



Reconstructing 90 years of anthropogenic activities in a subtropical reservoir: a chemometric and paleolimnological perspective

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Abstract

Environmental reference conditions (RC) and historical trends are crucial for assessing the degree of freshwater impact and formulating restoration measures. This is particularly relevant for freshwater systems used as potable water sources. Using sediments from the Carlos Maggiolo reservoir (Minas, Uruguay), located in a watershed with a mining history, this study aimed to (1) establish metal (As, Cr, Cu, Ni, Pb, and Zn) RC using a predicted interval (PI) chemometric technique; (2) evaluate metal enrichment and toxicity over time and space; and (3) assess environmental changes examining geochemical proxies. Surface sediments from 29 stations were used to establish RC and a core from the dam area was sampled to infer past conditions. The sediments were submitted to partial digestion and analyzed by inductively coupled plasma optical emission spectrometry- ICP-OES. Enrichment factor (EF) calculated using both PI and bottom core values did not show significant differences over time. Over space and time, most metals primarily originated from natural sources ($EF < 2$). The PI in mg/kg was Cr: 23.74–37.32; Cu: 25.75–48.99; Ni: 16.29–25.55; Pb: 7.63–13.75; and Zn: 94.34–174.80. A stratigraphically constrained cluster analysis corroborated by a permutational multivariate analysis of variance categorized the reservoir into two zones: Zone I, before reservoir operation to ~1996, and Zone II from ~1997 to 2017. The average concentrations of the main metals of toxicological interest in zones I and II, respectively, were as follows: Cr 37.60 ± 1.59 , 34.54 ± 1.49 mg/kg; Cu 49.76 ± 2.84 , 44.55 ± 2.70 mg/kg; Ni 24.11 ± 0.67 , 22.53 ± 1.22 mg/kg; Pb 12.40 ± 0.63 , 13.52 ± 0.82 mg/kg; Zn 99.25 ± 3.12 , 93.86 ± 4.42 mg/kg; Mn 1160.56 ± 68.88 , 1441.61 ± 83.55 mg/kg; and P 1243.21 ± 271.56 , 1128.42 ± 183.10 mg/kg. According to a principal component analysis, the period preceding reservoir operation until ~1985 was linked to mining activities and application of Cu_2SO_4 , and the period from 1985s to 2000 was influenced by C and P concentrations due to increasing agricultural and afforestation activities in the watershed that consume P fertilizers. The most recent period, from 2000 to ~2017, was characterized by an increase in sedimentation rates mainly associated with erosion, particularly in the agricultural areas. This subsequent soil loss in the watershed could compromise the reservoir's useful life. This study contributes to a better understanding of metal geochemistry in subtropical reservoirs and aids in formulating effective recovery and restoration measures.

Keywords Reference condition · Paleolimnology · Chemometric · Enrichment factor · Sediment rate · Drinking water

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Introduction

Establishment reference conditions for assessing anthropogenic impacts and implementing recovery and restoration measures in aquatic ecosystems is a critical step (Cardoso-Silva et al. 2013). Typically, in water management systems, reference conditions are associated with periods of minimal human impact, often returning to the pre-industrial era (Bennion et al. 2011; Smol 2019). Various methods can be used to derive reference conditions, including the “reference site approach” (Poikane et al. 2010; Bailey et al. 2014), mathematical modeling (EC - European Commission 2000), and historical data acquired through monitoring, literature sources, or paleolimnological studies (EC- European Commission 2000; Poikane et al. 2010).

Each method has advantages and limitations, and a combination of techniques can be employed whenever possible. The reference site approach is rarely applied because pristine ecosystems often seen as models of reference are increasingly impacted by anthropogenic activities (Moss et al. 2003; Hering et al. 2010). Although promising, mathematical models require a substantial amount making their application unfeasible in data-scarce situations (da Silva et al. 2022). Monitoring and literature data often fail to provide sufficient information on reference conditions and rarely capture the onset of human impact (Heinsalu and Alliksaar 2009; Paterson et al. 2020). Paleolimnological studies have been successfully utilized to bridge data gaps in monitoring programs and establish reference conditions (Bennion et al. 2011; Smol 2019; de Oliveira Soares Silva Mizaël et al. 2020; Halac et al. 2020; Cardoso-Silva et al. 2021). Paleolimnology assumes that aquatic ecosystems record past watershed activities in their sediment layers (Smol 2008, 2019). Thus, sediment accumulation zones serve as historical records, and by analyzing multiple proxies, it becomes possible to discern historical trends (Smol 2008) and identify past conditions suitable as targets in a management system (Bennion et al. 2011).

Given the accelerated introduction of metals into freshwater ecosystems through human activities global metal pollution is a significant environmental concern (Smol 2008). Therefore, the use of metals as proxies for reconstructing anthropogenic impacts and reference conditions is widespread. These elements persist in aquatic environments and may exert adverse and toxic effects when their concentrations exceed certain thresholds (Cardoso-Silva et al. 2016, 2022) for long periods, even when the sources of contamination have been removed. In reservoirs used for public water supply, careful monitoring of metals is essential, as both the biological communities and the population supplied by the affected source can be at risk.

When geochemical proxies such as metals are used in paleolimnological studies, this approach can be further strengthened by combining it with chemometric techniques. Chemometrics involves the application of mathematical and statistical methods to analyse chemical data and can help identify patterns and sources of metal contamination (Inobeme et al. 2022). Researchers can differentiate between natural and anthropogenic metal contributions by applying chemometric analysis and establishing accurate reference conditions (Kim et al. 2017; Inobeme et al. 2022). When these techniques are applied together, they enable the interpretation of complex data sets, providing a more comprehensive understanding of metals’ temporal and spatial distribution. Integrating chemometric analysis with paleolimnological data can enhance the accuracy and reliability of reference conditions, ultimately supporting more effective management and restoration efforts in aquatic ecosystems.

