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Longitudinal Gradient and Historical Trends of Arsenic and Metals in a Tropical Reservoir

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This study aimed to establish the longitudinal gradient and historical trends of arsenic and metals in a tropical reservoir. Water and sediment samples were collected along the Rio Bonito reservoir (Espírito Santo, Brazil), and a sediment core was obtained from the lacustrine zone. Plasma spectrometric techniques were employed to determine concentrations of As, Cd, Co, Cu, Fe, Mn, Ni, and Pb in water and sediment samples, and the sediment samples were dated using high-resolution gamma spectrometry. Higher concentrations of elements were observed in surface water samples from the riverine zone and bottom water samples from the transition zone. Concerning surface sediment samples, elevated concentrations were noted in the transition and lacustrine zones, where deposition is more intense. The sediment core was dated to 1940, before the reservoir dam construction, utilizing ^{210}Pb dating. Certain elements exhibited progressively increasing concentrations over time. Enrichment factor, pollution load, and ecological risk indexes indicated the need for continuous monitoring of this reservoir.

Keywords: toxic metals, reservoir, sediment, water, plasma techniques, dating

Introduction

The trace element accumulation in aquatic ecosystems increased interest in several aspects, such as destination, effects, the behavior of these contaminants in food chains, and biogeochemical cycles. The concentration residual contaminant is continuously growing in the natural environment, both in quantity and diversity. Urban and industrial development are mainly responsible for the degradation of streams and rivers, decreasing ecological health in river basins.[1-3] Thus, establishing trace element concentrations is essential to assess environmental conditions.[4,5]

Water is the main transport route for trace elements in dissolved phases or bounded to suspended particles. Determining the concentrations of elements dissolved in water is important to assess the degree of contamination of an ecosystem. However, the determination of trace elements in water should always be followed by analysis of other matrices, such as sediments.[6]

Sediments are preferred monitoring compartments since their contaminant concentrations are higher than water.[7-9] They are recognized as an essential sink of trace elements in aquatic systems, providing short- and long-term memory of the contaminant load in water bodies.[10]

Along with the river network of a river basin, different aquatic ecosystems can function as sources or sinks of materials transported by the river flow, groundwater exchanges, and atmospheric deposition. Lakes, reservoirs, flooded areas, and estuaries act as retaining filters for materials such as organic matter, nutrients, and organic and inorganic contaminants.[11] Although the retention capacity is mainly controlled by lake morphometry (e.g., mean depth), lacustrine hydrodynamics (e.g., theoretical retention time), and chemical stratification, reservoirs can critically affect the sink of trace elements in bottom sediments.

Reservoirs are hybrid systems between rivers and lakes and show a longitudinal gradient that influences sedimentation processes, thermal and chemical

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stratification, and primary productivity.[12] Fluvial processes in the riverine zone bring high amounts of allochthonous materials and promote higher turbulence in shallower waters. The lacustrine zone is closest to the reservoir dam, where greater depths promote thermal and chemical stratification with the predominance of autochthonous fine sediments. The transition zone presents intermediate characteristics and its extension depends on river flow conditions.[12,13]

The deposition of trace elements along longitudinal gradients suggests higher concentrations near the reservoir dam, where deposition conditions are more favorable.[8,12,14] Reducing conditions due to anoxic bottom waters of tropical reservoirs promote the diffusion of trace elements from sediment porewater, enriching the concentration in the bottom waters of the reservoir and turning them bioavailable. The increased contaminant concentration becomes a diffuse pollution problem for bottom water discharges in the dam reservoir.[15]

The enrichment of elements along sediment profiles in lakes and reservoirs has been evaluated through sediment cores and layered sampling extrusion. The highest concentrations are typically found in surface layers, reflecting recent contamination from both point and diffuse sources, which are often linked to population growth, urbanization, and industrialization.[4,16] Furthermore, the chronology of trace element deposition has been determined using the lead isotope ^{210}Pb, based on the dating of extruded sediment samples.[17] This assessment also considered the influence of upstream land use and land cover changes within the river basin, in addition to reservoir morphometry and hydrodynamics.[16,18-20]

The objective of this study was to establish the longitudinal gradient and historical trends of trace elements in a tropical reservoir evaluating the concentration of As, Cd, Co, Cu, Fe, Mn, Ni, and Pb in sediment and water from the riverine, transition, and lacustrine zones. Moreover, the geochronology of these elements was established by analyzing a sediment core sample from a region next to the reservoir, as a historical record of pollution.

Experimental

Instrumentation

The determination of trace elements in water and sediment samples was performed by inductively-coupled plasma mass spectrometry (ICP-MS, NexION 300D, PerkinElmer, Waltham, United States) and inductively-coupled plasma optical emission spectrometry (ICP-OES, Optima 7000 DV, PerkinElmer, Waltham, United States). Argon gas with a purity of 99.9992% (White Martins, Cariacica, Brazil) was used for the generation and maintenance of the plasma, nebulization of the sample, and as auxiliary gas. Table 1 shows the instrumental parameters used to determine trace elements.

