Periódico Eletrônico "Fórum Ambiental da Alta Paulista"
Electronic Journal "Environmental Forum of Alta Paulista"

ISSN 1980-0827 – Volume 20, Number 1, Year 2024

Analysis of potentially toxic elements in waters and sediments of the Sorocaba River following its environmental recovery

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ISSN 1980-0827 – Volume 20, Number 1, Year 2024

ABSTRACT
The presence of potentially toxic elements (PTEs) in aquatic environments deserves attention, mainly due to the adverse effects they can have on water quality and ecological and human health. In this context, this study aimed to analyze and evaluate PTEs in waters and sediments of the Sorocaba River at different sampling points distributed throughout its urban extension. Element quantifications were performed by microwave plasma atomic emission spectrometry (MP-AES), after acid digestion of the samples. The PTEs Al, Fe, and Mn were above the maximum value allowed (MVA) by Brazilian legislation for waters, and As, Cu, and Cr was above the MVA for sediments. Based on the aforementioned results as well as the assessment of land use around the sampled sites, it is possible to demonstrate that the high concentrations of PTEs are probably caused and/or intensified by human activities. Additionally, the applied Enrichment Factor index (EF) indicated moderate anthropogenic enrichment for As, Cr, Cu, and Zn in three points in the study area, and very high for Zn in one location. This investigation alerts us to the parameters of attention that must be investigated in the ecosystem since the Sorocaba River has already been subjected to a program to clean up its waters.

KEYWORDS: Water quality. Urban rivers. Inorganic contaminants.

1 INTRODUCTION

Potentially toxic elements (PTEs) represent a significant portion of inorganic contaminants introduced into aquatic ecosystems by anthropogenic sources. Additionally, the sediment can be a sink as well as a source of PTEs, due to the ability to complex these trace elements with organic matter, sulfides, and other particulate forms (LI, J. et al., 2023). Therefore, evaluating the presence of PTEs in a body of water is extremely important, as they are considered one of the most harmful environmental contaminants due to their potential toxicity, accumulation, and non-biodegradability, which result in negative ecological effects and health risks of living beings that establish contact with the contaminated ecosystem (LI, Q. et al., 2023; OBAYOMI et al., 2023). Some PTEs are essential from a biological point of view, but when at levels above what is tolerable for living organisms, they can have negative impacts on the environment (JOSHI et al., 2022; CARVALHO et al., 2022).

As a consequence of the intensification of urbanization and industrialization, there was a great contribution to the increase in the entry of contaminants into river ecosystems, originating from domestic and industrial effluents. This environmental panorama is worrying, since concentrations of contaminants above tolerable levels can result in the degradation of water resources, compromising their multiple uses and, consequently, a series of environmental and public health problems (BANDARI; SADHUKHAN, 2021; CETESB, 2015; YADAV et al., 2021). Anthropogenic activities were mainly responsible for the degradation of aquatic environments in several countries (ABDULLAH et al., 2022; AITHANI et al., 2020; GETU; BHAT, 2021; MERHABY et al., 2021; OBIAHU et al., 2021; ROJAS et al., 2022). Similarly, human interferences listed in the Sorocaba River and its associated ecosystems negatively affected their quality levels (CETESB, 2023; FERNANDES et al., 2016, 2017; SILVA et al., 2020).

The Sorocaba River belongs to the Sorocaba and Middle Tietê hydrographic basin (RBC-SMT), which was included in the list of basins that presented critical quality levels in the National Water Resources Information System (SNIRH, 2015). Much of the basin's extension presents high rates of urbanization and industrialization and extensive vegetation fragmentation. Furthermore, the river is the main source responsible for providing water to the population located in its drainage area. These issues highlight the great relevance and importance of developing studies related to the environmental conditions of the aquatic ecosystem (BORTOLETO et al., 2016; FABH-SMT, 2022; SAAE SOROCABA, 2022; SILVA et al., 2020).

A program aimed to clean-up the waters of the Sorocaba River was implemented between 2000 and 2016, in which 17 pumping stations and 7 Sewage Treatment Plant (STP) were built, which together have the installed capacity to treat 100% of the sewage generated in Sorocaba (SAAE SOROCABA, 2022). Therefore, considering the environmental history of the Sorocaba River, it is necessary to evaluate the quality parameters of its waters and sediments, as well as the anthropogenic occupations in its surroundings. It is important to highlight that in addition to quantifying metals, other factors must be considered to determine the degree of sediment pollution (DUNG et al., 2013). In this sense, the Enrichment Factor (EF) index is a reliable tool for evaluating the presence and intensity of anthropogenic deposition of contaminants in sediments (BARBIERI, 2016).