Despite its importance, studies employing paleolimnological approaches in South American countries are still scarce, with most research conducted in high-latitude regions (Escobar et al. 2020). Even fewer studies have focused on contamination and pollution by metals and/or eutrophication. A search in the Scopus database (July 2024) using the keywords “paleolimnology” AND “eutrophication” OR “contamination” OR “pollution” OR “metal” yielded a total of 789 publications. The field is most prominent in Northern Hemisphere countries, particularly Canada, the United States, the United Kingdom, and China. Only 50 studies were conducted in South American countries (Argentina, Brazil, Chile, Colombia, Ecuador, Peru, Uruguay). This highlights a significant gap in information for the region, which has unique ecosystem characteristics, underscoring the need for further research.

In Uruguayan reservoirs (e.g., Halac et al. 2020), for example, no published research has delved into the history of metal contamination in these environments. The region features an extensive river network with numerous reservoirs that require further investigation. In the Santa Lúcia watershed, which supplies water to 60% of the national population (Zabaleta et al. 2023), agricultural and mining activities represent potential risks to both biological communities and public health. The application of pesticides and fertilizers can elevate the introduction of metals into aquatic ecosystems, thereby posing a potential threat to local wildlife. Agricultural activities have also resulted in increased soil erosion and nutrient pollution. It is estimated that 75% of the total nitrogen load and 62% of the total phosphorus load entering reservoirs originate from fertilizer application (Sabaj and Saravia 2023).

In Uruguay, most studies have focused on evaluating metal concentrations in the estuarine region of the Río de La Plata, near the capital Montevideo. In these areas there are records of some metals with concentrations between the empirical

Sediment Quality Guideline' (SQG) TEL (Threshold Effect Level) or ISQG (Interim Sediment Quality Guideline) and PEL (Probable Effect Level) (CCME-Canadian Council of Ministers of the Environment 2001) (e.g., As, Cr, Cu, Ni, Pb, and Zn- (Muniz et al. 2011, 2015, 2019) García-Alonso et al. 2017)) suggesting toxic effects are uncertain to occur. There is a risk of metal accumulation in organisms (Hutton et al. 2015), such as polychaete (Castiglioni et al. 2018). Increases in metal concentration in the Rio de la Plata estuary after 1917 have been registered (García-Rodríguez et al. 2010) and linked to anthropogenic pressures.

Using a subtropical reservoir used for public water supply (Ingeniero Carlos Maggiolo reservoir- Minas- Uruguay) as a study model, this study aimed to (1) establish sediment metal reference conditions using both chemometric and paleolimnological techniques; (2) assess the enrichment and toxic potential of metals over time and in surface sediments; and (3) evaluate environmental changes in the watershed through geochemical proxies. This study addresses the significant gap in paleolimnological studies in South American countries. Besides that, it contributes to the global body of knowledge on paleolimnology and chemometrics, demonstrating their applicability and benefits in diverse ecological contexts, thereby encouraging similar studies in other regions.

Material and methods

Study area

The Ingeniero Carlos Maggiolo dam (hereafter Maggiolo reservoir) is situated in the San Francisco stream, in the upper basin of the Santa Lucía river in the county of Lavalleja (Uruguay). The catchment covers 140 km² in a hilly area, reaching the highest point of the landscape about 260 m above reservoir level. The average annual temperature is 17°C, and the year is rainy and partly cloudy, with heavier precipitation occurring from October to March, with a total annual precipitation of approximately 1250 mm (Gliemmo 2014). Throughout the year, the temperature typically ranges from 5°C to 30°C and rarely drops below -2°C or rises above 36°C.

Constructed in 1934, this reservoir is the main drinking water supply for the city of Minas, which had an estimated population of 38,446 inhabitants in 2011, supplying water to approximately 18,000 homes. The waterbodies within this watershed are generally assessed to be in good to moderate environmental conditions based on water physical–chemical variables and the structure of the main biological communities (Meerhoff et al. 2017).

The reservoir has a storage capacity of 670,000 m³, yet it has experienced substantial reductions in volume during

drought periods, as exemplified in 2015 when it decreased to 162,000 m³ (Meerhoff et al. 2017) operating at 10% of its capacity in 2023. The water surface area is 31.35 ha, with a maximum depth of 9.5 m in the dam area, and the average depth (estimated as the ratio between volume and area) is 2.10 m (Meerhoff et al. 2017). The country is vulnerable to high winds (World Bank 2024), which, combined with the shallow depth of the reservoir, can promote the mixing processes of the water column. The reservoir's basin is predominantly characterized by a crystalline geological base, marked by the abundant presence of crystalline limestones and dolomites. This region exhibits rugged terrain with varying slopes, encompassing the San Francisco River, a tributary of the Santa Lucía River, and it receives effluents from both mining operations and a hotel-tourism complex (Fornaro et al. 2014).