Study area

The Rio Bonito reservoir (RBR), located 640 m above sea level in the Santa Maria da Vitória River basin, Espírito Santo, Southeast Brazil, has an area of 2.4 km^2 and a maximum depth of 30 m (Figure S1, presented in the Supplementary Information (SI) section). The São Luiz

Table 1. Instrumental conditions and parameters of ICP-MS and ICP-OES

Instrumental parameter	Operating condition	
	ICP-MS	ICP-OES
Nebulization chamber	glass cyclonic with bulkpar	glass cyclonic with bulkpar
Nebulizer	concentric meinhard, type C	concentric meinhard
Cone (i.d.) / mm	nickel 1.1	–
Torch	quarZTZTo easyglideTM torch	1 slot
Radio frequency power / W	1450	1250
Sample introduction	peristaltic pump	peristaltic pump
Torch configuration	–	axial
Observation height / mm	–	15
Auxiliary gas flow rate / (L min^{-1})	1.2	1.2
Plasma gas flow rate / (L min^{-1})	16.0	16.0
Nebulizer gas flow rate / (L min^{-1})	1.1	1.1
Replicate	3	3
Spectral line / nm	–	Fe (II) 239.562 Mn (II) 257.610
Isotopes measured	^{208}Pb, ^{112}Cd, ^{59}Co, ^{75}As, ^{60}Ni, ^{63}Cu, ^{55}Mn	–
Internal standard	Rh, Sc, Ir	–

ICP-MS: inductively-coupled plasma mass spectrometry; ICP-OES: inductively-coupled plasma optical emission spectrometry; i.d.: internal diameter.

stream, as a tributary of the Santa Maria da Vitória River, drains the municipality of Santa Maria de Jetibá (31,176 inhabitants in 2010), including its urban area, which lacks a proper sewerage system, and flows into the upper part of the RBR.

The climate is tropical, with a mean annual rainfall of 1,339 mm and two distinct seasons: hot and wet summer (mean maximum temperatures from 27.8 to 30.7 °C) and dry winter (mean minimum temperatures from 9.4 to 11.8 °C).[21] The local geology is characterized by gneiss and migmatite from the Paraíba do Sul Complex.

The reservoir has a drainage basin of 617.3 km^2 with rough topography (mean slope of 30.1%), reaching up to 76% slope near the reservoir. Its water is used for hydroelectric power production and irrigation. The construction of the reservoir began in 1952 and since 1959, it has been operating. In 2010, the land use and cover in the reservoir watershed were composed of forests (44%), agriculture (25%), and *Eucalyptus* forestry (22%), the remaining was urbanized.

Due to nutrient inputs from domestic effluents and the leaching of cropland soils and sewage inputs from the urban area of Santa Maria de Jetibá, by the São Luiz River, a tributary of the Santa Maria da Vitória River, the RBR is meso-eutrophic.[22] According to the National Sewerage Atlas,[23] in 2013, Santa Maria de Jetibá presented 41.3% of domestic sewage without treatment, which produced 342 kg BOD (biological oxygen demand) *per* day.

Field sampling, preparation, and analysis of samples

Three sampling sites were selected along the longitudinal axis of the RBR for water and surface sediment sampling. These sampling sites were located in the lacustrine zone (LZ), located 238 m from the dam (20°3'40.94"S and 40°38'43.48"W), the transition zone (TZ) located 3.1 km upstream (20°2'6.23"S and 40°39'10.86"W), and the riverine zone (RZ), located 6.3 km upstream (20°1'45.85"S and 40°40'3.86"W). These sampling sites were selected during the high-water period (wet season). During the low water period, the RZ had to be relocated 3.0 km downstream (20°1'51.93"S and 40°41'24.88"W) (Figure S1, SI section).

Surface sediment and water samples were collected in March (late rainy season) and November (early rainy season) 2016 with a stainless-steel (Ekman Bottom Grabs, Royal Eijkelkamp, Giesbeek, Netherlands) and a bottle of 2.8 L (External Spring Niskin, General Oceanics, Miami, United States), respectively. The surface sediment aliquots were collected in the central part of the sample without touching the grab, while the water samples were on the surface of each site. In the TZ, water samples were collected from the middle and bottom of the water column. Temperature, physicochemical variables of dissolved oxygen, Eh, and electrical conductivity were evaluated every 1 m with a multiprobe (Horiba U-50, Kyoto, Japan).

The sediment core was collected in the LZ zone in November 2016 using a hammer core with a 120 cm long and 8 cm diameter tube (Uwitec Single Corer, Mondsee, Austria). In the laboratory, the 80-cm sediment core was sliced every 2 cm up to the 40-cm depth, every 4 cm from the 40- to the 60-cm depths, and every 10 cm until the bottom 80-cm. The surface and core sediment samples were dried in an oven (Ethik, São Paulo, Brazil) at 60 °C for 72 h, sieved (2 mm), and packed in plastic bags.

