Environ Monit Assess (2025) 197:250
https://doi.org/10.1007/s10661-025-13712-4

RESEARCH

Assessment of potentially toxic elements in sediment cores from reservoirs in the Upper Tiete River Basin, Brazil

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Received: 25 November 2024 / Accepted: 29 January 2025 / Published online: 6 February 2025
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Abstract This study evaluated concentrations of potentially toxic elements (PTEs)—As, Sb, Co, Cr, Zn, U, and Th—in sediment cores from the Jundiai and Taiaçupeba reservoirs in the Upper Tiete Water Basin, Sao Paulo, Brazil. These reservoirs are vital for supplying water to the São Paulo metropolitan area but face risks from agricultural and industrial activities. The research aimed to determine whether PTE enrichment in sediments is due to natural or anthropogenic factors, assess the influence of sediment geochemistry and grain size, and evaluate risks to public health and biota. Granulometric analysis and enrichment factors were used to interpret the results, with As, Cr, and Zn compared to sediment quality guidelines. Significant Zn contamination was found in the Taiaçupeba reservoir, exceeding the Probable Effects Level (PEL), suggesting mining-related contamination. This highlights the need for further research on Zn's spatial distribution, ecological risks, and bioavailability in the Taiaçupeba reservoir. Conversely, Sb, Co, Cr, U, and Th were linked to natural processes. Arsenic showed a local geologic anomaly in both reservoirs. This research emphasizes the importance of geochemistry as a critical tool for interpreting PTEs in trace element environmental monitoring. Geochemical parameters, including Hf, Ta, Sc, and K, and rare earth elements, were essential for understanding sedimentary dynamics and anthropogenic impacts. This approach enhances the effectiveness of PTE impact assessments and can be applied to other dam reservoirs worldwide.

Keywords Potentially toxic elements · Trace elements · Geochemistry · Environmental monitoring · Sediments · Dam reservoirs

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10661-025-13712-4.

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Introduction

Many researchers have reported the risks associated with human exposure to trace elements considered potentially toxic elements (e.g., PTEs—As, Cd, Cr, Ni, Cu, Se, Th, U, Pb, Zn, and Hg) (Tkalec et al., 2014; Xiao et al., 2020). However, there are

relatively few studies focusing on the distribution of trace elements in the sediment cores from Brazilian water supply reservoirs (e.g., Frascareli et al., 2018; Lima et al., 2014, 2021; Nascimento, 2003; Souza & Wassermann, 2015). In contrast, many studies in the international literature have reported the trace element contents in sediments and also in soils in the catchment area of water reservoirs (e.g., Ahmad et al., 2022; Hahn et al., 2019; Han et al., 2017; Sedláček et al., 2012). The content of trace elements in sediments is influenced by many factors, such as rock parent material, pedogenesis, weathering, and erosion, as well as the physical, chemical, and biological processes. However, anthropogenic inputs of trace elements have increased dramatically since the second industrial revolution (Kabata-Pendias, 2000; Yang et al., 2020).

Trace elements are those that occur naturally in the environment at low concentrations (< 100 mg/kg) (Pierzynski et al., 1994). Biomagnification and persistence of the trace elements result in adverse effects on water quality, aquatic life, human health, and overall biodiversity (Peter et al., 2020). Therefore, these elements are classified by the United States Environmental Protection Agency (USEPA) and the International Agency for Research on Cancer (IARC) as some of the most hazardous environmental pollutants (Peter et al., 2021), as stated by Tadesse et al. (2018).

Trace element contamination in dam reservoir sediments is a global concern because this compartment has multiple and complex ecological interactions, posing significant risks to public health and the biota (Cyriac et al., 2021; Yang et al., 2020). In the last decades, the São Paulo metropolitan area has faced water scarcity due to reduced rainfall (Dobrovolski & Rattis, 2015) and increased water demand (Côrtes et al., 2015). Loss in water quality, exacerbated by insufficient rainfall and distribution challenges associated with large metropolitan areas, is an ongoing environmental concern. In addition, conventional water treatment systems in São Paulo are not fully effective in removing all pollutants. Certain dissolved trace elements can be found in the residue after treatment (Voltan et al., 2016).

The two reservoirs selected for this study are part of a cascade system located in the Upper Tiete Water Basin (UTWB), one of the most stressed hydrographic basins in the State of Sao Paulo. The reservoirs are part of the Upper Tiete Production System (UTPS) and are formed by the impoundment of the Tiete River. This river is influenced by the waters from the Ponte Nova and Paraitinga reservoirs. After the release of the water from these reservoirs, a pumping station was built on the banks of the river to transport the water to the Biritiba-Mirim reservoir. The final recipient of the cascade system is the Taiaçupeba reservoir, which receives water from the Jundiai reservoir. On the outlet tributary of the Taiaçupeba reservoir, there is a water treatment station of the Sao Paulo State Basic Sanitation Company (SABESP). These reservoirs supply millions of people in the Sao Paulo Metropolitan area and experienced several dry cycles in 2014 and 2015.

A major concern is the intense agricultural and industrial activities that characterize the surrounding areas. The Taiaçupeba reservoir is particularly vulnerable to anthropogenic impacts due to its proximity to the São Paulo metropolitan area. Furthermore, its proximity to mining operations, paper manufacturing, electroplating, and smelting activities increases this vulnerability (Ussier, 2007). Since this reservoir is the final destination within the cascade system, there is a potential risk of accumulation of trace elements transported from other reservoirs. The Jundiai reservoir is located amidst agricultural activities, as evidenced by the presence of farms and rural estates, which naturally increase the risks associated with the use of pesticides and agrochemicals.

The main objective of this work was to evaluate the concentrations of the PTEs—As, Sb, Co, Cr, Zn, U, and Th—in sediment cores from the Jundiaí and Taiaçupeba reservoirs. This work aims to serve as a database for future research on Brazilian dam reservoirs and to discuss the geochemical signatures of the sediments, providing a hypothesis on the nature of the occurrence of PTEs, whether geogenic or anthropogenic. The geochemical parameters evaluated in this study were Sc, Hf, Ta, La, Ce, Nd, Eu, Sm, Tb, Yb, Lu, Fe, Na, and K. The study was developed to answer the following questions:

- Is there evidence for anthropogenic or natural enrichment of PTEs in the sediments after flooding of the reservoirs?

- Does sediment geochemistry and grain size influence the behavior of PTEs?
- What are the major risks to the biota and public health from PTE concentrations in sediments?

To interpret the results and answer the above questions, the granulometric analysis and the enrichment factor (EF) were used, which was calculated by comparing the results of the elements determined with three reference values: UCC—Upper Continental Crust (Rudnick, 2005); NASC—North American Shale Composition (Gromet et al., 1984), and WRSS—World River Suspended Sediments (Viers et al., 2009). The concentration results obtained for the trace elements As, Cr, and Zn were compared with threshold effect level (TEL) and probable effect level (PEL) values to assess the quality of the sediment.

Material and methods

Sampling

The contextualization of the study area is shown in Fig. 1. The Jundiai reservoir is located in the municipality of Mogi das Cruzes (23°40′ S and 46°10′ W). This reservoir has a drainage area of 111 km^2, and its flooded area is about 17.5 km^2. The Taiaçupeba is located between the municipalities of Mogi das Cruzes and Suzano (23°35′ S and 46°17′ W). It has a drainage area of 224 km^2 and a flooded area of 19.4 km^2. The local climate is classified as C_{wa} according to the Köppen Climate Classification System. This type of climate is characterized by a tropical altitude climate with distinct wet summers and dry winters (Sorrini, 2015).