Historical activities along the San Francisco stream watershed

Mineral extraction and processing have been prominent economic activities in the area since the mid-nineteenth century (Álvarez et al. 2015). Nowadays, the primary economic activities within the watershed encompass extensive livestock production and natural grasslands, covering an area of 98 km² (70% of the total area). Afforestation occupies 20 km² (14%), tourism and recreation parks span 4.2 km² (3%), olive tree plantations and non-irrigated agriculture cover 3.2 km² (2%), and there is a current mining activity on 0.53 km² (0.4%) (Meerhoff et al. 2017; Burwood et al. 2021). Native forests comprises approximately 11% of the area (Perez 2023). The name of the capital town, Minas, reflects the area's mining history, with lead and manganese among the extracted metals. Additionally, until the late 1980s, the waterworks company frequently applied Cu₂SO₄ (copper sulfate) to control harmful phytoplankton growth in the reservoir, a practice discontinued due to the ecotoxicological impacts of Cu.

Regarding mining, notably, operations at the Valencia Mine, located approximately 8 km from the city of Minas and the Ing. Carlos Maggiolo reservoir, have been significant. This mine had two distinct periods of exploitation: the first focused on the extraction of metals, especially lead and zinc, and the second on dolomite extraction (Galgo 2017). Between the late nineteenth century and early twentieth century, mining was centered on extracting various minerals, such as galena (lead sulfide), lime, copper, and zinc (Galgo 2017). From 1936 to 1938, the main mineral extracted was galena, mined underground through galleries and trenches (Galgo 2017). These activities were halted around 1938, but open-pit mining began in the 1940s (Galgo 2017). From 1943 to 1986, the primary exploitation at the Valencia Mine was of dolomite,

with periods of mining expansion in 1955, 1969, and 1974 (Meerhoff et al. 2018). From 1986 to 2011, the mine remained closed due to bankruptcy in early 1986 and was auctioned in 2011 (Galgo 2017). In 2015, a new concession for dolomite mining was obtained at the Valencia Mine (Meerhoff et al. 2018). Manganese was not the main mineral extracted at the Valencia Mine or the watershed; it was mined in other locations, as shown in Fig. 1b (Alvarez et al. 2015).

In addition to mining, agriculture is another principal economic activity that can impact the watershed water quality. Family farming activities have historically characterized the region, concentrating mainly on the San Francisco stream banks upstream of the Ing. Carlos Maggiolo reservoir (Pérez-Brum 2023). The area designated for agriculture was 144 ha in 1969, 2003 ha in 2000, and 304 ha in 2008 (Alvarez et al. 2015). In 2009, there was an intensification in the sector with the cultivation of olives (Alvarez et al. 2015).

Other events, between 1934 and 2017, that may have directly affected the water and sediment quality and sedimentation rate of the Ing. Carlos Maggiolo reservoir are described as follows. Between the 1940s and 1950s, the UTE-ANTEL Park was established for tourism purposes, with reforestation of the region. Periods of drought were recorded in 1989, 1995, 2000, 2012, and 2015. Conversely, the year 2002 was marked by flooding along the watershed (Alvarez et al. 2015). In that same year, the country entered an economic recession, which may have led to a relaxation of environmental protection. Forest fires were recorded in 2004, 2005, and 2007 (Alvarez et al. 2015). In the supplementary material (Fig SM1), there is a graph with a timeline of the main impacts on the watershed that may have affected the concentration of elements and parameters evaluated in this research.

Sampling

Surface sediments at 29 sampling stations located randomly to cover all the reservoir areas and two cores in the dam area were collected in the Maggiolo reservoir (Minas-Uruguay) in October 2017 (Fig. 1a). The points were georeferenced using the UTM coordinate system, WGS84, using a Garmin 72 GPS model.

A gravity corer was released twice in the dam area of the reservoir (Ambühl and Bührer 1975). The choice of the sedimentary profile collection point is because the sampling area should ideally reflect an “average” accumulation of material from the entire watershed (Birks and Birks 2006; Smol 2008). As a result, the samples were collected from the deepest areas of the reservoir, known as the lacustrine zone, where sedimentation rates are usually higher and less susceptible to bioturbation or other mixing processes (Smol 2008). Each core (total depth ranged between 36 and 40 cm) was sliced at intervals of 2 cm stored in sterilized plastic bottles and kept in the dark at low temperature until the laboratory analysis was performed. One of the cores (core I, 40 cm depth totaling 20 samples) was used for dating using the ^{210}Pb method and the respective determination of the concentration of metals and phosphorus and for the determination of organic matter (by loss on ignition, LOI). The other core was stored (core II, 36 cm depth totaling 18 samples). The core slices were numbered in ascending order, from the top of the core to the bottom.

Surface sediments were sampled with a Lenz-type grab (400 cm²) which was deployed two times at each site. The sediment fraction from 0 to 4.0 cm depth was collected in each deployment. A portion was removed for the determination of metals and total phosphorus (TP), and another portion was removed for analyses of organic matter (OM).