The EPA 3051A method[24] was used to prepare the sediment sample. In this process, 0.250 g of the sample was heated with 10 mL HNO_3 68% m m^{-1} P.A. (Sigma-Aldrich, Saint Louis, United States), previously purified in distiller sub-boiling (DistillAcid BSB-939-IR, Berghof Products, Germany) using microwave radiation heating (Multiwave GO, Anton Paar, Switzerland). For decomposition, the following heating program was used: (*i*) 3 min to reach a temperature of 100 °C, (*ii*) 2 min maintaining heating at 100 °C, (*iii*) 5 min to reach a temperature of 180 °C and (*iv*) 10 min maintaining heating at 180 °C. All sediment samples were decomposed in triplicate. Water samples (1 L) were filtered in cellulose acetate membranes (0.45 µm porosity), acidified with HNO_3 at 2% v v^{-1}, and stored in polypropylene flasks for further analysis, according to the EPA 3015A method.[25] A spike and recovery test for water analysis evaluated the accuracy of the method. The certified reference material NIST RM 8704 (Buffalo River Sediment) from National Institute of Standard and Technology (NIST, Gaithersburg, USA) was used to assess the accuracy of the sediment analysis.

Sediment core dating

Sediment samples were dated by measuring the radioelements determined by high-resolution gamma spectrometry using a spectrometer with a hyperpure Ge detector (HPGe) (model GMX25190P, Ortec, Oak Ridge, United States).

The experimental model used for analyses in gamma spectrometers is based on measuring sediment samples in cylindrical polyethylene containers (21.7 cm^2 base area, 1.1 cm height, and 23.9 cm^3 volume) during 70,000 s. The method, previously presented by Figueira *et al.*,[26] is based on the daily calibration of the detector with calibrated sources of ^{60}Co and ^{137}Cs, measurement of background radiation, and counting efficiency analysis with the determination of radionuclides in certified reference materials. The ^{210}Pb photopeak was 46.52 keV.

Organic matter content

To determine the organic matter content in sediment core samples, about 1.0 g of sample was weighed in a porcelain crucible, and placed in the muffle furnace (model LF0612, Jung, Blumenau, Brazil) at 550 °C for 3 h.[27] After removing the crucible from the muffle furnace, it was placed in a desiccator to cool until room temperature. Then, the sample was weighed and the percentage of organic matter was calculated.

Granulometric analysis

In total, 5 g of sediment samples were weighed (0.1 mg) in polyethylene terephthalate (PET) bottles, right away the addition of 50 mL of 0.1 mol L^{-1} NaOH (Neon Comercial, Suzano, Brazil), and agitation for 16 h in an agitator (TE-160/24 Wagner, Tecnal, Piracicaba, Brazil). After shaking, sand fractions were sieved (63 µm) and weighted. Clay and silt fractions were stirred in distilled water and, after 3 h of rest, 25 mL of each sample were pipetted, dried, and weighed (0.1 mg). Sand, clay, and silt contents were calculated.

Mineralogy

In the mixture of clay and silt, from sediment core samples of the Rio Bonito reservoir, X-ray diffraction analysis was performed using an X-ray diffractometer (XRD-6000, Shimadzu, Chiyoda-ku, Japan) equipped with a Cu tube (Kα1 = 1.5418 Å). The speed of analysis was 2° min^{-1} and the step was 0.02° for a 10 to 70° sweep. Diffractograms were treated in the Origin software version 9 (OriginLab)[28] and the XPowder software[29] was used to identify mineral phases.

Pollution indices and parameters for the evaluation of trace elements

The contamination of aquatic ecosystems by trace elements was evaluated by indicators such as enrichment factor (EF),[30,31] pollution load index (PLI),[32] ecological risk index (ERI),[33] and indexes established by the Canadian Sediment Quality Guidelines (SQGs), threshold effect level (TEL) and probable effect level (PEL).[34] EF, PLI and ERI were calculated according to equations 1-4, respectively.

$$\text{EF} = (\text{M}/\text{X}_{\text{sample}})/(\text{M}/\text{X}_{\text{reference}}) \qquad (1)$$

where M is the analyzed element concentration, and X is the normalizing element. In this work, Fe was used for this purpose.

$$\text{PLI} = \sqrt[n]{\text{FC}_1 \times \text{FC}_2 \times \text{FC}_3 \times \ldots \text{FC}_n} \qquad (2)$$

where FC is the concentration factor for the analyzed element, and n is the number of elements studied, calculated using equation 3.

$$\text{FC} = [\text{Element}_i]/[\text{Element}_{\text{BG}}] \qquad (3)$$

where [Element]$_i$ is the concentration of the element in slice i of the sediment or concentration in the sediment and [Element]$_{\text{BG}}$ is the concentration of the element at the bottom of the sediment/background.

$$\text{ERI} = \text{T}_{\text{ri}} \times \text{FC} \qquad (4)$$

where FC is the sample concentration factor, ERI the monomial of the potential risk factor for each element $(\text{RI} = \sum_{i=1}^{n} \text{E}_{\text{ri}})$ and T$_{\text{ri}}$ the toxic weight of the element. In this work, T$_{\text{ri}}$ = 5 was used for Cu, Ni and Pb and T$_{\text{ri}}$ = 10 for As.[33]

Statistical analysis

Metal concentration data in water and sediments at each location were expressed as mean values and standard deviations (n = 3). The concentration of metals in water was evaluated from a regulatory perspective based on the values from CONAMA 357/2005.[35] For sediment, this assessment was carried out based on TEL and PEL values. To establish a correlation between the trace elements quantified in the core sediment samples, a correlation analysis was performed using Spearman distances between the data. The software package used was Microsoft Office Excel, version 2019.