In view of the above, the objective of the present work was to verify the influence of human activities on the quality of water and sediments in the Sorocaba River in relation to PTEs levels. For this, the study of land use and occupation was carried out and the concentrations of PTEs in the waters and sediments of the Sorocaba River were evaluated by comparing them with the legislation CONAMA n° 357/05, CONAMA n° 344/04 and Ordinance GM/MS no. 888/21 and with the Enrichment Factor (EF) index.

2 METHODOLOGY

2.1 Study area

The Sorocaba River, formed by the Sorocabuçu and Sorocamirim rivers, is the main river that crosses the city of Sorocaba, located in the southeast of the state of São Paulo. The municipality has a high degree of urbanization, approximately 99% (FABH-SMT, 2016). The water body is one of the main rivers belonging to the CBH-SMT, which has a drainage area of 11.829 km², in addition to being one of the main tributaries on the left bank of the Tietê River, measuring approximately 227 km in length until its confluence (FABH-SMT, 2016, 2022; FERNANDES et al., 2016).

2.2 Reagents and Solutions

For the development of this work, analytical grade reagents HNO_3 65% (m/m) P.A. from Qhemis and HCl 37% (m/m) P.A./ACS from NEON were used. Standard solutions of Fe of 1000 mg L^{-1}, Cd of 1000 mg L^{-1} and multi-elemental G180V (Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Sr and Zn) of 5.00 mg L^{-1} and (K) of 50 mg L^{-1} from SpecSol, were used to prepare the analytical curves.

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2.3 Instrumentation

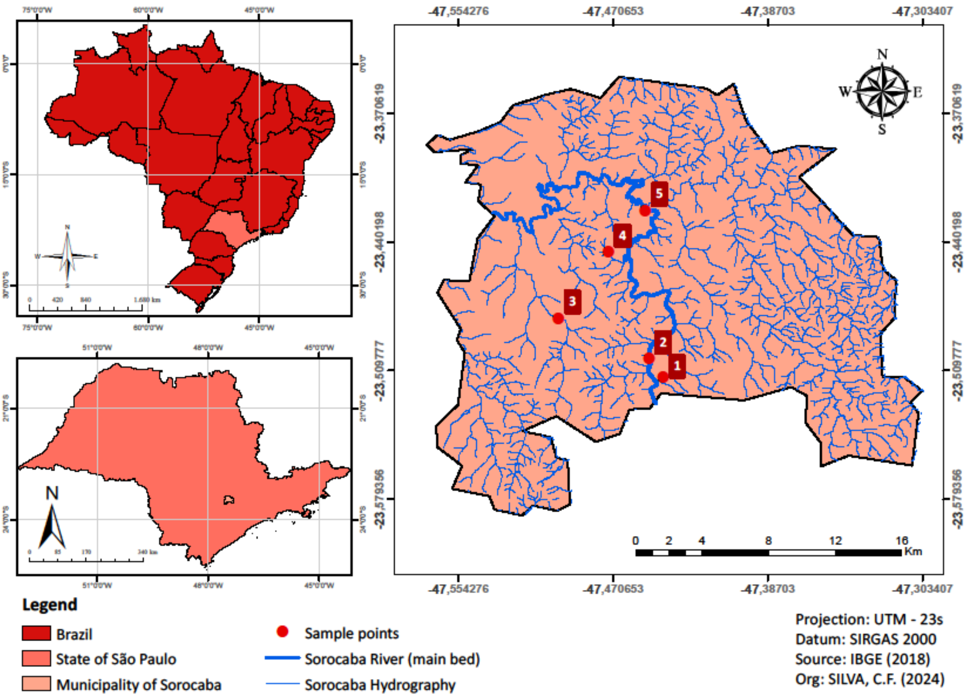
The pH values and water temperature were measured in situ with the *AKSO* pH meter (model: AK90), previously calibrated with standard solution pH 4.0 and pH 10.

The digestion of the sediment samples was carried out in a microwave digestion system (Anton Paar, model: Multiwave PRO) and the determination of PTEs levels in the water and sediment samples was carried out on a microwave plasma atomic emission spectrometer (Agilent, model: 4200 MP-AES).

2.4 Sampling procedures

Water and sediment samples were collected in October 2022, in five locations in the urban stretch of the Sorocaba River (Figure 1). Points 1, 3 and 4 were demarcated in smaller tributaries, and the others, in the main river bed (Figure 1). The coordinates of the sampling points and their respective surrounding characteristics are presented in Table 1.

Figure 1 - Location map of Sorocaba city (SP), municipal hydrography and sampling points



Source: Prepared by the author (2023).