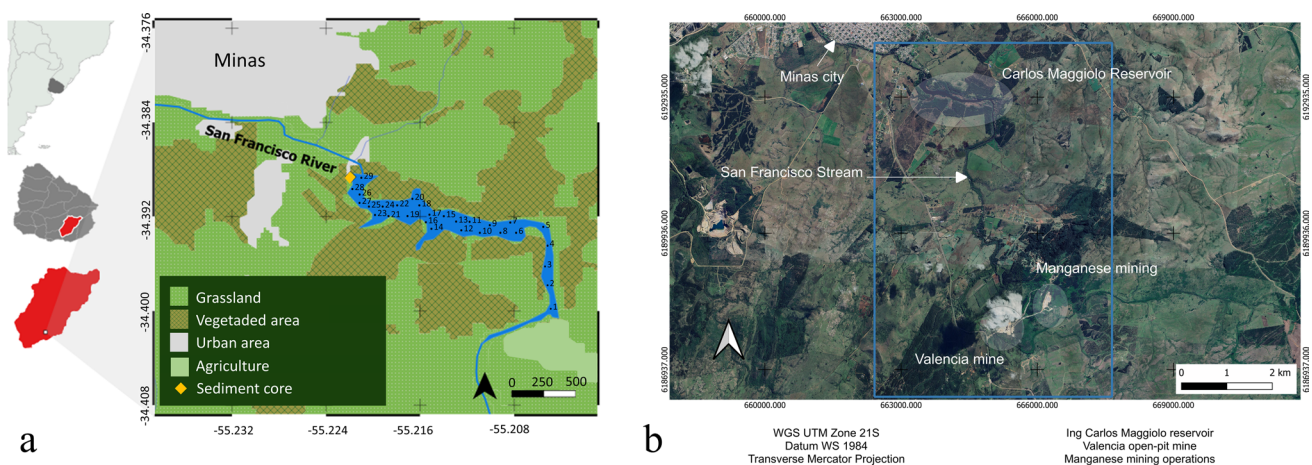


Fig. 1 Location of the hydrographic basin of the Carlos Maggiolo reservoir (Minas-Uruguay) and the sampling point of the sedimentary profile (a). Highlighted are the main mining areas over time (b)

The sediments were stored in sterilized plastic bottles and kept in the dark at low temperatures.

Laboratory analyses

The sediments were dried in a forced aeration oven at 50 °C until a constant weight, followed by grinding using a glass mortar and pestle. In core I, one portion of the sediment was designated to determine the organic matter (OM) content by the loss on ignition (LOI) method, which involves the combustion of the OM in an oven at 550 °C for 4 h (Heiri et al. 2001). The organic carbon content (C) was estimated from the OM value, assuming that the OM contained 58% carbon by weight (Meguro 2000).

Another portion of the sediment in core I was used for the analysis of the elements: Al, As, Ba, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Se, Sr, and Zn, according to US EPA method SW-846 3050 B (US EPA United States Environmental Protection Agency 1996). The method involves a strong acid digestion of the sediments with additions of nitric acid, hydrogen peroxide, and hydrochloric acid and then heating the mixture at 90 °C for about 4.5 h. Subsequently, the samples were stored at 4 °C prior to analyzing the metals and P content by inductively coupled plasma optical emission spectrometry (ICP-OES) using an Agilent Series 720 instrument. Analytical grade reagents (obtained from Merck and Sigma-Aldrich) were used in all analyses. All glassware and equipment used for the storage and processing of the samples for metal analysis were left in 10% nitric acid for at least 24 h and rinsed with ultrapure water.

The accuracy of the data obtained was evaluated in recovery assays performed using sample solutions fortified with metals. These assays employed SpecSol® G16 V standard solutions containing 100 mg/L of the metals in 2% HNO₃. A value between 75 and 125% was considered the acceptance criterion. The recovery efficiencies ranged from 79.8 to 116.9%. The metal data were expressed as milligrams per kilogram of dry weight (mg/kg dw). The same methodology was applied to surface sediments.

The age-depth model and the sedimentation rates for the sediment core were calculated using the CRS (constant rate of supply) model (Appleby and Oldfield 1978). This model uses trends on atmospheric-originated ²¹⁰Pb (also called unsupported ²¹⁰Pb, considered as the difference between ²¹⁰Pb and ²²⁶Ra) levels to estimate changes in the sedimentation rate and the age of each sediment layer. The results were validated by comparing the core depth of the layer with the highest ¹³⁷Cs level. It is widely accepted that the sediment layer with the maximum ¹³⁷Cs activity corresponds to the year of 1964, the maximum global radioactive fallout from past nuclear tests made during the Cold War (Ferreira et al. 2016). The adoption of this model observed the guidelines of Fontana et al. (2022). The radionuclides of interest (²¹⁰Pb,

²²⁶Ra, and ¹³⁷Cs) were analytically determined by gamma spectrometry in a high resolution, low background hyperpure Ge detector (ORTEC, model 25190P). In short, 10–15 g of dry sediment was ground into a fine powder using a porcelain mortar and pestle and then transferred into air-tight polyethylene containers for gamma counting for approximately 20 h (Ferreira et al. 2020).

Reference conditions

Reference conditions for metals of toxicological interest (As, Cr, Cu, Ni, Pb, and Zn) were determined through a chemometric technique (Kim et al. 2017). The technique is based on a linear regression between the concentration of a metal and a conservative element, which is not influenced by anthropogenic activities (Dung et al. 2013). Aluminum was employed as a conservative element because it is a component associated with clay minerals (Förstner and Wittmann 1981; Luoma and Rainbow 2008) an important metal-binding phase (Devesa-Rey et al. 2011). This statistical method establishes a prediction interval (PI) in which future observations would fall within 95% of probability given what has already been observed (Kim et al. 2017). Data that fall beyond the confidence interval (95%) are considered as anthropogenic loads while the data that are well-fitted with the linear regression conditions represent the background values (Covelli and Fontolan 1997; Matschullat et al. 2000; Aloupi and Angelidis 2001). In the method, a linear regression curve is generated ($p < 0.05$) to obtain the predicted value by $\hat{Y} = b_1 + b_0 \times X$. Therefore, the estimated y would lie in the range by $\hat{y} - E < y < \hat{y} + E$, where E represents the margin of error (Kim et al. 2017). This technique is advantageous when there are a large number of samples. It gives a more realistic result because it determines a range of values instead of a single value (Dung et al. 2013). In addition, even if some sediment samples are contaminated it is possible to establish the reference condition.

To evaluate the efficiency of the technique we compared the results with the mean of the bottommost values of the dam core representing the pre-industrial era (de Mahiques et al. 2009; Cardoso-Silva et al. 2021).