Results and Discussion

Thermal, physical, and chemical parameters of the water column

Higher thermal and chemical stratification in the LZ, with a difference of 4.2 °C between surface and bottom; hypoxia (< 2.0 mg L^{-1} dissolved oxygen) from 16.0 m depth were observed. The anoxic and reducing bottom water (−100 mV) showed a 23% increase in electrical conductivity, (103 µS cm^{-1}). The pH showed slight variation between surface and bottom waters (7.89 at the surface and 7.05 at the bottom). Under anoxic and reducing conditions at the bottom of the water column, adsorbed substances in the sediment were diffused into the water column via interstitial water.[15,36-38]

In the TZ, the thermal stratification was 3.2 °C between surface and bottom waters (11.6 m), but it was observed no significant gradients for dissolved oxygen, Eh, pH, and electrical conductivity. For the RZ, the bottom and surface waters were mixed due to its reduced depth (1.0 m) and the turbulence associated with river flow. Figure 1 shows the variation of the temperature, dissolved oxygen, Eh, and electrical conductivity profiles in the transition zone of the RBR in November 2016.

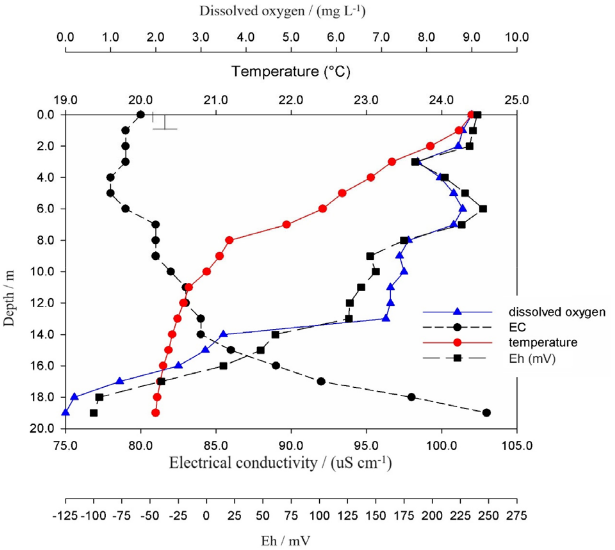

Figure 1. Temperature (°C), dissolved oxygen (mg L^{-1}), Eh (mV), and electrical conductivity (µS cm^{-1}) profiles in the transition zone of the Rio Bonito reservoir.

Determination of trace elements in water and surface sediments

The accuracy was evaluated with the spike and recovery tests for the water and certified reference material for the sediment. Recoveries determined at two concentration levels ranged from 86 to 114%, and recoveries level of the certified reference material ranged from 80 to 96%. Table 2 presents the results found for As, Cd, Co, Cu, Fe, Mn, Ni, and Pb in water samples from the RZ, TZ, and LZ. Samples collected on the surface of the RZ in both seasons presented higher trace element concentrations. Probably, this is because this site receives all contributions from the Santa Maria da Vitória River. After damming, water flow decreases, changing the vertical and horizontal distribution of biotic and abiotic characteristics and increasing its residence time,[13] which contributes to the sedimentation process, reducing the trace element concentration in the TZ and LZ.

In Table 2, it is noted that the Fe concentration is above the value established by CONAMA at points RZ (surface) and TZ (20 m) in the late rainy season. In the early rainy season, the Fe value is above the allowed limit at points RZ (surface), TZ (2 m), and TZ (9 m). In addition to the contribution of the Santa Maria da Vitória River, the high Fe value at the RZ point (surface) can be attributed to its origin as a result of weathering processes caused by the action of wind, water, and temperature.

The trace element concentration in the TZ increased as the depth increased. According to Mortimer,[36] the solubility of ions from sediments to the water column depends on several factors, but the most important is the dissolved oxygen concentration. Anoxic conditions promote a reducing environment with negative Eh, causing the diffusion of trace elements from sediments to the water column.[15,36,37] During summer, the thermal stratification is higher, causing an oxygen deficit in the hypolimnion, which leads to anoxic conditions at the bottom of the water column and increases the metal concentration.