Table 1 - Information on water and sediment collection points on the Sorocaba River

Sample points	Location (geographical coordinates: *Lat. and Long.)	Main uses and occupations around the sampling point
1	-23.514740° e -47.444630°	Urban park and urbanization
2	-23.506755° e -47.451020°	Welding and machining companies, gas stations and urbanization
3	-23.482556° e -47.498081°	Fragmentation of riverine vegetation, urbanization and metallurgical industries

4	-23.448701° e -47.471330°	Metallurgical industry and urbanization
5	-23.423796° e -47.448045°	Fragmentation of riverine vegetation, urbanization and engine, foundry, textile, boilermaking and metallurgical industries

Source: Prepared by the author (2023).
***Lat.** = latitude e **Long.** = longitude.

The cleaning and storage procedures for collection materials, as well as sampling, were carried out based on the U.S. Environmental Protection Agency protocol (USEPA, 2016). At each point, 500 mL of water was collected, which was acidified *in situ* to pH 2.0 with HNO_3 1:1 (65% m/m) and sediments, which were removed with the aid of a hoe and stored in zip lock bags. After each collection, the samples were placed in a thermal box with ice and transported to the laboratory.

2.5 Experimental procedures

Water samples were subjected to acid digestion in accordance with the procedures of the American Public Health Association section 3030E (APHA, 2000). In triplicates of 100 mL of water, 5 mL of HNO_3 (65% m/m) were added, which were digested at 120 ºC until the volume was reduced to approximately 10 mL.

The sediment samples were arranged to be air-dried in the laboratory. Subsequently, they were macerated in a polypropylene mortar and pestle and sieved on a 14 mesh (1.41 mm) particle size sieve to better detail the particle size. Then, the samples were subjected to microwave-assisted acid digestion according to USEPA method 3051A (USEPA, 2007). In triplicates of 0.5 g of sediment, 9 mL of HNO_3 (65% m/m) and 3 mL of HCl (37% m/m) were added, digested at a temperature of 175 ± 5 °C and pressure of 0.3 bar s^{-1} for 25 minutes.

After digestion, the water and sediment samples were transferred to 25 mL volumetric flasks, filled with ultrapure water from the Millipore Milli-Uni-Direct Q® 3UV system (18.2MΩ cm^{-1}) and stored in falcon tubes until determination of PTEs.

The emission lines used for the detection of PTEs, the Limits of Detection (LOD) and Quantification (LOQ), and the analytical curves constructed are presented in Table 2.

Table 2 - Emission lines used in MP-AES, analytical curves, LOD and LOQ of the PTEs analyzed

PTEs and Emission Lines	Sb	*m*	LOD (mg L^{-1}) [1]	LOQ (mg L^{-1}) [2]
Concentration range: 0; 0.05; 0.1; 0.5; 1.0; 1.5; 2.5 mg L^{-1}				
Ba 455.403	3.817	331384	0.0000	0.0001
Cd 228.802	12.640	14708	0.0026	0.0086
Co 340.512	5.057	6525.9	0.0023	0.0077
Cu 324.754	14.345	76009	0.0006	0.0019
Mn 403.076	5.982	31884	0.0006	0.0019
Mo 379.825	5.130	24423	0.0006	0.0021
Ni 361.939	4.042	5724.1	0.0021	0.0071
Sr 421.552	9.004	304770	0.0001	0.0003
Cr 425.433	2.219	31286	0.0002	0.0007
Pb 368.346	4.482	1721.5	0.0078	0.0260
Zn 213.857	23.146	9202.5	0.0075	0.0252

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Concentration range: 0; 1.0; 2.5; 5.0; 7.5; 10.0; 12.5 mg L^{-1}				
Al 396.152	6.675	27213	0.0007	0.0025
As 193.165	10.130	174.02	0.1746	0.5821
Fe 259.940	3.802	4589.7	0.0025	0.0083
Concentration range: 0; 0.5; 1.0; 5.0; 10.0; 15.0; 25.0 mg L^{-1}				
K 769.897	9.683	18016	0.0016	0.0054
K 766.491	26.612	37295	0.0021	0.0071

Source: Prepared by the author (2023).
Sb = standard deviation of the white curve of each EPT.
m = Wave-length.
[1] **LOD** = 3*Sb/m
[2] **LOQ** = 10*Sb/m