Contamination and toxicity

To evaluate the sediment contamination level, we analyzed the enrichment factors (EFs). The EFs help determine whether the analyzed metals originate from anthropogenic or natural sources (Devesa-Rey et al. 2011) and were calculated as follows:

$$EF = \left(\frac{Me}{EL} \right) / \left(\frac{Mer}{Elr} \right) \quad (1)$$

where Me/El is the ratio between the concentrations of the analyzed metal and the conservative element in the sample,

and Mer/Elr is the ratio of the background values for the metal to be analyzed and the conservative element. Aluminum was used as a conservative element (Förstner and Wittmann 1981; Luoma and Rainbow 2008) to represent a chemical tracer of aluminosilicates that are part of the composition of the fine-grained fractions ($< 63 \mu\text{m}$, silt, and clay). The enrichment classification according to (Sutherland 2000) varies between < 2 and > 40 :

- < 2 : *Absent or very low enrichment*
- $2 \leq EF < 5$: *Moderate enrichment*
- $5 \leq EF < 20$: *Considerable enrichment*
- $20 \leq EF < 40$: *High enrichment*
- > 40 : *Very high enrichment*

To assess the potential for toxicity, the SQG (CCME-Canadian Council of Ministers of the Environment 2001), TEL or ISQG, and PEL was employed. In this model, for each contaminant, there is a range of values, where above a given concentration (PEL), a toxic effect is likely to occur, while below a given value, TEL effects are unlikely. Values between TEL/ISQG and PEL and the effects are uncertain (CCME-Canadian Council of Ministers of the Environment 2001). Only metals of toxicological interest were evaluated (Cr, Cu, Ni, Pb, and Zn).

Statistical analysis

Basic descriptive and multivariate statistical analyses were performed for the core data. The data distribution was tested for normality and transformed using a Z score when needed. Relationships between metals, P, sedimentation rates (SR), and LOI were evaluated using Pearson correlations to better interpret the sediment geochemistry. A stratigraphically constrained cluster analysis (CONISS- Ward's method) was applied to define the main paleoenvironmental zones. A principal component analysis (PCA) was used for data ordination (Legendre and Legendre 1998). The PCA allowed us to summarize the environmental variables, evaluate whether the elements had similar sources, and identify periods of distinctive main anthropogenic impacts. The principal components can be considered indices and used to graphically sort the sampling units graphically (Legendre and Legendre 1998). A smaller number of variables can then evaluate the similarity pattern between the sampling units. A permutational multivariate analysis of variance (PERMANOVA) performed with 9999 random permutations was applied to evaluate if the main groups observed in the CONISS analysis were statistically distinct. The calculations were performed using PAST 2.7 (Hammer et al. 2001).

Results and discussion

The data are categorized into three main sections as follows. First, we examine historical trends in phosphorus and metal contamination, providing a comprehensive overview of the primary effects of metal contamination. This data lends additional insights into the current reservoir conditions. Next, we assess the general characteristics of surface sediments, a crucial analysis as no previous data exists for this specific reservoir compartment. These two approaches work in synergy to offer both a contemporary overview and a historical perspective of the impacts throughout the reservoir's operational history. Lastly, armed with this information, we propose management strategies and recommend avenues for future studies.

Historical trends

Geochronology and sedimentation rates

The vertical profile of the dam core showed episodes of dilution of unsupported ^{210}Pb in the topmost samples of the core (Fig. 2a), which can be related to increases in the sedimentation rate (SR); (Fig. 2d). The age-depth model developed for this core (Fig. 2c) was in agreement with the depth corresponding to the global fallout maximum observed at 26 cm (Fig. 2b). Since the beginning of reservoir operation in 1934 until the mid-1970s, SR remained relatively constant, exhibiting a large increase in the most recent sediment core layers (Fig. 2). The considerable change in land use and occupancy patterns in recent times, such as forestry, agriculture, and urbanization, have intensified the weathering and erosion process in the watershed (Meerhoff et al. 2017), thereby explaining the increment in SR observed in the core profile.

The first peak in the sedimentation velocity was observed in the 1980s and could be explained by the afforestation of the area surrounding the reservoir. Afforestation is a major source of disturbance and soil loss, resulting in the significant replacement of natural land cover (Huber et al. 2010; Huang et al. 2020) and consequent changes in watershed processes and ecosystem functioning. A subsequent peak in 2000 might be linked to an extreme forest fire in the watershed, potentially leading to an increased influx of soil into the reservoir.

Soil erosion has emerged as one of the main challenges associated with global change (Alaniz et al. 2021) and a management concern of both terrestrial and freshwater ecosystems worldwide. Nowadays, approximately 16.4% of the Maggiolo Reservoir watershed contains areas experiencing an average soil loss greater than 7 t/ha/year,