Table 2. Trace element concentrations (n = 3) and their standard deviations in water samples from the riverine (RZ), transition, (TZ) and lacustrine (LZ) zones of the RBR during the late rainy season (March 2016) and early rainy season (November 2016)

Zone	Trace element / (µg L^{-1})							
	As	Cd	Co	Cu	Fe	Mn	Ni	Pb
				Late rainy season				
RZ	0.120 ± 0.001	0.0158 ± 0.0001	0.124 ± 0.001	1.39 ± 0.01	947 ± 9	0.300 ± 0.001	0.450 ± 0.003	0.339 ± 0.007
TZ	0.125 ± 0.001	0.00177 ± 0.00001	0.0407 ± 0.0013	0.279 ± 0.004	28 ± 1	0.163 ± 0.002	0.216 ± 0.009	0.0504 ± 0.0011
TZ (5.0 m)	0.123 ± 0.001	0.00209 ± 0.00001	0.0425 ± 0.0004	1.65 ± 0.01	39 ± 1	0.170 ± 0.001	0.222 ± 0.011	0.0876 ± 0.0034
TZ (20.0 m)	0.161 ± 0.001	0.00136 ± 0.00001	0.474 ± 0.003	5.36 ± 0.05	2868 ± 57	0.242 ± 0.001	0.415 ± 0.016	0.110 ± 0.001
LZ	0.138 ± 0.001	0.00209 ± 0.00001	0.0425 ± 0.0016	0.510 ± 0.01	27 ± 1	0.170 ± 0.002	0.222 ± 0.007	0.0876 ± 0.0028
Range	0.120-0.161	0.00136-0.0158	0.0407-0.474	0.279-5.36	27-2868	0.163-0.300	0.216-0.450	0.0504-0.339
				Early rainy season				
RZ	0.146 ± 0.001	0.00397 ± 0.00001	0.109 ± 0.001	2.58 ± 0.18	715 ± 9	11.2 ± 0.1	0.493 ± 0.004	0.247 ± 0.001
TZ	0.131 ± 0.001	0.00298 ± 0.00001	0.0282 ± 0.0001	0.665 ± 0.040	98 ± 1	2.27 ± 0.04	0.195 ± 0.001	0.0142 ± 0.0001
TZ (2.0 m)	0.130 ± 0.001	0.00226 ± 0.00001	0.134 ± 0.001	0.636 ± 0.014	102 ± 1	2.17 ± 0.03	0.0829 ± 0.0003	0.0133 ± 0.0002
TZ (9.0 m)	0.135 ± 0.001	0.00298 ± 0.00001	0.175 ± 0.003	0.578 ± 0.012	499 ± 5	2132 ± 51	0.135 ± 0.001	0.0572 ± 0.0008
LZ	0.133 ± 0.001	< 0.000002	0.0213 ± 0.0001	0.569 ± 0.019	73 ± 2	2.84 ± 0.04	0.0748 ± 0.0004	0.00525 ± 0.00002
Range	0.130-0.146	0-0.00397	0.0213-0.175	0.569-2.58	73-715	2.17-2132	0.0748-0.493	0.00525-0.247
CONAMA[35]	0.14	1.00	50.0	9.00	300	100	25.0	10.0

CONAMA: Conselho Nacional do Meio Ambiente.

Surface sediment samples showed higher trace metal concentrations in the TZ and LZ, particularly during the late rainy season (Table 3). In these areas, the water flow is slower, which helps the sedimentation process.[8,12] In the early rainy season (November 2016), the concentrations of Mn, Co, Cu, and Cd were higher upstream, which was associated with the hydrological pulse of the reservoir. Moreover, it may also be associated with the geological characteristics of the site and levels of anthropic impact in the watershed since some trace elements present higher levels downstream of the reservoir, in the site near the reservoir (LZ).

Determination of trace elements in the sediment core

The granulometry of sediment core samples presented a predominance of clay (Figure S2, SI section). These sedimentological characteristics of the reservoir show the type of material transported in suspension and the sediment fraction deposited in the sampling site. From the fine sediment fraction (i.e., clay and silt), it was performed X-ray diffraction analysis in sediment core samples (Figure S3, SI section). Similar diffractograms were obtained for all samples, which shows that the mineral contribution is the same over the years. The main mineral phases observed were kaolinite, goethite, gibbsite, illite, and mica.

In the Santa Maria da Vitória River basin, latosols and cambisols constitute the largest cluster of soils.[39] These soils present minerals such as kaolinite, gibbsite, goethite, hematite, mica, and illite.[40] Therefore, these minerals are of allochthonous origin. According to Pires *et al.*,[41] latosols present a high capacity to retain Pb. It may explain the high levels of Pb found in the sediment core. The presence of Al, Fe, or Mn oxides increases the adsorption of trace elements, decreasing their mobility. Mn and Fe oxides are strongly associated with Co, Ni, As, and Pb.[42]

Organic matter content (Figure S4, SI section) was similar until 60-cm depth, however, in depths of 70 to 80 cm, they were different. These values correspond to a period before the construction of the reservoir, which may show that this higher content is of allochthonous origin and the organic matter from plant debris are from fragments of leaves and tree branches of the flooded and surrounding area. Thus, these results allow us to classify the sediment core as organic, as it presents more than 10% dry weight of organic matter, according to Håkanson and Jansson.[43]