Between 2015 and 2018, sediment cores were collected from the margins of the Jundiai and

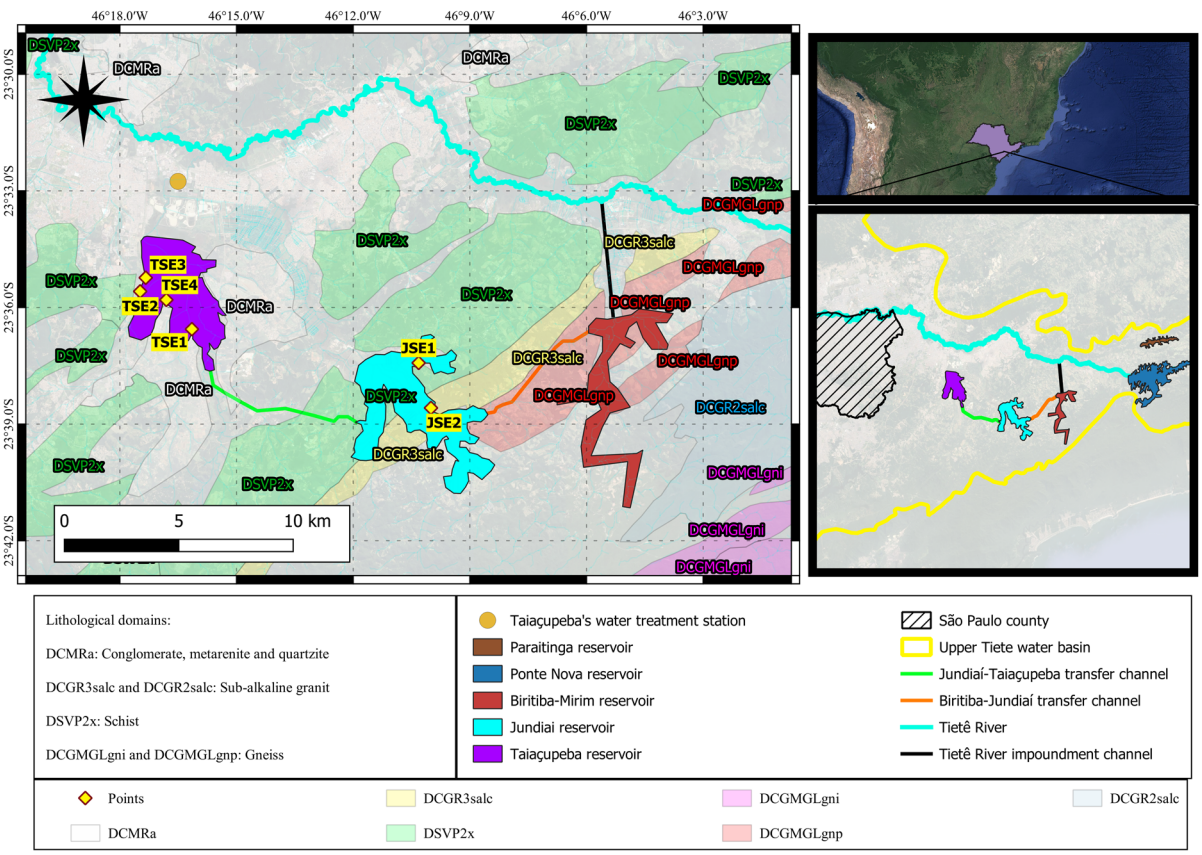

Fig. 1 Map of the sampling points and information on the location of the Upper Tiete hydrographic basin and its lithology. *The QuantumGIS (QGIS) software was used to create this artwork

Taiaçupeba reservoirs. Two points were selected in the Jundiai reservoir (JSE1 and JSE2), and four points in the Taiaçupeba reservoir (TSE1, TSE2, TSE3, and TSE4). Sediment was sampled with a manual polyvinyl chloride core sampler, and the depth varied between 28 and 61 cm. Additional information about the sampling sites, such as the coordinates, lithology, and core depths, is presented in Table 1.

In the laboratory, the sediment cores were carefully opened. After describing the morphology, sediment samples were taken by slicing the sediment cores every two centimeters. Sediment drying was performed in an oven at 50 °C due to the high humidity of the samples. The samples were then sieved through a 10-mesh (2.00 mm) sieve, and a quarter was taken as an aliquot for the chemical analysis. These fractions were pulverized in a glass mortar and passed through a 115 mesh (0.127 mm) sieve for complete homogenization.

Sediment grain size was determined according to the Soil Manual of Chemical Analysis (Donagemma et al., 2011) of the Brazilian Agricultural Research Corporation (EMBRAPA). Approximately 5 g of each sample was sieved with type 1 water in a set of sieves of 30, 60, 230, and 635 mesh, respectively. The particles were classified as sand (diameter between 2 mm and 0,06 mm), silt (diameter between 0.06 mm and 2 µm), and clay (diameter less than 2 µm).

Instrumental Neutron Activation Analysis (INAA)

The concentrations of the elements—As, Sb, Co, Cr, Zn, U, Th, Sc, Hf, Ta, Fe, Na, K, La, Ce, Nd, Eu, Sm, Tb, Yb, and Lu—were determined using Instrumental Neutron Activation Analysis (INAA). The comparative method was used, and three certified reference materials (CRM) were selected: Lake Sediment (SL3) from the International Atomic Energy Agency (IAEA), Inorganic Marine Sediment (2702), and Montana Soil II (MII) from the National Institute of Standards and Technology (NIST). Approximately 150 mg of samples and CRM was irradiated for 6 h in the IPEN Research Reactor IEA-R1, with a thermal neutron flux of 10^{12} n/cm, and the concentrations were measured by gamma-ray spectrometry, using a coaxial HPGe detector, ORTEC.

Element concentrations were calculated using the method well described by Franklin et al. (2016). To evaluate the precision of the method, 10 analyses were performed using MII from NIST as the certified reference material. MII was selected for its applicability to most elements determined, as shown in Supplementary Material Table S1. The concentrations in MII were determined using the comparative method with the other two certified reference materials, SL3 and 2702.

Geochemical signatures

The geochemical signatures of the sediments were determined in order to deepen the discussion of the results obtained for the analytes specified in the objectives of the study. The signatures were compared to classical background references: UCC—Upper Continental Crust (Rudnick, 2005); NASC—North American Shale Composition (Gromet et al., 1984);

Table 1 Coordinates, lithology, and depths of sediment cores sampled

Core point	Geographical coordinates	Lithological domain[a]	Depth
JSE1	23°37′25″S 46°10′19″ W	Schist	29 cm
JSE2	23°38′35″ S 46°10′0″ W	Sub-alkaline granite	28 cm
TSE1	23°36′33″ S 46°16′8″ W	Conglomerate, metarenite, and quartzite	42 cm
TSE2	23°35′35″ S 46°17′28″ W	Schist	51 cm
TSE3	23°35′13″ S 46°17′20″ W	Schist	47 cm
TSE4	23°35′48″ S 46°16′48″ W	Conglomerate, metarenite, and quartzite	61 cm

[a]Geodiversity database: Geological Brazilian service (SGB, 2024)

PAAS—Post- Archean Australian Shale (Pourmand et al., 2012); and WRSS—World River Suspended Sediments (Viers et al., 2009).

Rare earth elements and cerium/europium anomalies

Cerium (Ce) anomalies are used as a tracer of the environmental redox conditions because Ce has a specific characteristic that differs from other trivalent state Rare Earth Elements (REEs). This element has two different oxidation states (Ce^{3+}/Ce^{4+}), and the tetravalent state is less soluble, which affects the mobility of the element in soils, mainly in the presence of Fe–Mn oxides, which can adsorb Ce^{4+} under oxic conditions (Rétif et al., 2023). Europium (Eu) has two different oxidation states (Eu^{2+}/Eu^{3+}), and the bivalent form can replace Ca^{2+} by isomorphic substitution of the plagioclase mineral. Usually, negative Eu anomalies can be associated with higher plagioclase alteration and chemical weathering indexes. This event is more expressive in warm and humid tropical environments (Temga et al., 2021).

Cerium anomalies (Ce/Ce*) were calculated using the equation cited by Rétif et al. (2023): $Ce/Ce^* = [3Ce(N)/(2La(N) + Nd(N))]$. The calculations of europium anomalies (Eu/Eu*) were performed using another equation described by Rétif et al. (2023): $Eu/Eu^* = [Eu(N)/(0.67Sm(N) + 0.33\ Tb(N))]$. REEs were normalized (N) using a simple ratio with the Post Archean Australian Shale (PAAS) reference values (Pourmand et al., 2012).