2.6 Assessment of sediment contamination by enrichment factor (EF)

The degree of contamination of sediments in the Sorocaba River was estimated based on the evaluation of element enrichment factors. The Enrichment Factor (EF) (Eq. 1) consists of an index used to identify and quantify anthropogenic contamination by PTEs in sediments (REIMANN; CARITAT, 2000) (Table 3). EF establishes normalization by comparing the concentration of the element under evaluation with that of a reference metal, usually Al, Fe, or Mn. In this study, the Al was used as a reference, since it is the most commonly used normalization element in geochemical literature (BARBIERI, 2016; SUTHERLAND, 2000). Furthermore, Al is one of the markers of natural metal-binding phases and the second most abundant in the Earth's crust, which generally correlates with the clay content in sediments. Therefore, it provides a reasonable representation of the natural variability of metal concentrations in fine-grained sediments (MIL-HOMENS et al., 2007).

$$EF = \frac{(C_n/C_M)\ sample}{(C_n/C_M)\ background} \quad \text{Eq. (1)}$$

On what:

- *(C_n/C_M) sample* = Ratio between the concentration of element n (C_n) and the concentration of the reference element (C_M) in the sediment sample; It is
- *(C_n/C_M) background* = Ratio between the background value of element n (C_n) and the background value of the reference element (C_M).

Table 3 - Classifications for Enrichment Factor (EF)

EF	**< 2** Minimum enrichment	**2 - 5** Moderate enrichment	**5 - 20** Significant enrichment	**20 - 40** High enrichment	**> 40** Extremely enriched

Source: Adapted from Sutherland (2000).

When evaluating anthropogenic contamination in sediments using indices, it is necessary to use reference values, also called background values, which represent the natural concentrations of elements in a specific location (REIMANN; CARITAT, 2000). The concentrations of PTEs in natural environments are heterogeneous and are based on the geological attributes of the region, therefore, the use of references obtained in regions close to the study area is recommended (NASCIMENTO; MOZETO, 2008).

The background values of PTEs, as well as the value of the reference metal (Al), used were defined by Cardoso-Silva et al. (2021) (Table 4), based on data on the dynamics of metals present in deep sediment samples from an aquatic ecosystem located in the same geographic region as the study area (Itupararanga reservoir). The Itupararanga reservoir is located at the top of the Sorocaba River (FRASCARELI et al., 2015). The EF index was calculated only for the elements included in the paleolimnological study by Cardoso-Silva et al. (2021), being: Al, As, Cr, Cu, Fe, Mn, Ni, Pb, and Zn (Table 4).

Table 4 – Reference values of PTEs (mg/kg dw) defined by Cardoso-Silva et al. (2021) for the Itupararanga dam and standard deviation (±SD)

Al*	As	Cr	Cu	Fe*	Mn	Ni	Pb	Zn
43.5 ± 2.1	3.0 ± 0.9	32.7 ± 1.7	19.2 ± 0.9	61.0 ± 11.0	583.9 ±131.6	8.7 ± 0.6	25.8 ± 2.1	40.8 ± 4.4

Source: Cardoso-Silva *et al.* (2021).
*g/kg dw

3 RESULTS AND DISCUSSION

3.1 Physicochemical parameters of water

The temperature of water samples from the Sorocaba River varied between 22.4 and 26.7 °C and pH values between 6.8 and 9.3 (Table 5), the latter being above the maximum value established in the CONAMA resolution No. 357/05 for Class 2 – Fresh Waters. However, the pH value recorded is within the range permitted by Ordinance GM/MS No. 518/04 for water intended for human consumption (pH from 6.0 to 9.5). Therefore, the value obtained complies with at least one of the laws in force for the study ecosystem.

Table 5 - Results of the physical-chemical parameters of the 5 sampling points on the Sorocaba River

Parameters	P1	P2	P3	P4	P5	CONAMA [1]
Temperature (°C)	22.4	23.1	23.8	23.7	26.7	40
pH	7.3	7.1	7.0	6.8	9.3	6 – 9

Source: Prepared by the author (2023).
[1] Maximum value allowed (MVA) established by CONAMA no. 357/05 for Class 2 – Fresh waters.

3.2 Potentially toxic elements in the waters of the Sorocaba River

The determination of PTEs in water samples from the Sorocaba River was carried out for the elements: Al, As, Ba, Cd, Co, Cr, Cu, Fe, K, Mn, Mo, Ni, Pb, Sr, and Zn. The PTEs Ni, Co, Pb, and As were not detected in water samples at any sampling point. The average concentrations of PTEs were compared with two Brazilian laws, namely: CONAMA resolution no. 357/05, which establishes the conditions and standards for releasing effluents into waters (BRASIL, 2005), and Ordinance GM/MS no. 888/21, which establishes control and surveillance procedures for the quality of water for human consumption and its potability standard (BRASIL, 2021) (Table 6).