Considering the trace element contents obtained from the sediment core and the fractions of clay, silt, sand, and organic matter (OM), we performed a Spearman correlation (Table 4). Results showed that the trace element behavior in the sediment is influenced by interactions between the elements themselves and also between them and clay, silt, and organic matter contents. Among the main correlations, we observed a positive correlation between the clay fraction and the elements Ni, Mn, and Fe, as well as between silt and Cu, and a negative correlation between the elements and the sand fraction. Moreira[44] shows the strong interaction between trace elements and clay and silt. Moreover, we observed a positive correlation between the organic matter

Table 3. Trace element concentrations (n = 3) and their standard deviations in surface sediment samples from the riverine (RZ), transition (TZ), and lacustrine (LZ) zones of the RBR during the late rainy season (March 2016) and the early rainy season (November 2016), and TEL and PEL values for reference

Zone	Trace element / (mg kg^{-1})							
	As	Cd	Co	Cu	Fe	Mn	Ni	Pb
Late rainy season								
RZ	2.39 ± 0.19	0.0549 ± 0.0068	4.93 ± 0.30	12.8 ± 0.8	72401 ± 1610	237 ± 6	12.2 ± 0.6	22.9 ± 1.1
TZ	2.67 ± 0.09	0.00563 ± 0.00089	5.23 ± 0.21	12.0 ± 0.4	83698 ± 2340	369 ± 9	13.2 ± 0.8	26.4 ± 0.8
LZ	3.28 ± 0.14	0.00599 ± 0.0011	2.90 ± 0.23	10.3 ± 0.4	96872 ± 2730	144 ± 3	9.80 ± 0.51	15.1 ± 0.7
Range	2.39-3.28	0.00563-0.0549	2.90-5.23	10.3-12.8	72401-96872	114-369	9.80-13.2	15.1-26.4
Early rainy season								
RZ	2.18 ± 0.05	0.104 ± 0.001	5.51 ± 0.13	16.3 ± 0.5	54036 ± 291	402 ± 3	6.13 ± 0.21	14.9 ± 0.2
TZ	2.99 ± 0.06	0.0734 ± 0.0013	4.79 ± 0.10	13.7 ± 0.3	63796 ± 1005	252 ± 3	7.00 ± 0.36	16.5 ± 0.4
LZ	3.26 ± 0.05	0.0457 ± 0.0014	4.13 ± 0.09	11.6 ± 0.5	63819 ± 6092	283 ± 21	4.95 ± 0.12	16.3 ± 0.4
Range	2.18-3.26	0.0457-0.104	4.13-5.51	11.6-16.3	54036-63819	252-402	4.95-7.00	14.9-16.5
Reference values								
TEL	5.90	0.60	–	35.7	–	–	18.0	35.0
PEL	17.0	3.50	–	197	–	–	34.9	91.3

TEL: threshold effect level; PEL: probable effect level.

Table 4. Spearman correlations for trace elements in the sediment core

	Cu	Pb	Ni	As	Co	Cd	Mn	Fe	Clay	Silt	Sand	OM
Cu	1.000											
Pb	0.402[a]	1.000										
Ni	0.593[b]	0.490[b]	1.000									
As	0.734	0.049	0.498[b]	1.000								
Co	0.239	–0.445[a]	–0.029	0.590[b]	1.000							
Cd	0.392[a]	–0.129	0.540[b]	0.574[b]	0.361	1.000						
Mn	–0.211	–0.500[b]	–0.218	–0.016	0.440[a]	0.077	1.000					
Fe	0.159	–0.207	–0.363	0.179	0.410[a]	–0.227	0.390[a]	1.000				
Clay	–0.476[a]	–0.227	0.542	–0.419	–0.281	–0.353	0.672	0.781	1.000			
Silt	0.489[b]	0.229	0.340	0.429[a]	0.277	0.350	0.062	–0.073	–0.998[b]	1.000		
Sand	–0.171	–0.360	–0.467[a]	–0.169	0.339	–0.308	0.449[b]	0.431[b]	0.154	–0.173	1.000	
OM	0.199	–0.200	0.308	0.181	0.322	0.328	0.433[a]	0.663	–0.360	0.349	0.560	1.000

[a] The correlation is significant at the 0.05 level (two extremes); [b] the correlation is significant at the 0.01 level (two extremes). OM: organic matter.

content and Fe and between Ni with Cu, As, Cd, and Pb, and As with Cu, Co, and Cd.

Figure 2 shows the distribution of trace elements in relation to the depth of the sediment core and the corresponding year (estimated dates). The mean age of the samples was calculated from the sedimentation rate value (0.42 cm $year^{-1}$) (Constant Initial Concentration model, CIC), which provided a value in the 1940s for the 80-cm depth of the dam. This value shows that the sediment core is from a period prior to the construction of the Rio Bonito reservoir (1952).