The total REEs ($\sum$REEs) content was defined as the sum of La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu concentrations in the samples.

Geochemical tracers

The trace elements Hf, Ta, and Sc, along with rare earth elements (REEs), are commonly used in geochemical studies as tracers of sedimentary provenance processes (Ahmad et al., 2022; Sutherland, 2000). Hf, Ta, and Sc are lithophile elements; particularly, Hf and Ta are immobile in the environment and can reflect weathering conditions of felsic granitic rocks (Fernández-Caliani et al., 2020), which significantly influence the Upper Tiete hydrographic basin (Sorrini, 2015; Urakawa, 2011). The element Sc, on the other hand, is associated with mafic rocks (Fernández-Caliani et al., 2020), but it is often used as a normalizer for the calculation of enrichment factors of PTEs, as it accumulates from lithological and natural processes, making it a reliable tracer of natural enrichments of trace elements (Ahmad et al., 2022; Loska et al., 2003; Sutherland, 2000).

REE patterns, such as the fractionation of LREEs (light rare earth elements) over HREEs (heavy rare earth elements), reflected by the (La/Yb)N ratios, and the fractionation of LREEs over MREEs (medium rare earth elements)—(La/Sm)N—are also used in geochemical studies. In addition to fractionation providing evidence of sediment provenance (Liu & Han, 2021), greater fractionation of LREEs over the remaining REE classes can indicate anthropogenic influence in the sediment. This occurs because LREEs are naturally enriched in phosphate fertilizers (Gao et al., 2024), which are widely used by farmers in the areas surrounding the reservoirs (Goto et al., 2024). Fertilizers can be a significant source of trace element accumulation in soils and sediments (Bolan et al., 2014).

Major elements

The enrichment pattern of the major elements Na and K may reflect the Chemical Index of Alteration (CIA) of sediment samples (Roser & Korsch, 1988). These major elements undergo rapid alteration processes during chemical weathering and are easily leached and mobilized in tropical climates, which are generally associated with high chemical weathering indices (Ahmad et al., 2022; Sorrini, 2015). The accumulation of these elements may reflect the entry of less weathered materials into the reservoir and, in particular, K, may be a tracer of atmospheric pollution (Qu et al., 2024). The influence of atmospheric processes on sedimentation must be considered. The reservoirs are located in a region with high wildfire activity (Goto et al., 2024), which may affect the dispersion of allochthonous chemical elements (Beyene et al., 2023).

Enrichment factor

The enrichment factor (EF) is a parameter that is commonly used in sediment quality testing. These indices are obtained by comparing the contents of an element of interest and the normalizing element with their reference values. Usually, the elements

Sc, Al, Mn, Ti, Y, and Li are selected as the normalizing element for the analysis (Loska et al., 2003; Sutherland, 2000), and in this work, Sc was chosen.

In this paper, the UCC, NASC, and WRSS reference values were used for the EF calculation, in addition to the sediment lower core layer (SLC), determined for the sediment cores that presented clear transition zones associated with the reservoir flooding.

EF calculations were performed using the expression: $[(C_i/C_N)$ sample$/(C_i/C_N)$ reference], where C_i is the concentration of the element of interest and C_N is the normalizing concentration. According to Sutherland (2000), there are five classes of enrichment: no enrichment when $EF < 2$; moderate enrichment when $2 < EF < 5$; significant enrichment when $5 < EF < 20$; very high enrichment when $20 < EF < 40$; and extremely high enrichment when $EF > 40$.

Sediment quality guidelines (SQGs)

Sediment quality guidelines (SQGs) are commonly used to assess the ecological risks associated with metals and metalloids in sediments. In this study, the concentrations of trace elements in sediment samples were compared to the threshold effect level (TEL)—below which adverse biological effects are unlikely to occur—and the probable effect level (PEL)—above which adverse biological effects are likely to occur (Cyriac et al., 2021; Long & MacDonald, 1998; MacDonald et al., 1996). The trace elements analyzed in this reference were As, Cr, and Zn.

Statistical analysis

The principal component analysis (PCA) was performed using the IBM (International Business Machines Corporation) SPSS (Statistical Package for the Social Sciences) 26. This test was applied to show the behavior of the analytes in the sediment, investigating possible correlations between the PTEs and natural (Hf, Ta, and Sc) or anthropogenic indicators (La/Yb, La/Sm, and K). Furthermore, correlations with the grain size of the samples were tested to enhance the discussion of the results.

Results and discussion

General results

The results of grain size analysis and the trace/major element concentrations in the sediment cores from the Jundiai and Taiaçupeba reservoirs are shown in Table 2. The comparisons with reference values and neighboring reservoirs are also presented in this Table.

Geochemical signatures

The results of the geochemical parameters of the sediments from the Jundiai and Taiaçupeba reservoirs are presented in Fig. 2. The figure presents the geochemical signatures of the sediments and comparisons with background references. The sampled cores and the reference values were categorized by color, size, and shape of the symbols. The UCC, NASC, and WRSS reference values were not included in the (La/Yb)N × (La/Sm)N and Ce/Ce* × Eu/Eu/plots because these indices were calculated by normalization to the PAAS reference. The plot between Ta and Hf does not include the PAAS reference, since these elements are not present in the values revised by Pourmand et al. (2012).

A significant portion of the samples presented normalized La/Yb ratios below 1.0, suggesting a greater fractionation of HREEs relative to LREEs. In particular, the Jundiaí reservoir showed samples with lower trends of LREEs accumulation, which may be attributed to the preservation of this aquatic system, as LREEs can serve as indicators of agricultural activity. On the other hand, TSE3 samples from the Taiaçupeba reservoir presented an opposite trend, with a strong accumulation of LREEs over HREEs. Most of the samples show no significant fractionation between LREEs and MREEs, as indicated by the normalized La/Sm ratios. Fractionation includes the TSE4 core (MREE accumulation) and parts of the JSE2 and TSE2 cores (LREE accumulation).

Regarding the Ce anomalies, a significant portion of the samples showed weak or strong positive anomalies, reflecting the oxidizing conditions present in the cores. Samples TSE1 and mainly TSE3 were the only ones with negative Ce anomalies, indicating reducing conditions. Concerning the Eu anomalies, almost all samples presented negative anomalies, typical of

Table 2 General results of the sediment cores collected in the reservoirs of Jundiai and Taiaçupeba, comparisons with the reference levels and with the neighboring reservoirs of Ponte Nova and Ribeirão do Campo

Dependent variable		Jundiaí reservoir	Taiaçupeba reservoir	Ponte Nova reservoir[a]	Ribeirão do Campo reservoir[b]	TEL|PEL[c]
Clay		8–30	5–74	nd	nd	nd
Sand	%	50–80	14–88	nd	nd	nd
Silt		8–22	4–17	nd	nd	nd
Ce/Ce*		1.1–2.9	0.7–2.5	nd	nd	nd
Eu/Eu*		0.6–2.9	0.4–1.6	nd	nd	nd
∑REEs		38.6–58.8	101–404	nd	nd	nd
(La/Sm)N		0.7–1.3	0.5–1.5	nd	nd	nd
(La/Yb)N		0.1–0.3	0.3–2.0	nd	nd	nd
As	mg/kg	14.0–39.6	3.5–40.3	15–28	7.7–24	5.9|17
Sb		0.9–1.7	0.3–2.9	nd	nd	nd
Co		3.4–6.4	1.3–22	17–23	17–24	nd
Cr		67–148	18.4–112	29–50	26–45	37.3|90
Zn		28.8–57.2	23.3–38,200	67–89	66–107	123|315
U		3.39–6.45	1.36–13.8	6.30–8.60	13–21	nd
Th		19.4–34.9	10.6–44.2	15–25	23–28	nd
Sc		13.2–28.2	2.5–32.2	nd	nd	nd
Hf		12–35.4	1.8–24.2	nd	nd	nd
Ta		1.4–2.3	0.5–5.4	nd	nd	nd
Fe	%	4.12–7.41	0.62–4.81	nd	nd	nd
Na		0.052–0.080	0.039–0.47	nd	nd	nd
K		0.61–1.37	0.013–2.68	nd	nd	nd

*Not determined (nd)

[a,b]Sediment samples analyzed in the Ponte Nova and Ribeirão do Campo reservoirs, located at the Upper Tiete water basin (Nascimento, 2003)

[c]Threshold effect level (TEL) and probable effect level (PEL) (Long & MacDonald, 1998; MacDonald et al., 1996)

the climatic conditions of the area, which favor Eu leaching. However, a few samples from TSE3, a single sample from TSE2, and the entire JSE2 samples showed positive Eu anomalies, which may indicate the input of less weathered material at these sampling points.