Al and Fe presented average concentrations above the maximum value allowed (MVA) in CONAMA no. 357/05 and also above the potability standards established in Ordinance GM/MS no. 888/21 at all sampling points. The Cd was quantified only at collection point 1, however, within the MVA of the two legislations used. Mn presented concentrations above the

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MVA at points 3 and 4 and the other PTEs Zn, Ba, Cu and Cr presented values within the MVA established in both legislations in all sampled locations (Table 6).

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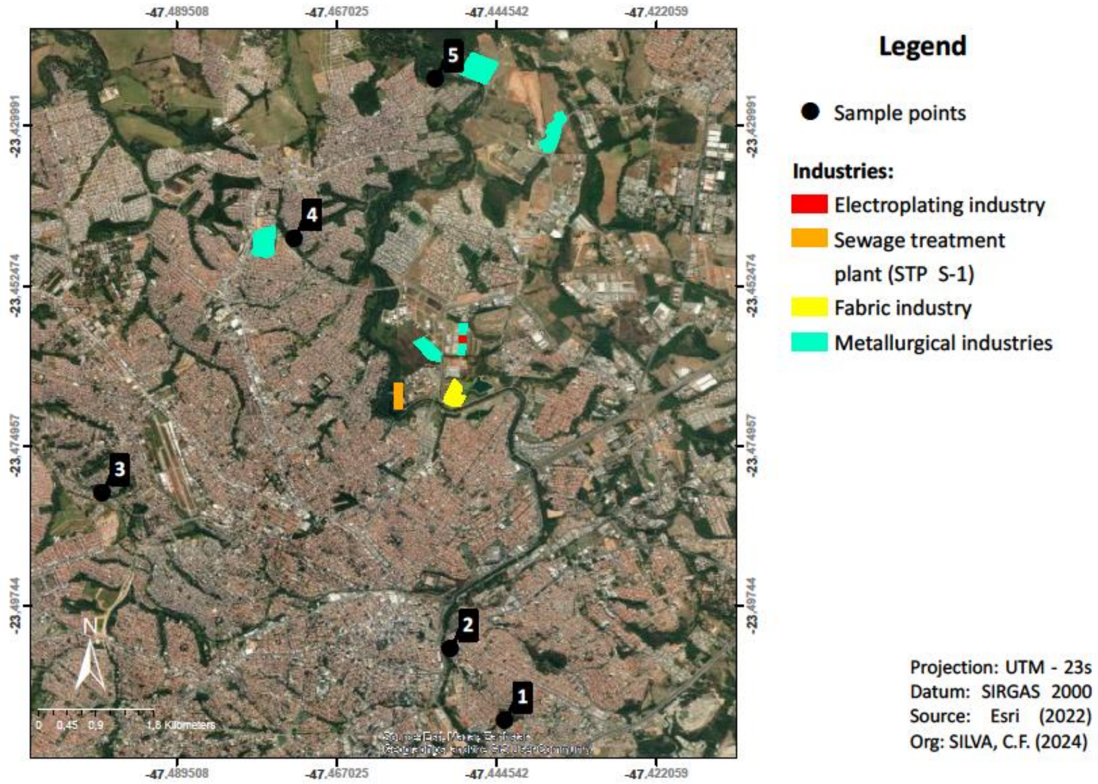
Table 6 - Average concentrations (mg L^{-1}) and standard deviation (±SD) of PTEs analyzed in the waters of the Sorocaba River

PTEs	P1	P2	P3	P4	P5	CONAMA [1]	GM/MS [2]
Al	**1.4556** ± 0.3936	**4.6578** ± 0.9837	**4.1953** ± 2.5522	**1.7400** ± 0.5246	**0.3924** ± 0.3859	0.1	0.2
As	< LOD	< LOD	< LOD	< LOD	< LOD	0.01	0.01
Ba	0.171 ± 0.0046	0.0492 ± 0.0031	0.0608 ± 0.0031	0.0875 ± 0.0055	0.0376 ± 0.0012	0.7	0.7
Cd	0.001 ± 0.001	< LOD	< LOD	< LOD	< LOD	0.001	0.003
Co	< LOD	< LOD	< LOD	< LOD	< LOD	0.05	SR
Cr	0.0037 ± 0.0024	0.0054 ± 0.0018	0.0059 ± 0.0009	0.0045 ± 0.0007	< LOD	0.05	0.05
Cu	0.0058 ± 0.0006	0.0073 ± 0.0018	0.0088 ± 0.0008	0.0038 ± 0.0005	0.001 ± 0.0008	0.009	2
Fe	**0.7678** ± 0.0454	**4.3402** ± 1.2304	**3.3715** ± 0.6173	**1.6254** ± 0.1823	**0.344** ± 0.2246	0.3	0.3
K	14.1096 ± 2.5434	46.2776 ± 2.1851	15.6272 ± 0.4967	7.4068 ± 0.4665	2.2307 ± 1.9399	SR	SR
Mn	0.0357 ± 0.002	0.09058 ± 0.0083	**0.1113** ± 0.0031	**0.2395** ± 0.0161	0.0522 ± 0.0022	0.1	0.1
Mo	0.0036 ± 0.0026	< LOD	0.0008 ± 0.0007	0.0069 ± 0.0005	< LOD	SR	SR
Ni	< LOD	< LOD	< LOD	< LOD	< LOD	0.025	0.07
Pb	< LOD	< LOD	< LOD	< LOD	< LOD	0.01	0.01
Sr	0.0684 ± 0.0014	0.0356 ± 0.0016	0.0475 ± 0.0013	0.0813 ± 0.0044	0.0256 ± 0.0017	SR	SR
Zn	0.0392 ± 0.0012	0.0349 ± 0.0064	0.0427 ± 0.0087	0.151 ± 0.0103	0.011 ± 0.0095	0.18	5