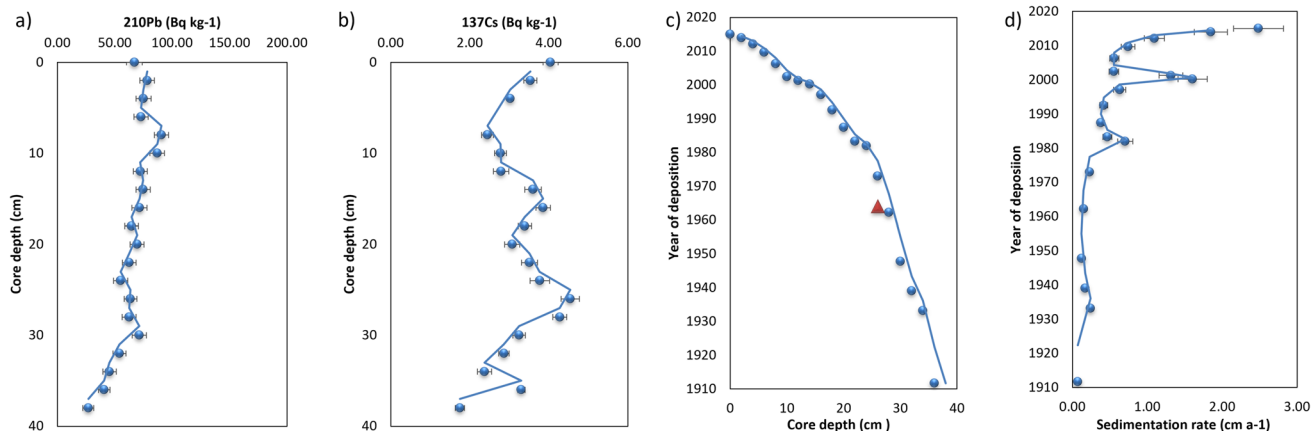


Fig. 2 Sedimentary profiles showing the activities of ^{210}Pb (a) and ^{137}Cs (b), the age-depth model obtained from the CRS technique (c), and the sedimentation rate (d) in the lacustrine area of the Maggiolo

which surpasses the upper limit recommended by the local Ministry of Agriculture for ensuring productive soil recovery (Meerhoff et al. 2018). The significant increase in SR in the most recent layers of the sediment core (~2010 to 2017) coincided with the expansion of agricultural and tourist activities in the watershed where soil loss is estimated to exceed in some points 16 t/ha/year (Meerhoff et al. 2018). The expansion of these activities, in combination with the features of the landscape with steeper slopes, makes this region more susceptible to erosion (Meerhoff et al. 2018). To gauge the growth in agricultural activities, consider that in 1969, agricultural areas encompassed 144 hectares of the reservoir's hydrographic basin. By 2000, cultivated areas were estimated at 203 hectares, and they progressively expanded to 304 hectares in 2008 and 320 hectares in 2011, representing a remarkable 122% increase in cultivated areas by 2011 (Álvarez et al. 2015).

LOI, metals, and nutrients

The sediment profiles showed a uniform dark color, characteristic of environments with a predominance of organic matter. The sediments could be considered organic with LOI values > 10% (Ungemach 1960) ($15.70 \pm 0.72\%$). No significant variations in organic matter content were observed over time (coefficient of variation of 4.57%).

The Mo and Se contents were below the detection limit and the As contents were below the QL. For most other metals, there were no significant variations over time (Table 1, Fig. 3). However, the concentrations of Cr, Cu, Al, and Fe tended to decrease over time. Several factors are linked to the deposition and release of metals into the water column, including physical, chemical, and biological influences. Changes in oxidative processes and pH, the decomposition of organic material, and sediment disturbance, whether

reservoir. The triangle, in Fig. 3c, marks the core depth corresponding to the past nuclear fallout of 1964

caused by wind, mechanical action, or bioturbation driven by benthic organisms, can facilitate the release of metals retained in the sediments into the water column (Förstner and Wittmann 1981; Luoma and Rainbow 2008), thereby explaining the decrease in these elements within the sedimentary profile. Also, the regulation and establishment of polluting sources can be linked to decreases and increases in metal pollution. The decreases in Cu and Cr may be linked to the reduction in copper sulfate application, which is used as an algacide. Chromium (Cr) may be present in the algacide formulation due to the general lack of absolute purity in these herbicides. Additionally, Cu and Cr exhibited significant linear correlations ($r=0.95$), indicating a common source of origin. The decline in Al and Fe levels in the late 1980s may also be associated with an intense drought in 1989 (Meerhoff et al. 2017). This is because precipitation episodes influence the input of terrigenous elements into aquatic ecosystems (Stuut et al. 2007), and under drier conditions, the delivery of lithogenic elements to the catchment is usually reduced (Bueno et al. 2021).

The decrease in metal levels observed in 2002 (Fig. 3) may be associated with a flooding period in the watershed, which could have increased the transport of larger particles, resulting in a lower concentration of metals in the sediments. Fine-grained sediments, such as silt and clay with particles smaller than $63 \mu\text{m}$, are crucial for metal retention. This is because their smaller size offers a larger surface area for metal binding (Förstner and Wittmann 1981; Luoma and Rainbow 2008). The influx of material can be corroborated by the increased sedimentation rate during this period (Fig. 2).

We found significant Pearson correlations between most elements with Al, Fe, and Mn (Tab. SM 2), which reveals the affinity of these metals to clay minerals and Fe–Mn oxyhydroxides. In addition, the correlations of

Table 1 Basic descriptive statistics for the contents of metals (mg/kg DW), phosphorus (mg/kg DW), and LOI (%) and enrichment factors (EF) in sediments from a core in the dam area of the Maggiolo res-

ervoir (~90 years). ISQG (Interim Sediment Quality Guideline) and PEL (Probable Effect Level) values established by CCME (2001)