The Ta×Hf plot indicates that a significant portion of the samples followed a distribution similar to UCC, NASC, and WRSS, suggesting that these elements may serve as reliable environmental indicators for the study area. However, the JSE1 samples showed strong Hf anomalies relative to the reference values, and Ta showed anomalies in the TSE4 core. To understand these anomalies, the Na×K plot is presented in Fig. 3.

The results presented in Fig. 3 suggest a significant accumulation of K in some samples from the TSE3 core compared to others, with these samples approaching the K concentrations found in UCC, a characteristic pattern of unweathered rock. The JSE1 core, which showed Hf anomalies, also presented high concentrations of K. Since K mobilization and subsequent accumulation in sediments can be traced back to atmospheric events, the Hf anomaly found in this core may be due to remobilization from atmospheric dust. The sandy texture of the JSE1 core (Fig. 4) also influences the Hf accumulation, as the sandy sediments are likely to accumulate this element in greater proportions. The mineral zircon, commonly present in soils and sediments after the granite weathering, is enriched in Hf and may be trapped in coarser sediments (Fernández-Caliani et al., 2020). This profile also showed higher concentrations of Sc compared to the reference values,

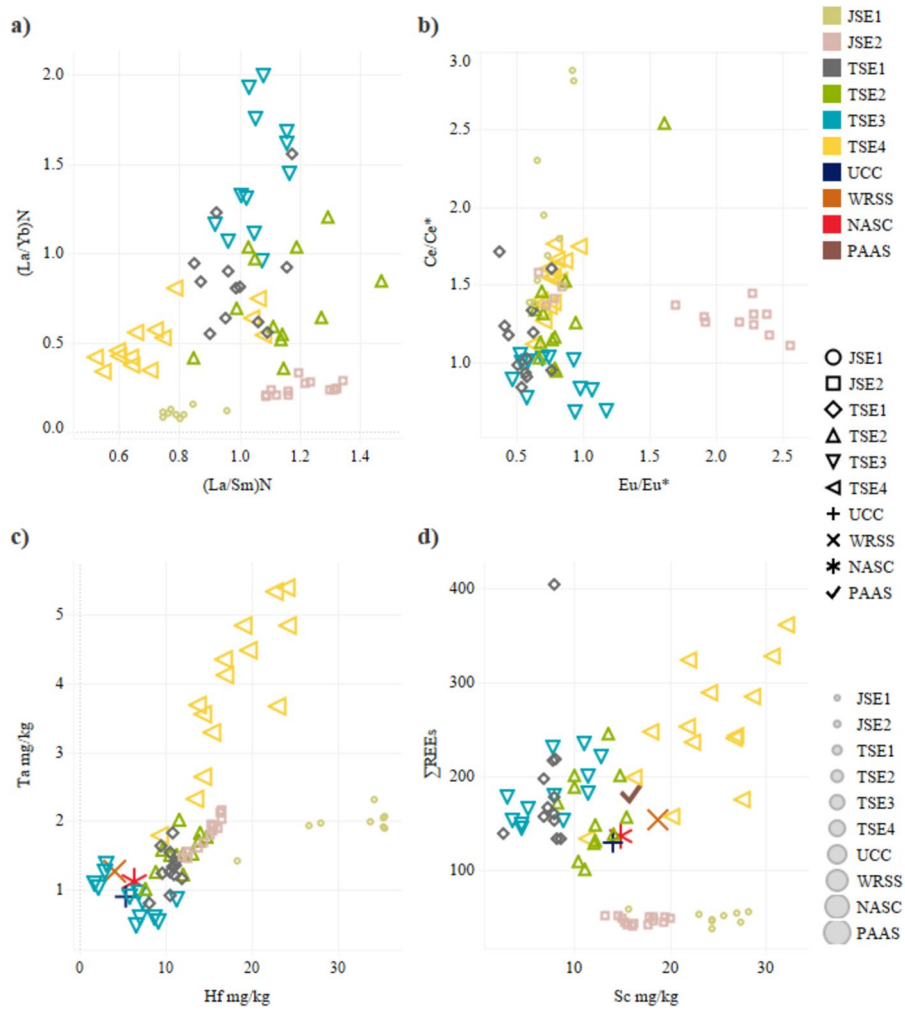

Fig. 2 (La/Yb)N × (La/Sm)N (**a**); Ce/Ce* × Eu/Eu* (**b**); Ta x Hf (**c**); and ∑REEs × Sc (**d**) in sediments from the Jundiaí and Taiaçupeba reservoirs. *The sampled cores and the reference values were categorized by color, size, and shape of the symbols. *The Tableau software was used to create this artwork

reinforcing the large accumulation of geochemical tracers in the JSE1 core.

Concerning the Ta anomaly presented in the TSE4 profile, it is important to note that the K concentrations in this core were below detection limits, indicating intense weathering and complete removal of this alkaline metal at this particular sampling location. Since Ta is highly immobile and is associated with weathering, the anomaly that was found for this core may be due to geogenic conditions. The clay texture of this core (Fig. 4) may contribute to the accumulation of Ta, which is favored in fine sediments (Fernández-Caliani et al., 2020).

In terms of total REE accumulation, there was a greater availability of these elements in the Taiaçupeba sediments than in the Jundiaí reservoir. Among the cores with higher REE values are the samples from TSE3 and TSE4.

Sediment core transition zone (TZ) determination

The sediment core transition zone (TZ) determination was based on the evaluation of four parameters: clay, sand, silt, and Fe percentages of the samples. This determination is crucial to the understanding of the environmental impact of the reservoir post-flooding period. The results of the grain size analysis and the Fe concentrations of the sediment cores are shown in Fig. 4.

During the initial filling phase of a reservoir, fine fluvial particles, such as clay and fine silt, are typically deposited at high depths in the water column of

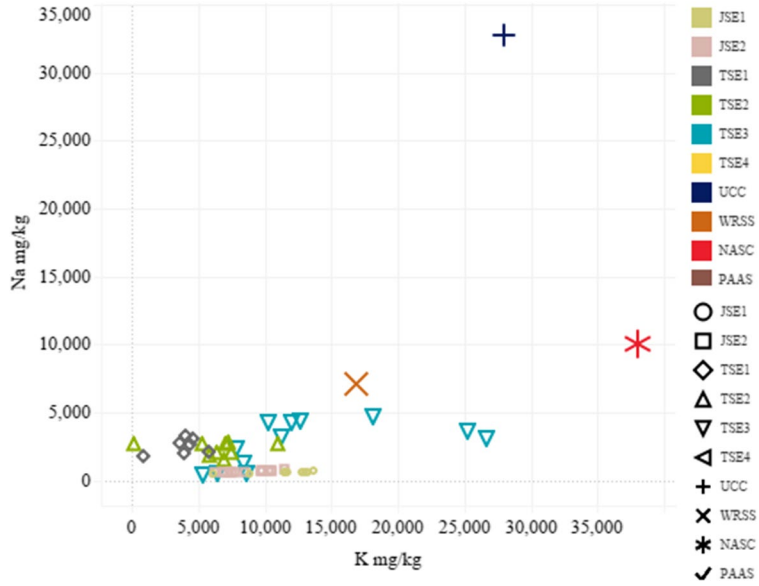

Fig. 3 Na × K plot in sediments from the Jundiai and Taiaçupeba reservoirs. *The sampled cores and the reference values were categorized by color, size, and shape of the symbols. *The graph does not include the PAAS reference, as the Na and K elements are not found in the values revised by Pourmand et al. (2012). *The Tableau software was used to create this artwork

the reservoir. Nevertheless, coarser particles, including gravel, sand, and coarse silt, are generally deposited along the reservoir margin (Carvalho et al., 2000; Hahn et al., 2019), where the sediment cores were sampled. In the JSE1 core from the Jundiai reservoir, a notable peak in sand percentages was identified at 18 cm. In this reservoir, an increase in silt percentage was observed in the JSE2 core at the same depth range where the sand peak was detected in the JSE1 core. These peaks coincided with an upward Fe-depletion in both cores. This Fe depletion could be related to the oxic conditions reflected by the positive Ce anomalies calculated for these cores (Fig. 2). Normally, an upward Fe-migration is expected in reducing environments (Burgin & Loecke, 2023; Hahn et al., 2019), and the redox conditions of the Jundiai sediments traced by the Ce anomalies suggest the opposite, as reflected by the Fe-depletion in the upper part of the core. Given this, the sedimentary transition zone (TZ) for the Jundiai reservoir was determined at the 18 cm depth.