Source: Prepared by the author (2023).
[1] Maximum value allowed (MVA) established by CONAMA no. 357/05 for Class 2 – Fresh waters.
[2] Maximum value allowed (MVA) established by Ordinance GM/MS No. 888/21 for Human Consumption.
SR = No reference in the legislation analyzed.

Mn occurs naturally in surface waters. However, human activities also contribute to the entry of the element into aquatic ecosystems, which is a matter of warning, as despite being an element necessary for the human body, it presents toxicity at excessive levels, causing clinical symptoms similar to Parkinson's disease (CETESB, 2021). Although PTE was quantified at concentrations above the MVA of legislation (Table 6), the recorded content is in accordance with concentrations considered natural for surface waters (≤ 0.2 mg L^{-1}) in points 1, 2, 3, and 5 (CETESB, 2021). Collection point 4, where the highest concentration of Mn was detected, is close to three companies in the industrial sector in which manganese and its compounds are widely used, namely: electroplating, machining, and metal fasteners companies (CETESB, 2021), showing that these activities may be responsible for the presence of PTE above the MVA of legislation in the waters of the Sorocaba River (Figure 2). Furthermore, one of the Sewage Treatment Plant (STP S-1) is located close to point 4, which is another potential source of PTEs and other contaminants for the river waters (Figure 2).

Figure 2 – Map of potential sources of aquatic contaminants (industries) and sampling points



Source: Prepared by the author (2023).

Al concentrations above the MVA of CONAMA legislation no. 357/05 and GM/MS no. 888/21 were also recorded at the 5 sampling points (Table 6). This result deserves environmental and public health attention, due to the element's toxic potential to living organisms and due to its presence in the environment being associated with anthropogenic activities, mainly industrial and agricultural (SENZE et al., 2021). The presence of Al in water has been associated with Alzheimer's disease and the International Agency for Research on Cancer (IARC) classifies the production of Al as carcinogenic, due to cases of cancer in workers in this industrial sector (CETESB, 2017).

Fe was also found in concentrations above the MVA of CONAMA legislation no. 357/05 and GM/MS no. 888/21 in the 5 sampling points (Table 6). The occurrence of anthropogenic iron in surface waters can be attributed to the contribution of industrial effluents from metallurgical plants, potential sources present in the study area (CETESB, 2021). Fe is an essential element for most living organisms (BAEZ et al., 2022), however, Fe concentrations above 0.1 mg L^{-1} can lead to aquatic biological contamination due to iron bacteria, impart color and flavor to water and cause damage to species present in the environment (CETESB, 2021; DEY et al., 2022).

The Sorocaba city presents a highly fragmented landscape, in which a large part of the land uses is destined for urbanization (≈34%), agriculture (≈18.58%), livestock (≈16.07%), and, only a small portion (≈23.47%) corresponds to native vegetation (SILVA et al., 2020). Therefore, it is possible to infer that the high urbanization surrounding the study area is probably the main responsible for the negative changes in the waters of the Sorocaba River, configuring sources of PTEs for the natural environment.

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3.3 Potentially toxic elements in the sediments of the Sorocaba River

The determination of PTEs in sediment samples from the Sorocaba River was carried out for the elements: Al, As, Ba, Cd, Co, Cr, Cu, Fe, K, Mn, Mo, Ni, Pb, Sr, and Zn. The PTEs Ni, Co, Pb, and Cd were not detected in the sediment samples at any sampling point, and As was quantified only at points 2 and 4 (Table 7). The Brazilian legislation used to evaluate the levels of PTEs in the sediments of the Sorocaba River was CONAMA resolution no. 344/04, which establishes the general guidelines and minimum procedures for the evaluation of material removed or displaced from the bed of jurisdictional bodies of water. Brazilians (BRAZIL, 2004). As presented a concentration above the MVA of the legislation in point 2 (Table 7). Cu and Cr were also found in concentrations above the legislation MVA in points 1 and 5, respectively (Table 7).