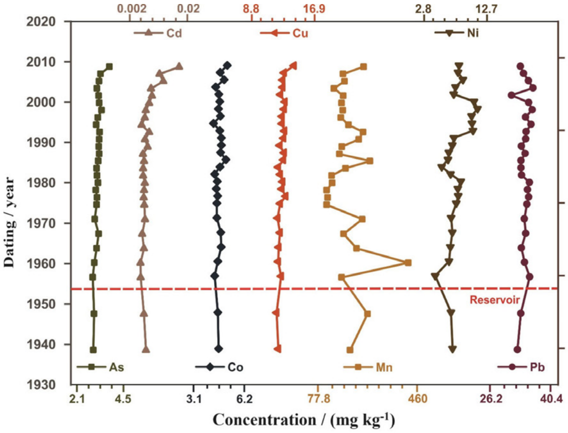

Figure 2. Trace elements profiles of sediment core of the Rio Bonito reservoir.

As, Cd, Co, Cu, and Pb contents did not present great differences along the sediment core, except for surface samples. The concentration of As, Cd, Co, and Cu increased in the sediments collected on the surface of the sediment core, showing recent sources of these elements in the Rio Bonito reservoir system. Although the Pb content in the surface sediment decreased, the values obtained were higher than TEL at many different times. The concentration of Mn and Ni showed large variations along the sediment core. Mn showed a high concentration in the period of construction of the reservoir (460 mg kg^{-1}) at a 56-cm depth (1958), which be associated with sediment deposition that occurred in the form of oxide and sulfide. The concentration of Ni presented a positive variation in depths of 14- to 20-cm (11.3-12.7 mg kg^{-1}), showing higher deposition from 1992 to 2000. This increase in Ni may be related to a period of significant demographic increase in the city of Santa Maria de Jetibá. Moreover, the Ni content decreased in surface sediments while Mn increased.

The EF was considered to evaluate the trace element accumulation over time. Figure 3 presents the degree of pollution by the calculated EF content: EF < 2 means minimum contamination, 2 > EF > 5 moderate contamination, and 5 > EF > 20 significant contamination. In this study, we used Fe as a normalizing element.[31,45]

Although As and Cu showed slight variations in EF, this increased over the years, which shows the increase

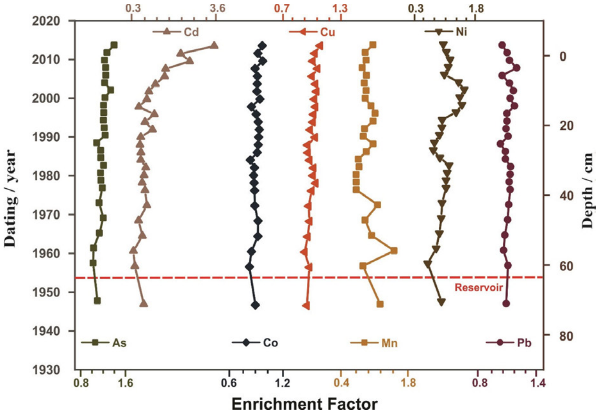

Figure 3. Enrichment factor for trace elements of sediment core of the Rio Bonito reservoir.

in chemical contamination by As and Cu of the bottom sediment over time. Even with this increase, EF values remained below 2, showing minimal contamination. Pb and Co showed more significant variations, presenting periods of increase and decrease in the availability. However, Co increased and Pb decreased in recent years, in the upper part of the sediment core. This increase in Co may be related to the increase in economic activities in Santa Maria de Jetibá. Considering that the RBR is located near a highway, the traffic of motor vehicles could be a possible source of Pb until the 2000s, due to the effects of tetraethyl lead along with gasoline. In 1992, the addition of Pb on petroleum was prohibited in Brazil.[46]

Ni presented significant variations in EF. After the construction of the reservoir, EF decreased, but in the following years, it significantly increased (from 1958 to 1976, which corresponds to the construction of connecting roads between Santa Leopoldina and Santa Maria de Jetibá). After this period, EF decreased again until the mid-1980s, the period of urbanization of Santa Maria de Jetibá, which promoted a new increase in EF. In the most superficial sediments of the sediment core, we observed again a decrease in EF, which may be related to the expansion of domestic sewage treatment in the municipality.

Mn presented a large variation in EF, which increased significantly mainly during the construction of the reservoir, reaching values close to 2. After the period of construction of the reservoir (1952-1959) and the road network in the following years, EF decreased, with small variations. In the sediments, EF increased. Cd presented few variations in EF until the mid-1990s. From this period on, EF significantly increased, and it is probably related to the population growth in Santa Maria de Jetibá and the increase in economic activities in this municipality. The value of Cd in surface sediments is higher than 2, which shows moderate contamination.

Pollution indexes (PLI and ERI) allowed the sediment quality analysis concerning contamination by trace elements, as well as an increase in deposition over the years and its reflection on the environment. PLI shows how many times the trace element concentration in the sediment exceeds the background concentration and provides a general indication of the level of trace elements in a sample.[32,47] On the other hand, ERI assesses the risk of bioaccumulation and biomagnification of trace elements along the trophic chains of the aquatic ecosystem.[33]

Figure 4 shows the calculated PLI value for the sediment sample: PLI = 0 indicates an uncontaminated region, 0 < PLI < 1 region with low pollution, and PLI > 1 deteriorated region. In this study, the PLI value is slightly above 1, indicating that the ecosystem is suffering an anthropic contribution. Moreover, the increase in pollution rates over the years is evident, especially after constructing the reservoir, roads, and bridges that connect the municipalities of Santa Leopoldina and Santa Maria de Jetibá. Population growth and the development of Santa Maria de Jetibá were factors for this increase, mainly due to the release of domestic and industrial effluents into the river, increasing the PLI value. The 2-cm depth presented one of the highest PLI values (1.88), showing recent reservoir contamination that is probably due to population growth and an increase in fruit and vegetable activities.