In the Taiaçupeba reservoir, the sand peaks were identified at the 41 cm depth in cores TSE2 and TSE3. An interesting behavior observed in these cores, mainly in TSE3, was the increase in clay after the TZ, associated with the flooding of the reservoir. The change in the sedimentary conditions will be discussed later in this manuscript for the TSE3 core. In contrast to the Jundiai reservoir sediments, the TSE3 core showed a clear upward Fe migration after the TZ. This result is explained by the strong negative Ce anomalies in the upper TSE3 core (Fig. 2), which favors Fe accumulation under reducing and anoxic conditions. The fine particle deposition (clay) in this core creates favorable conditions for reducing environments, as the dissolved oxygen (DO) in the sediment–water interlayers can be scarce under this scenario (Hahn et al., 2019).

For cores TSE1 and TSE4, no clear transition was observed and the evaluated parameters showed relative homogeneity throughout the cores. These cores also showed the lowest Fe concentrations compared to the other cores analyzed.

PTE assessment

The PTE enrichment factors (EFs) in the analyzed cores are presented in Fig. 5. The PTEs—Cr and Co—showed low enrichment in both reservoirs and were not included in the graphs. The Sediment Lower Core (SLC) was established as the last analyzed layer for the cores that presented TZ (JSE1, JSE2, TSE2, and TSE3).

It is important to note that the elements presented a higher enrichment pattern in the UCC (mainly) and NASC compared to the other references. The parameters considered more conservative for the environmental impact assessment are WRSS since it serves

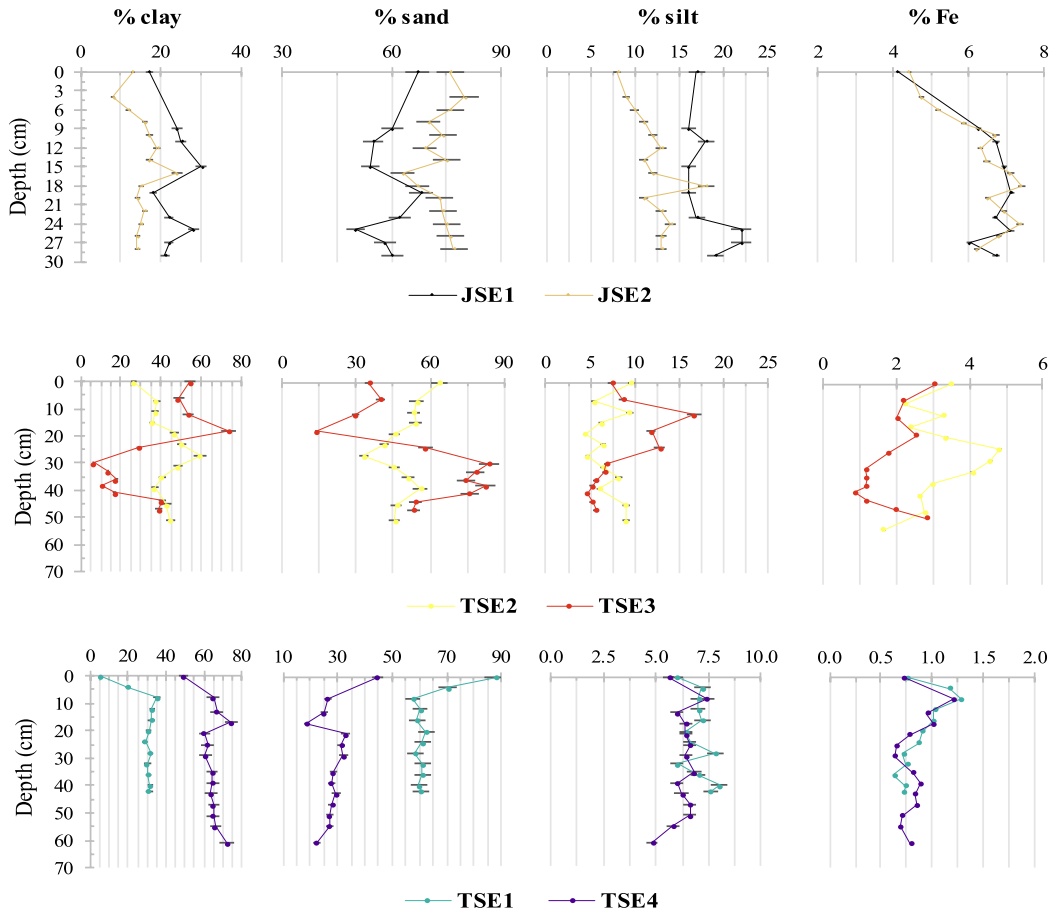

Fig. 4 Grain size analysis and Fe percentages in the sediment cores from the Jundiaí and Taiaçupeba reservoirs. The graphs are plotted on two axes: the x-axis is the result of clay, silt, sand, and Fe; the *y*-axis is the core depth, in cm. *The Microsoft Excel software was used to create this artwork

as a reference for sediments, and SLC, which evaluates the geochemical background of the area before the flooding of the reservoir. For instance, the element As showed an extremely high enrichment in the UCC assessment. In the WRSS and SLC categories, these enrichments were predominantly moderate or low. Overall, the sediments from the Jundiai reservoir showed significantly lower enrichments of PTEs compared to the Taiaçupeba reservoir. A significant finding of the study was the extremely high EFs calculated for the element Zn in the sediment core TSE3 from the Taiaçupeba reservoir (Fig. 5b). This enrichment was pronounced in all the reference values considered. In addition, the sediments from this reservoir presented moderate to significant enrichments for the elements As, Sb, U, and Th in the WRSS and SLC parameters. Figure 6 shows the vertical distribution of these elements through the four cores collected to better illustrate their behavior.

*Graphs were organized using the enrichment categories proposed by Sutherland (2000): no enrichment if $EF < 2$; moderate enrichment if $2 < EF < 5$; significant enrichment if $5 < EF < 20$; very high enrichment if $20 < EF < 40$; and extremely high enrichment if $EF > 40$. These categories were separated by reference lines and background colors. *Sampled cores were categorized by color, size, and shape of the symbols. *The element Zn was not evaluated by the NASC reference (Gromet et al., 1984). *The Tableau software was used to create this artwork.