Table 7 - Average concentrations (mg L^{-1}) and standard deviation (±SD) of PTEs analyzed in sediments from the Sorocaba River

PTEs	P1	P2	P3	P4	P5	CONAMA [1]
Al	10393.20 ± 7.64	15489.22 ± 1095.80	15819.9 ± 1878.73	4048.20 ± 336.69	14620.88 ± 1612.51	SR
As	< LOD	**12.32** ± 1.26	< LOD	1.25 ± 0.035	< LOD	5.90
Ba	56.97 ± 1.26	102.50 ± 2.02	60.84 ± 2.52	43.47 ± 31.06	61.80 ± 1.53	SR
Cd	< LOD	< LOD	< LOD	< LOD	< LOD	0.6
Co	< LOD	< LOD	< LOD	< LOD	< LOD	SR
Cr	14.00 ± 3.04	27.46 ± 1.32	15.47 ± 0.87	17.00 ± 5.07	**41.06** ± 0.29	37.30
Cu	**43.17** ± 3.01	19.14 ± 0.29	7.15 ± 0.58	6.17 ± 0.29	8.98 ± 0.01	35.70
Fe	11119.99 ± 708.68	22989.33 ± 597.52	16219.21 ± 645.32	8296.65 ± 37.53	12071.13 ± 37.75	SR
K	1050.17 ± 34.15	1786.79 ± 83.27	1474.56 ± 186.03	662.67 ± 62.35	1144.95 ± 37.81	SR
Mn	207.84 ± 183.33	433.93 ± 8.66	140.89 ± 2.89	232.84 ± 169.21	174.05 ± 5.00	SR
Mo	0.001	< LOD	< LOD	< LOD	< LOD	SR
Ni	< LOD	< LOD	< LOD	< LOD	< LOD	18.00
Pb	< LOD	< LOD	< LOD	< LOD	< LOD	35
Sr	7.5 ± 0.87	8.32 ± 0.29	6.65 ± 0.29	3.17 ± 0.29	10.14 ± 0.29	SR
Zn	74.5 ± 5.89	75.07 ± 2.36	34.26 ± 0.58	77.17 ± 3.88	48.04 ± 1.53	123.00

Source: Prepared by the author (2023).
[1] Maximum value allowed (MVA) established by CONAMA no. 344/04 for the material to be dredged in Fresh waters (Level 1 – Low probability of adverse effects)
SR = No reference in the legislation analyzed.

Several PTEs occur naturally in the environment, originating from rock weathering processes (BI et al., 2014). However, the concentrations of PTEs Cu, Cr, and As above the maximum values allowed in the legislation used, constitute aspects of attention due to the presence of these elements in high concentrations in the aquatic environment, mostly resulting from anthropogenic emissions. Among the main sources, we can mention mining, metal components industries, agricultural pesticides, and vehicle emissions (CETESB, 2015; LIU et al., 2019). The presence of industries in the aforementioned sectors in the sampled extensions of the Sorocaba River indicates that they may be mainly responsible for the increase in the entry of these elements into the river's waters (Figure 2). Therefore, these possible sources must be

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studied, mainly due to the important role that sediments play in relation to aquatic contaminants.

Sediments have the ability to act as sinks for elements such as metals and, subsequently, as a source of these for the water column, since inorganic contaminants are not subject to degradation and can easily resuspend or dissolve in surface waters, representing a serious long-term threat to both the environment and aquatic species present, as well as humans (CHEN et al., 2017).

The elements identified in concentrations above those arbitrary by legislation (Cr, As, and Cu) (Table 7) have already been associated with runoff from urban roads, due to emissions and leaks from motor vehicles. In this sense, it can be inferred that this is also one of the main sources associated with the presence of the aforementioned elements in the sediments of the Sorocaba River, as a consequence of the intense urban traffic in its surroundings (BAEK; AN, 2010).

Therefore, the development of more studies and analyses related to the concentrations of PTEs in the Sorocaba River is important for identifying the sources of these elements for the ecosystem.

3.4 Assessment of sediment contamination by Enrichment Factor (EF)

From the calculation of the EF index (Eq. 1 and Table 2), carried out with the results of the quantifications of PTEs in the Sorocaba River presented in this study and the reference values defined by Cardoso-Silva et al. (2021) (Table 4) it was possible to evaluate the degree of anthropogenic contamination in sediment samples from the Sorocaba River for most of the PTEs studied. Based on the EF results obtained at the five sampling points of the Sorocaba River, it can be deduced that the recurrent anthropogenic activities in its surroundings are significantly affecting the enrichment of As, Cr, Cu, and Zn in the aquatic environment (Table 8).

