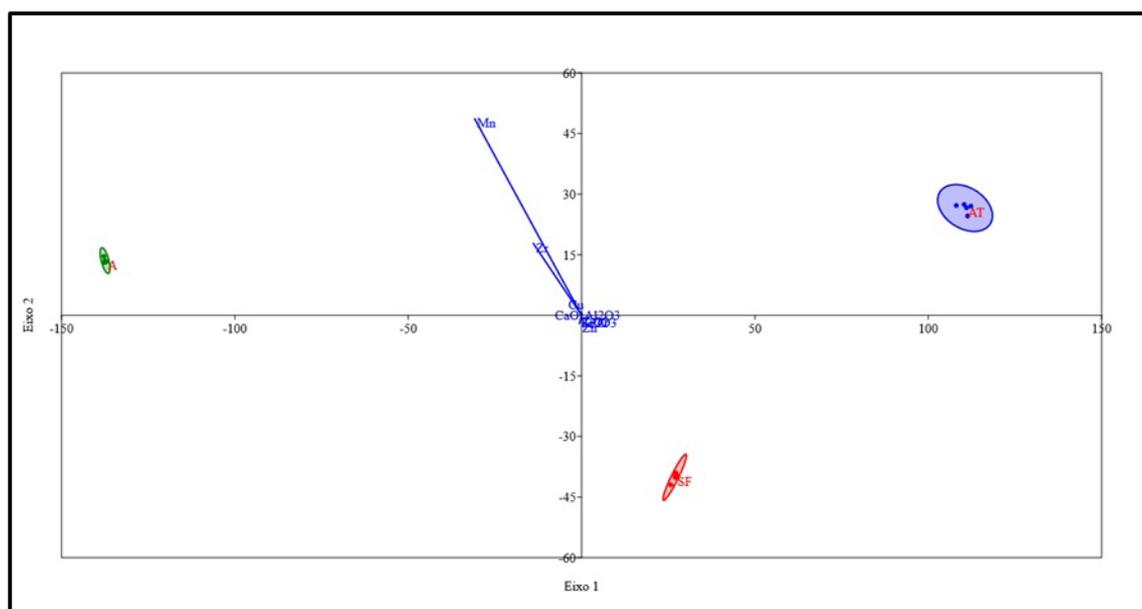


Figure 6. Graph of the Discriminant analysis for the sampling points of Araucária (A); Santa Felicidade (SF); Almirante Tamandaré (AT).

**Table 6.** Discriminant analysis scores and loadings.

ESCORES					
	Axis 1	Axis 2		Axis 1	Axis 2
1	-137.1	13.3	Al <sub>2</sub> O <sub>3</sub>	0.002754	0.016639
2	-137.8	14.6	Fe <sub>2</sub> O <sub>3</sub>	-0.00386	0.022848
3	-137.3	13.2	TiO <sub>2</sub>	0.013246	0.051759
4	-137.6	13.0	K <sub>2</sub> O	-0.00088	0.002903
5	-137.5	13.6	CaO	0.001389	0.004255
6	27.0	-40.2	Zr	-2.3494	3.0051
7	25.7	-42.0	Mn	-5.2061	8.2124
8	27.4	-39.6	Zn	-0.104	-0.34094
9	27.2	-39.0	Cu	-0.00474	0.12865
10	27.0	-39.7	Axis	Eigval	Percent
11	111.0	26.6			
12	111.3	24.6	1	13270	92.73
13	110.3	27.4			
14	108.1	27.2	2	1040.6	7.272
15	112.3	27.0			

A 400-year sedimentary record of the Barigui River was investigated using fecal biomarkers by Machado et al. (2014a). Human fecal contamination in the Barigui River was observed more markedly from 1930 onwards due to the beginning of Curitiba's population growth associated with a lack of sanitary conditions, causing pollution of the water body by human sewage. Furthermore, Machado et al. (2014b) demonstrated the direct relationship between local socioeconomic development and the presence of polycyclic aromatic hydrocarbon (PAH) concentrations in a sediment core collected from the Barigui River in Curitiba.

Gomes & Gomes (2025) presented the contamination of the Barigui River by psychiatric medications excreted into the storm drain system that is drained by the river due to the lack of a local sewage system. These studies attest to the compromised environmental quality of the water system, a conclusion that our study also reaches when evaluating the average concentrations of inorganic chemical elements in sediment samples from the Bargüi River, considering their spatial and temporal variability in the face of landscape changes and urbanization.

## CONCLUSIONS

This study assesses the geochemical contamination in the sediments of the Barigüi River, employing a multi-methodological approach that integrated ED-XRF analysis, statistical modeling, and established environmental quality indices. The Contamination Factor (CF) index indicated sediment contamination by the elements TiO<sub>2</sub> and K<sub>2</sub>O, significant pollution of Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and moderate contamination by Cu, particularly at the Araucária sampling point.

The contribution of chemical elements was confirmed by the Enrichment Factor (EF) for Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and K<sub>2</sub>O in Araucária; K<sub>2</sub>O in Santa Felicidade; and TiO<sub>2</sub> in Almirante Tamandaré. The Geoaccumulation index (IGEO) scores classified the sediment samples as moderately polluted for Fe, and heavily polluted for TiO<sub>2</sub> and K<sub>2</sub>O in Araucária.

They were classified as heavily polluted to very heavily polluted for TiO<sub>2</sub>, and moderately polluted for K<sub>2</sub>O in Santa Felicidade, and heavily polluted to very heavily polluted for TiO<sub>2</sub>, and moderately to heavily polluted for K<sub>2</sub>O in Almirante Tamandaré. The Metal Pollution Index (PLI) indicated total contamination in all areas, but with significant contributions in Araucária when compared to Santa Felicidade and Almirante Tamandaré. The strong correlations statistics between Fe<sub>2</sub>O<sub>3</sub>, Mn underscore their pivotal role as key scavengers and carriers of contamination within the sedimentary matrix, likely through mechanisms of adsorption and co-precipitation. The integration of instrumental data with geochemical indices proved to be a robust strategy for diagnosing environmental stress in a region lacking specific legislative benchmarks for sediment quality.

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**Contribuições dos autores:**

Paulo Roberto Bairros da Silva: curadoria de dados, investigação, metodologia, supervisão, redação (versão inicial), revisão e edição.

Cleyton Nascimento Makara: investigação, revisão e edição.

Ana Paula Munaro: investigação, revisão e edição.

Lurian Aparecida Domingos da Cruz: investigação, revisão e edição.

Arci Dirceu Wastowski: supervisão e infraestrutura.

Danielle Caroline Schnitzler: supervisão, infraestrutura, metodologia, redação (versão inicial), revisão.

## **Supplementary Material**

Supplementary material accompanies this paper.

Supplementary Table S1. Grubbs and Kolmogorov-Smirnov tests to evaluate MRC sample

Supplementary Table S2. Kolmogorov-Smirnov Normality Test (95% confidence,  $p > 0.05$ )

Supplementary Table S3. Background values were obtained from the Geochemical Atlas of the Curitiba Sheet, provided by the public company Minerais do Paraná S.A.

Supplementary Figure S1. Recovery against certified reference material (MRC).

This material is available as part of the online article from <https://doi.org/10.21168/rega.v22e25>