The concentration of Zn in the upper part of core TSE3 from the Taiaçupeba reservoir has significantly

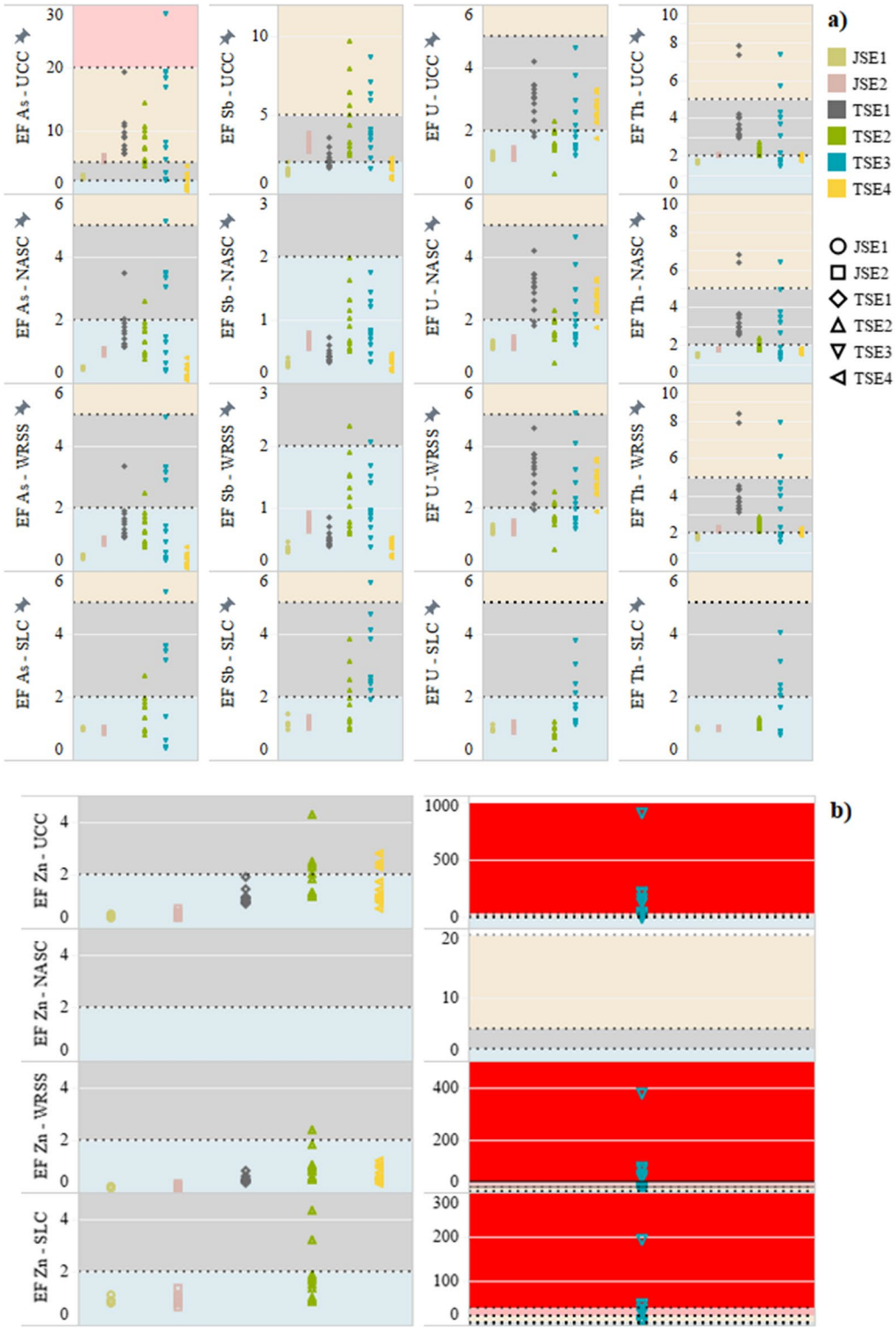

Fig. 5 PTEs—As. Sb, U, and Th (**a**), and Zn (**b**)—enrichment factors (EFs) in the sediments from the Jundiaí and Taiaçupeba reservoir

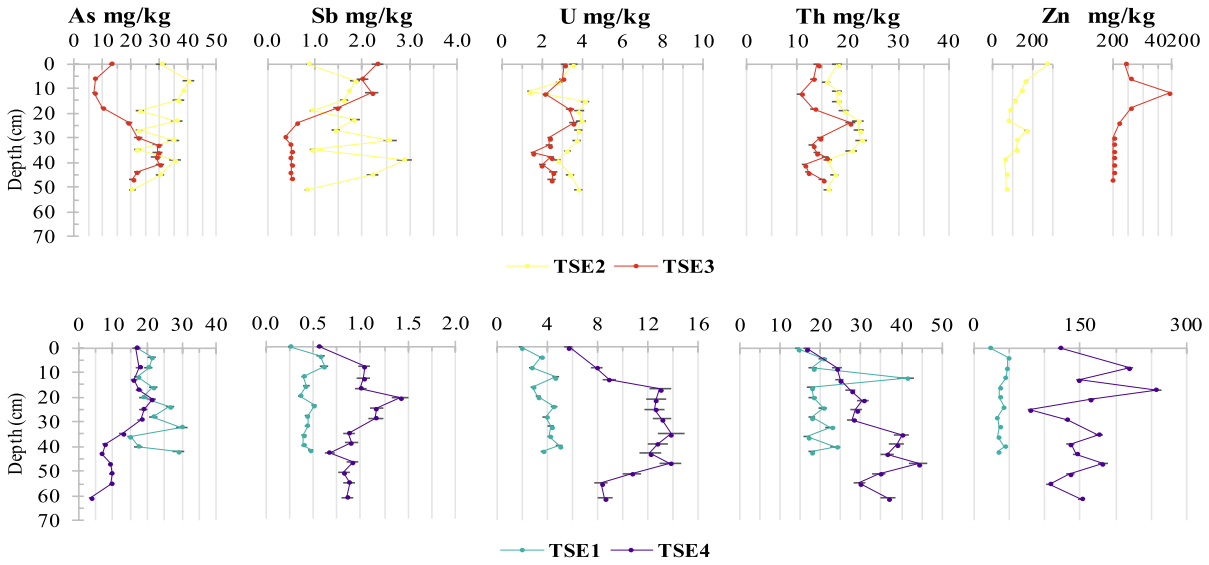

Fig. 6 Vertical distribution (mg/kg) of As, Sb, U, Th, and Zn in the sediment cores from Taiaçupeba reservoir. *The Microsoft Excel software was used to create this artwork

exceeded the PEL values (> 315 mg/kg), with a peak at a depth of 12 cm where the concentration reached 38,200 mg/kg. The study by Xie et al. (2019) suggests that Zn in the form of carbonates and sulfates has a higher bioavailability. Typically, the presence of these phases is associated with the oxidation of ZnS, which is more common during water oxygenation events, leading to the oxidation of S^{2-} to SO_4^{2-}. In this core, the redox conditions traced by the negative Ce anomalies suggest the possible occurrence of water with low dissolved oxygen up to the TSE3 core, which may be a consequence of the anthropogenic environmental impact on the Taiaçupeba reservoir. Reducing and anoxic conditions favor the immobilization of Zn in the form of sulfide (ZnS), which is less bioavailable. As reported by Esteves (2011), reservoirs in tropical areas often undergo cycles of stratification/destratification, which can lead to changes in redox conditions due to the cyclical availability of oxygen in the water column. Zinc levels above the PEL found in this core are of concern because the increased bioavailability of Zn during oxygenation events poses significant ecological risks to the aquatic community in the area. To understand the behavior of Zn in the TSE3 core, the linear regression models with clay percentages, Hf and K concentrations, and the (La/Yb)N ratios are shown in Fig. 7.

Positive weak correlations between Zn, clay, and (La/Yb)N were observed in Fig. 7. The negative trend with Hf may indicate the anthropogenic nature of the Zn concentration in this core. The inverse pattern with K reduces the likelihood of atmospheric deposition. The Zn concentrations found in TSE3 are consistent with the results reported by Van Damme et al. (2010), where total Zn concentrations in sediments contaminated by mining and smelting activities ranged from 10,000 to 69,000 mg/kg. The tremendous increase in the Zn concentrations in the upper core found in this study may indeed be a result of the mining activities around the reservoir. Figure 8 provides detailed geographic information on the Taiaçupeba reservoir and the location of the sampling sites near mining and agricultural areas.