The PTEs As and Cr that showed significant enrichment in points 2 and 4 (Table 8), respectively, were classified as priority pollutants by the USEPA due to their toxicity potential (USEPA, 2002). Both elements have their anthropogenic sources associated with the textile (As) and metallurgical (Cr) industries (CETESB, 2021), occupations that are present in the surroundings of the two sampling points (Figure 2) and, therefore, consist of potential sources of these elements for the aquatic ecosystem.

Cu, which also showed significant enrichment at sampling point 1 (Table 8), consists of an element with the potential to be toxic to humans and can reach organs such as the liver. EPT can also cause extremely harmful to lethal poisoning for aquatic organisms above tolerable levels. Sources of copper for the environment include effluents from sewage treatment plants and atmospheric precipitation from industrial sources (CETESB, 2021). Therefore, Sewage Treatment Plant (STP S-1) and the industries present around the study area (Figure 2) are likely contributors to the enrichment of Cu in the sediments of the Sorocaba River.

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Table 8 – Classifications of enrichment Factor (EF) in the 5 sampling points of the Sorocaba River

PTEs	P1	P2	P3	P4	P5
Al	1.000	1.000	1.000	1.000	1.000
As	< LOD	**11.533**	< LOD	4.477	< LOD
Cr	1.792	2.358	1.301	**5.586**	3.736
Cu	**9.411**	2.800	1.024	3.453	1.392
Fe	0.763	1.058	0.731	1.462	0.589
Mn	1.490	2.087	0.663	4.285	0.887
Ni	< LOD	< LOD	< LOD	< LOD	< LOD
Pb	< LOD	< LOD	< LOD	< LOD	< LOD
Zn	**7.643**	**5.167**	2.309	**20.324**	3.503

Source: Prepared by the author (2023).

Zn was the element most influenced by anthropogenic interference throughout the study area, especially at collection point 4 (P4), where it showed very high anthropogenic enrichment (Table 8). However, Zn concentrations in water samples were below the CONAMA MVA no. 357/05 in all sampled locations (including P4), showing that the EPT is probably complex with sulfides and organic matter. However, despite the probable non-bioavailability of the element, the result warns about factors of attention in the environment, since there is a risk of remobilization of the EPT into the water column (MARIANI; POMPÊO, 2008). Zn and its compounds are widely used in metal manufacturing industries (CETESB, 2021) and Zn inputs in urban watersheds have been attributed to tire wear on road surfaces (COUNCELL et al., 2004; MARZOLA et al., 2019), in this sense, the entry of the element into the aquatic ecosystem can be attributed to urban runoff. The aforementioned land occupations are present around the analyzed extension of the Sorocaba River, including next to point 4 (Figure 2).

4 CONCLUSION

From the analysis of the distribution of PTEs in the Sorocaba River, it was possible to verify that the ecosystem presents concentrations of Al, Fe, and Mn above the MVA of Brazilian legislation for waters and As, Cu and Cr above the MVA for sediments. These results characterize aspects of environmental attention, since the aforementioned PTEs have potential toxicity for living beings, and as a result of the river's waters being destined for public supply.

The EF index indicated significant enrichment for the elements As, Cr, Cu, and Zn in three of the sampled locations and very high enrichment for Zn in point 4. The levels of anthropogenic contamination in the studied sediments reflect the importance of controlling possible sources of contaminants present in the surroundings of the ecosystem, mainly in urban areas. It is also necessary to carry out further investigations of physical, chemical, and hydrobiological parameters important for water quality levels, to better identify the natural and anthropogenic sources of release of PTEs, as well as other contaminants throughout the river, especially in locations that showed high concentrations of PTEs. Most of the changes in the quality parameters of the Sorocaba River are probably associated with the intensification of recurrent human activities around the ecosystem.

The results obtained in the present investigation contribute to the formation of information regarding the evaluation of chemical parameters of the waters and sediments of the Sorocaba River and highlight the need for improvements in controlling the entry of contaminants into the source. The environmental scenario observed in the Sorocaba River requires attention, given that similar scenarios have caused damage to aquatic biodiversity in other regions of the world.

Acknowledgment

This study was funded by the Coordination for the Improvement of Higher Education Personnel - Brazil (CAPES) – Financing Code 001 (process no. 88887.629659/2021-00), pro-equipment project (proposal no. 189683) CAPES no. 11/2014, and research aid project from the São Paulo Research Foundation (FAPESP) process no. 2016/10796-5.

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