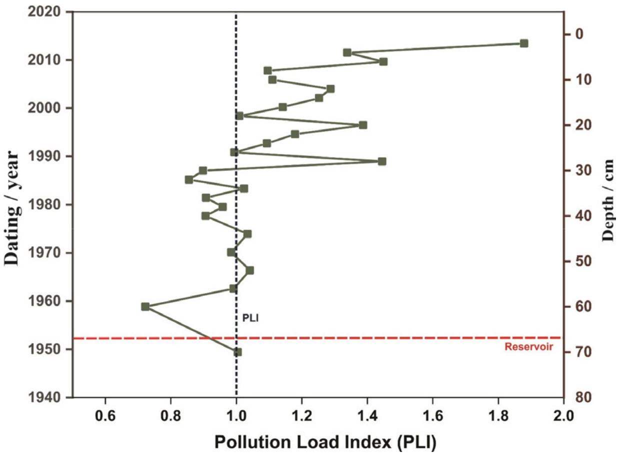

Figure 4. The pollution load index (PLI) of sediment samples from the Rio Bonito reservoir. PLI value > 1 indicates the deteriorated region.

The ERI pollution index was also calculated and presents an increase in the sediment core from its base to the surface (Figure 5), especially in the 1990s, which corresponds to the period of population growth. ERI value < 150 indicates sediment with low ecological risk, 150 < ERI < 300 moderate risk, and 300 < ERI < 600 considerable risk. The

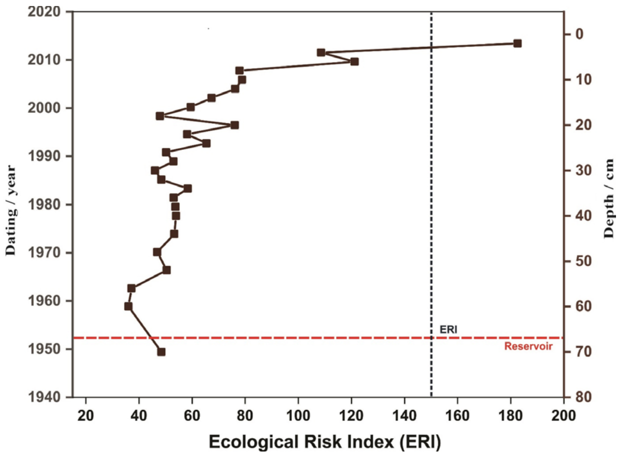

Figure 5. Ecological risk index (ERI) of sediment samples from the Rio Bonito reservoir. ERI value > 150 indicates sediments moderate ecological risks.

layer with the highest ERI value (183) is associated with a 2-cm depth. Therefore, this reservoir is suffering recent impacts and presents a moderate ecological risk.

Although PLI shows that the reservoir presents an interference (element contribution by anthropic routes) ERI values, in general, are not at the level of bioaccumulation and biomagnification in the aquatic food. However, indexes at the 2-cm depth (surface sediment) increased sharply, bringing concern to the reservoir quality, due to the possible contamination.

Conclusions

The water samples showed higher concentrations of trace elements in the riverside and transition zones of the Rio Bonito reservoir, while the surface sediment samples showed higher concentrations in the transition and lacustrine zones. The levels of trace elements in the core sediment samples indicate that the values originated from natural factors, as well as from anthropic activities present today and activities carried out decades ago. The distribution of elements in the environment is governed by interactions between the elements themselves, between the elements and the clay and silt fractions, and between the elements and organic matter. The levels of trace elements in the sedimentary core increased over the years, probably due to the increase in human activities around the reservoir. The PLI values corroborate the state of alertness regarding the management and care of the Rio Bonito reservoir, showing the need for frequent monitoring.

Supplementary Information

Supplementary information is available free of charge at http://jbcs.sbq.org.br as PDF file.

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Author Contributions

Roberta C. Salles was responsible for data curation, formal analysis, investigation, methodology, and writing original draft; Rafael Mantovaneli for investigation and writing (review and editing); Luana S. Moreira for investigation and writing (review and editing); Rubens C. L. Figueira for conceptualization and funding acquisition; Geisamanda P. Brandão for conceptualization; Gilberto F. Barroso for conceptualization, funding acquisition, project administration, and writing (review and editing); Renato Rodrigues Neto for conceptualization, supervision, and writing (review and editing); Maria Tereza W. D. Carneiro for conceptualization, supervision, funding acquisition and writing (review and editing).

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