The satellite image shows the influence of agricultural and mining areas along the margins of the reservoir. The image also shows the location of the streams that feed the reservoir. It is important to note that on the south bank of the reservoir, there is an area highlighted in yellow with exposed soil and some artificial ponds, where a mining company is located. This arm of the reservoir receives runoff from several tributaries of the Taiaçupeba River. Analyzing all the information from the area along with the results, the following hypothesis is

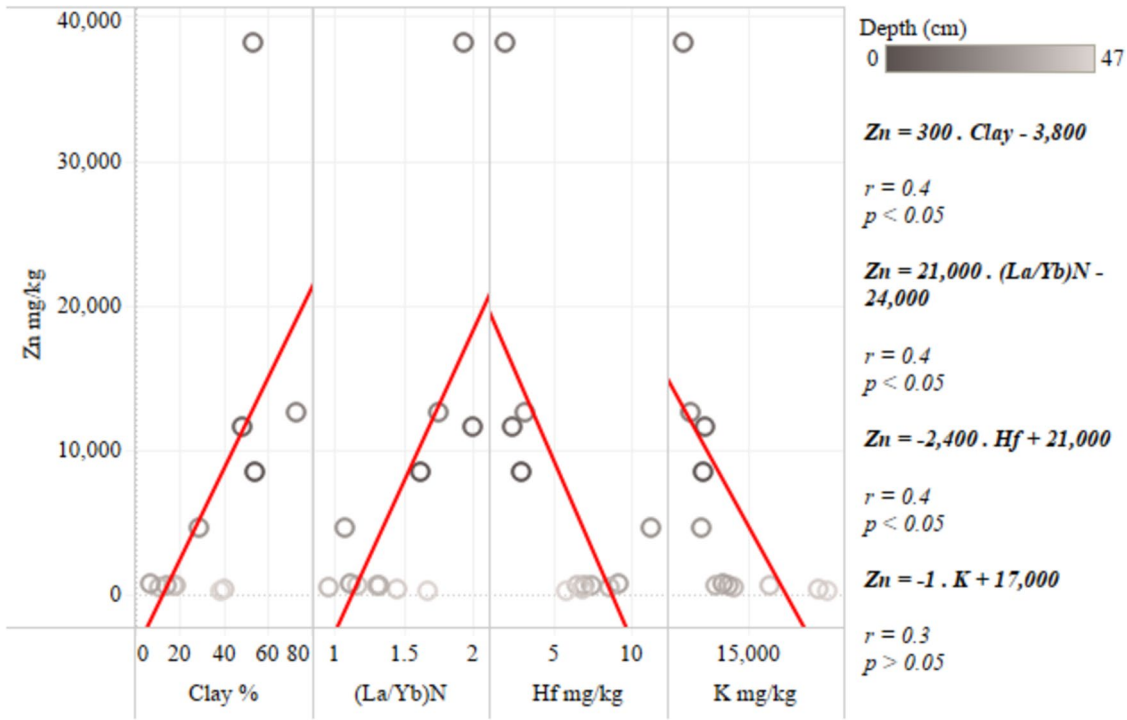

Fig. 7 Trend lines between Zn, clay, Hf, K, and (La/Yb)N in the TSE3 sediment core from the Taiaçupeba reservoir. *The Tableau software was used to create this artwork

proposed to explain the extremely high zinc enrichment found in the TSE3 core (Fig. 8: TA3):

- There was a drastic change in the grain size of this sediment core, with clay concentrations increasing significantly after a depth of 24 cm in TSE3. This increase was also observed in the adjacent core (TSE2), although less pronounced (see Fig. 4).
- The similar trend between Zn and clay, particularly in the upper portions of the TSE3 core, may indicate that the high concentration in the sediment is a result of the transport of clay particles contaminated with Zn due to soil disturbance and handling from mining activities on the southern margin of the reservoir.
- The preferential accumulation of this clay in TSE3 over TSE2 can be explained by the change in the course of the tributary stream, which directs the flow toward open water in the region where TSE3 was collected. Clay deposition is favored under these conditions of flow diversion to deeper areas. However, further studies with a larger number of samples should be conducted to validate this hypothesis.
- After this influx of clay contaminated with Zn, the concentrations of both parameters decreased in the upper part of the core and returned to the geochemical background levels for the area.

Figure 9 presents the PCA results for the entire data set to illustrate the overall behavior of PTEs in the sediment of both reservoirs.

Several considerations should be made regarding the results obtained from the PCA analysis:

- Considering the correlations in the first principal component (PC1), a clear grouping of the elements Cr, U, Th, Fe, Sc, Ta, and Hf was observed, together with silt particles. The REEs, especially the LREEs, and Na showed an inverse correlation with this group. These correlations suggest natural accumulation processes for the PTEs—Cr, U, and Th—in the sediments of the studied reservoirs. The moderate enrichment patterns for U and Th compared to the UCC,

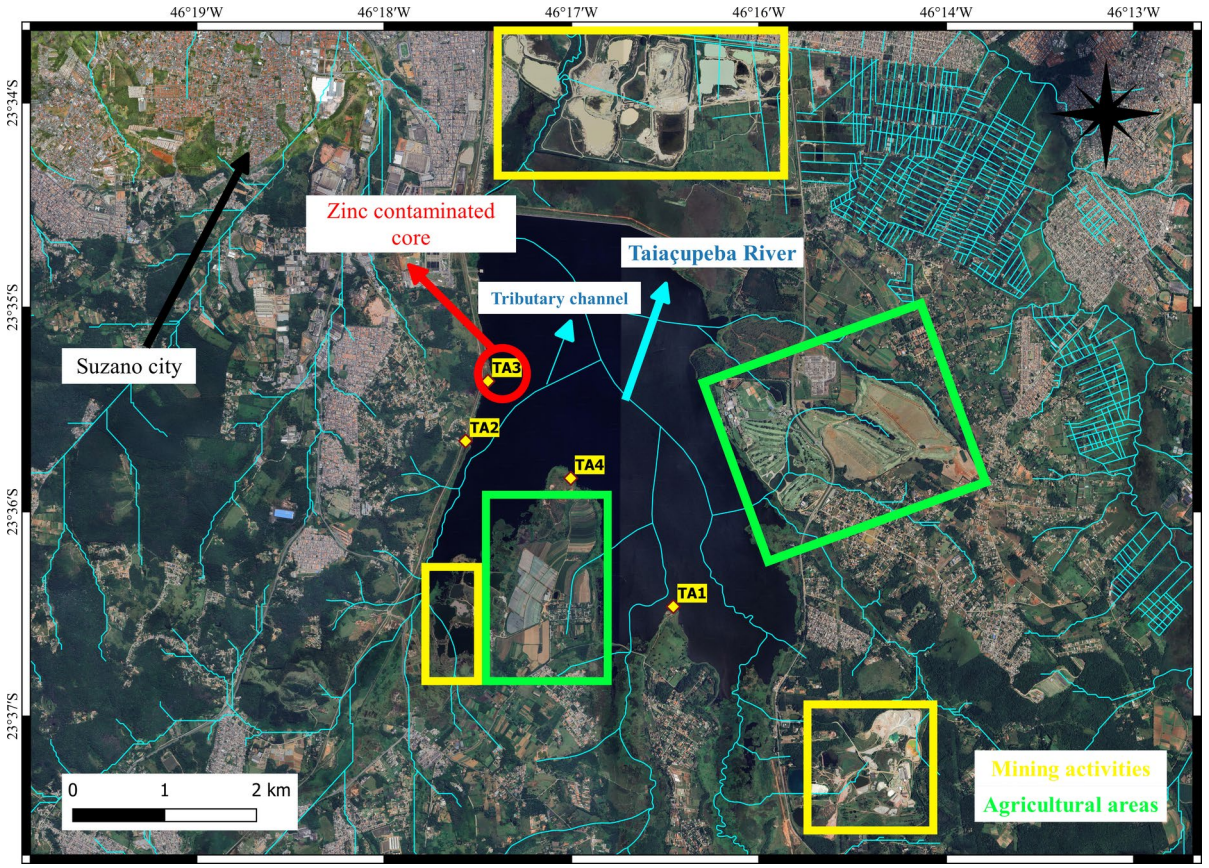

Fig. 8 Satellite map of the Taiaçupeba reservoir with detailed geographic information. *The QuantumGIS (QGIS) software was used to create this artwork

NASC, and WRSS references, mainly in the Taiaçupeba reservoir, can be explained by the high degree of weathering of the predominant granitic rocks in the Upper Tiete watershed. This hypothesis is supported by the correlations with Hf and Ta, which are signatures of weathering processes in the study area.