	N=20					EF						
	Range		Mean	SD	CV	Range		Mea n	SD	CV	ISQ G	PEL
Al	28401.1	37343.5	33412.3	2417.9								
Ba	5	6	9	2	7.24	-	-	-	-	-	-	-
Ca	231.08	290.60	266.65	13.89	5.21	1.17	1.31	1.22	0.04	3.21	-	-
Co	3697.97	4546.55	4216.66	188.74	4.48	0.98	1.3	1.09	0.09	8.36	-	-
Cr	14.39	16.86	16.08	0.57	3.54	0.99	1.17	1.08	0.06	5.71	-	-
Cu	31.34	39.80	36.07	2.17	6.01	0.98	1.05	1.02	0.02	1.87	37.3	90.0
	39.61	53.08	47.16	3.80	8.05	0.92	1.06	1.00	0.04	3.77	35.7	197.0
Fe	32105.2	40198.5	36904.5	1962.2		0.97	1.09	1.04	0.03	3.26	-	-
K	6	4	6	6	5.32							
Mg	2668.48	3620.26	3168.89	268.16	8.46	0.93	1.01	0.98	0.03	2.55	-	-
Mn	2845.76	3339.18	3169.07	102.15	3.22	0.96	1.17	1.07	0.06	5.74	-	-
Na	1055.85	1562.01	1301.09	162.30	12.47	0.84	1.16	0.99	0.09	8.72	-	-
Ni	128.56	167.95	148.44	8.31	5.60	0.99	1.25	1.06	0.07	6.85	-	-
P	20.11	25.42	23.32	1.26	5.39	0.99	1.11	1.05	0.04	3.48	18.0	36.0
Pb	847.22	1600.17	1185.82	232.98	19.65	-	-	-	-	-	-	-
Sr	11.26	14.94	12.96	0.92	7.09	0.95	1.08	1.02	0.04	3.84	35.0	91.3
Zn	16.40	20.27	19.06	0.92	4.85	0.98	1.22	1.05	0.06	5.85	-	-
LOI	85.56	104.29	96.55	4.64	4.80	0.98	1.12	1.04	0.04	3.48	123.0	315.0
	14.63	17.25	15.71	0.72	4.58	-	-	-	-	-	-	-

Green: toxicity unlikely to occur; yellow: toxicity is uncertain to occur

most metals with Fe and Mn suggest that their origin is the weathering of rocks and soils in the watershed (Mil-Homens et al. 2013). Future studies could be performed applying a sequential extraction metal analysis to better understand metal partitioning.

The enrichment factor did not indicate contamination over time ($EF < 2$), being the enrichment minimum and the source of metals mainly from crustal materials or natural weathering processes (Table 1). Although manganese, galena, and dolomite mining activities were recorded in the region, our results indicate that enrichment was minimal or absent for Pb (component of galena (Hernández et al. 2020)), Mg (component of dolomite— $\text{CaMg}(\text{CO}_3)_2$), and Mn. Lead levels showed significant Pearson linear correlations with these elements (Pb and Mg: $r = 0.57$ and Pb and Mn: $r = 0.61$) but exhibited a decreasing trend over time (Fig. 3). This decrease could be partially associated with a reduction in mining activities as well as a decrease in atmospheric input. In the atmosphere, lead could originate from industrial activities and motor vehicles. The use of tetraethyl lead as a gasoline additive was banned

in Uruguay only in 2004 (Renfrew 2011), which could explain the decrease over time.

Toxicity was unlikely to occur for the main elements of ecotoxicological interest, i.e., As, Cr, Cu, Ni, Pb, and Zn. Although the Cu and Ni contents fell within the range of the ISQG and PEL, these values exhibited no significant changes over time and remained close to the basal values. A water body situated in a mining area might not experience substantial impacts from the mining activities in the watershed due to various reasons. In the Maggiolo reservoir, in particular, the presence of a wide and old riparian forest along stream reaches in between the closest mine and the reservoir may have mitigated the input of contaminants. Also, it is possible that slow flow reaches upstream of the reservoir may have experienced relatively high sediment deposition, decreasing the amount of contaminants finally reaching the reservoir.

The variations in the pattern of phosphorus in the sediment profile can indicate alternation of periods of oxide-reduction at the sediment–water interface (i.e., conditions of oxygenation alternating with anoxic conditions) (Fig. 4).