- Regarding the REEs group, the inverse correlation with geochemical tracers (Hf, Ta, and Sc) in PC1 was mainly influenced by the results from the Taiaçupeba reservoir sediment, which showed low to high anomalies for this class of elements compared to the background geochemical references (Fig. 2). This increase may be due to the various stressors present along the reservoir margins, including agricultural and mining activities, as well as the proximity of large urban centers that contribute to atmospheric pollution and the release of liquid wastes into the reservoir's streams.
- The correlations in the second principal component (PC2) indicate a grouping of the elements Zn and Co, with an inverse correlation with As and sand. These results confirm the significant anthropogenic contribution of Zn in TSE3, since Co, which has a similar chemical behavior, showed low enrichments throughout the study area.
- The correlation between As and sand was also observed in the PC3 component, although this component had a lower variance in the results.
- The parameters depth, clay, (La/Sm)N, K, and Sb, as well as anomalies in Ce and Eu, showed low correlations in both principal components PC1 and PC2 (<0.4); therefore, it is not possible to infer their influence on the other PTEs.

Regarding the correlations of As it is important to note that the sandy sediment cores (TSE1 and TSE2) presented significant EF values for this element when

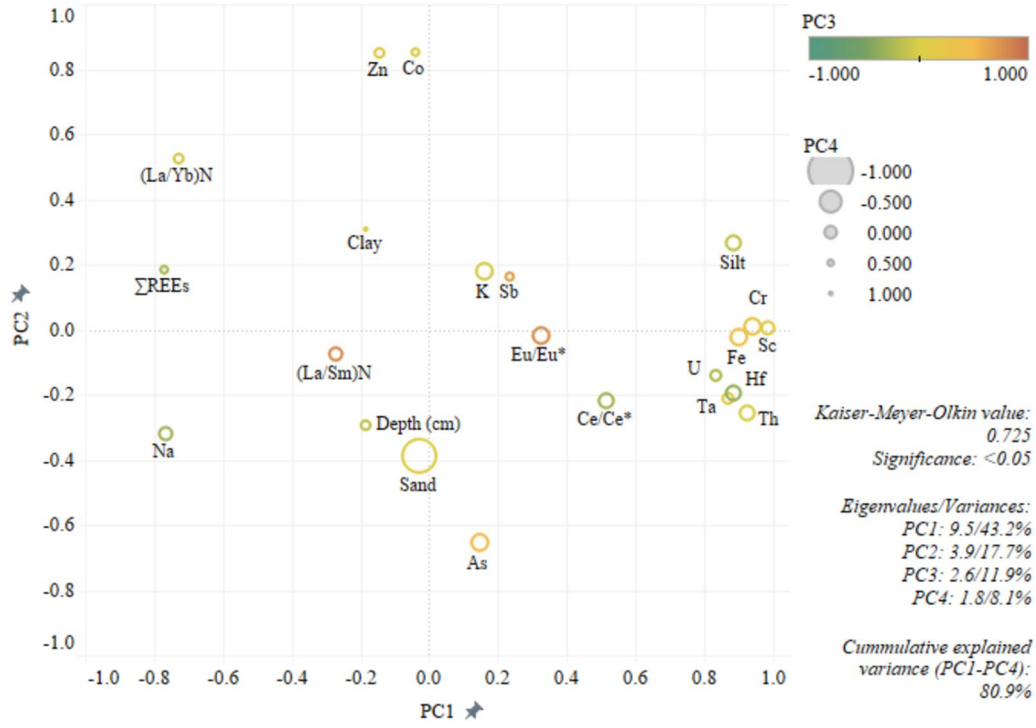

Fig. 9 Sediment PCA results for both reservoirs. *The Tableau software was used to create the artwork

compared to the UCC reference values. This enrichment was also pronounced in the pre-transition zone of the TSE3 core, which has remarkably sandy particles prior to the reservoir filling phase and clay inflows. This behavior is quite unusual, as trace elements are generally depleted in sandy sediments, however, there is a study developed by Mirlean et al. (2013) that indicates a high As sorption capacity in sandy-calcareous bioclasts. The presence of sedimentary rocks (conglomerate and arenite) in the catchment area of the Taiaçupeba reservoir could explain these correlations. The geological As enrichment compared to UCC values was also studied by Menezes et al. (2020). In this study, natural arsenic concentrations in Brazilian soils ranged from 15 to 24 mg/kg, exceeding the UCC value of 4.8 mg/kg and the PEL value of 17 mg/kg. Although the concentration in the sediment represents a positive lithological anomaly, the levels above the PEL in almost all cores from both reservoirs may pose a risk to the local biota.

For example, the apparent As depletion in the upper TSE3 core zone (Fig. 6), where it is clay-rich and contaminated with Zn, could be of concern due to the reductive/anoxic environmental conditions (Ce/Ce* < 1.0) in this core that could remobilize this element, triggering possible dissolution and subsequent availability in the reservoir water (Kneebone et al., 2002).

Conclusion

In this study, sediment analysis revealed severe Zn contamination in the Taiaçupeba reservoir, with concentrations well above the Probable Effects Level (PEL) and extremely high enrichments relative to background geochemical references. Zinc concentrations in one of the sediment cores sampled from this reservoir were compared to levels found in sediments known to be contaminated by mining activities, showing similar concentration ranges. The deposition of Zn-contaminated clay particles in core TSE3 occurred after the transition zone to the reservoir inundation area, where geographic features may have led to the accumulation of these Zn-contaminated fine

particles. Future research should focus on the spatial distribution of Zn in the reservoir through geostatistical analyses at different sediment and water points to confirm potential sources of contamination. In addition, detailed studies on the bioavailability and ecological risk of this element are needed to assess the damage this contamination may cause to the aquatic community of the reservoir.

The elevated REE concentrations in the Taiaçupeba reservoir compared to background references confirm the anthropogenic sources in this important water system for the supply chain of the most populated city in Brazil. Otherwise, the other PTEs, including Sb, Co, Cr, U, and Th, showed no evidence of anthropogenic influences in either reservoir. The concentrations of the geochemical tracers—Hf, Ta, and Sc—were very useful in explaining the sedimentary dynamics and the deposition of Cr, U, and Th. Thus, the Jundiaí reservoir showed the least anthropogenic influence on trace elements between the two reservoirs studied.

The positive As anomaly relative to the UCC reference values found in this study and in other Brazilian regions opens a wide scope for advanced local geochemical studies, as this element is of great interest in environmental monitoring due to its high toxic potential.

This research contributes significantly to the expansion of the database on trace element occurrence in dam reservoirs in Brazil, specifically addressing the distribution and chemical behavior of the elements As, Sb, Co, Cr, Zn, U, and Th in one of the most impacted watersheds in State of Sao Paulo, due to its proximity to Brazil's largest metropolitan area. Therefore, monitoring research and advances in environmental assessment techniques are of undeniable importance, as they provide data for decision-making by the water resource management agencies. This study also contributes to the dissemination of geochemical approaches for a better discussion of the results, generating more accurate impact assessments regarding the presence of PTEs in public water supply systems. Environmental protection measures and remediation of contaminated areas will be crucial to maintain the ecological balance of the reservoirs and ensure access to high-quality water for the population.

Acknowledgements We thank the Environmental Police of Mogi das Cruzes County for guaranteeing the fieldwork safety.

Author contribution Pedro do Nascimento Gonçalves: conceptualization, software, validation, formal analysis, investigation, writing—original draft, and visualization. Sandra Regina Damatto: conceptualization, methodology, resources, writing—review and editing, supervision, project administration, and funding acquisition. Joseílton Marques de Souza: validation, formal analysis, investigation, and visualization. Lucio Leonardo: conceptualization, resources, and writing—review and editing.

Funding Two funding agencies supported this research: the National Council for Scientific and Technological Development (CNPq) and the Coordination for the Improvement of Higher Education Personnel (CAPES).

Data availability No datasets were generated or analyzed during the current study.

Declarations

Competing interests The authors declare no competing interests.

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