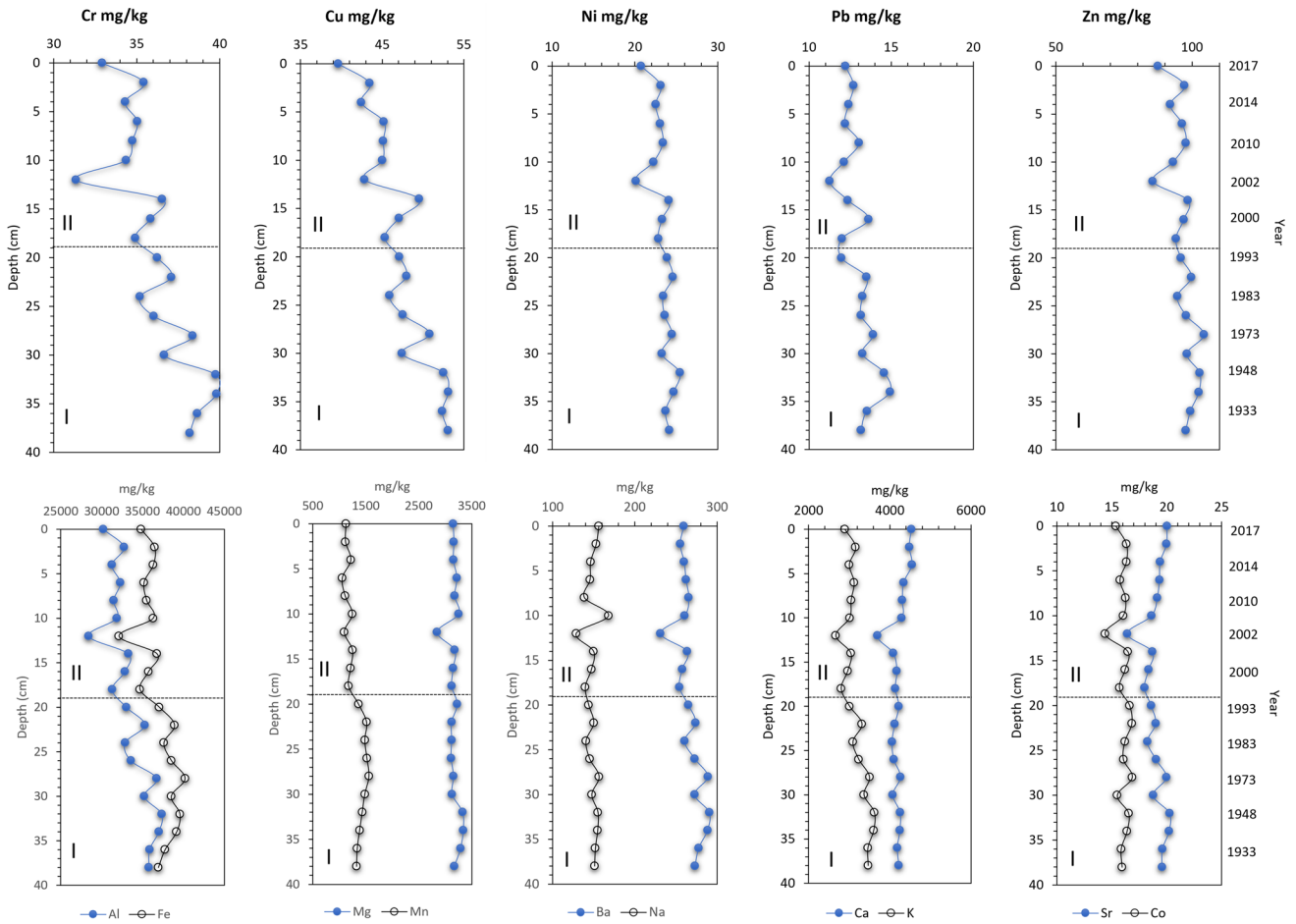
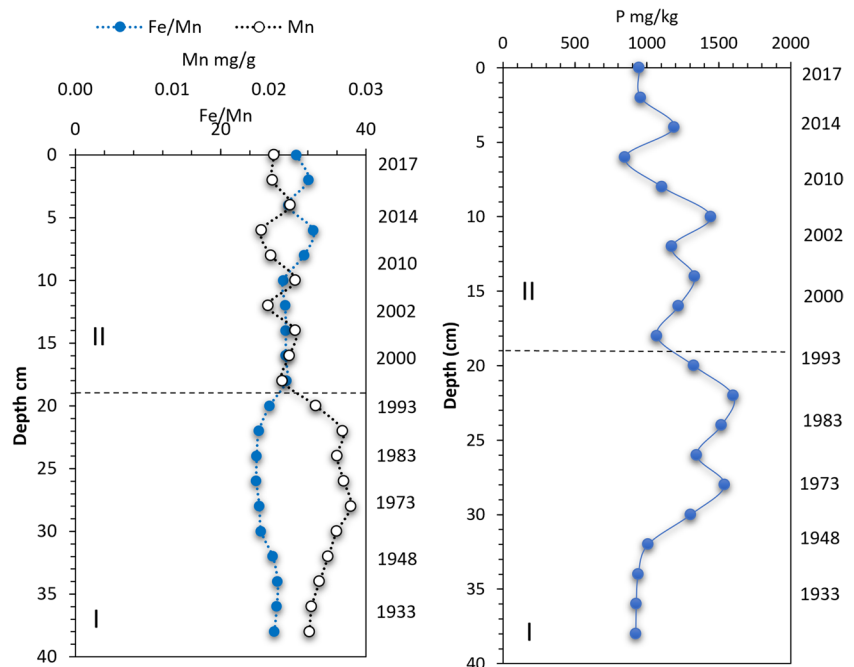


Fig. 3 Concentration of metals in a sediment core sampled in the dam area of the Maggiolo reservoir (Minas, Uruguay). Two main periods (I; II) were obtained through a CONISS analysis

Fig. 4 Fe/Mn ratio and Mn (left) and TP (right) concentration in the core sediments collected in the dam area of the Maggiolo reservoir (Minas-Uruguay). Two main periods (I; II) were obtained through a CONISS analysis



In general, oxygen can considerably affect P flux from sediments (Wetzel 2001; Anderson et al. 2021). Under anaerobic conditions, there is a decrease in the redox potential, and the reduction of Fe (III) to Fe (II) leading to Fe–P release from the sediment occurs (Steinberg 2011). To reconstruct past redox conditions, changes in the Fe/Mn ratios are usually analyzed (Mackareth,1966; Cardoso-Silva et al. 2022; Neugebauer et al. 2022). This is because, under oxic conditions, Fe and Mn are highly insoluble. Under anoxic and reducing conditions, the solubilities of both elements increase, and they are mobilized to the water column (Ladwig et al. 2017). However, Mn is more soluble than Fe, and the mobility of these elements is closely associated with the reduction potential of the environment (Boyle 2001; Smol 2008; Mackereth 1966; Neugebauer et al. 2022).

More pronounced changes in the Fe/Mn ratios and consequently in the redox potential were primarily observed in the sediment core layers at 20–22 cm (~1993) and in the 18–20 cm (~1997), 10–12 cm (~2006), and 4–6 cm (~2014) (Fig. 4). The decrease in *p* values towards the top of the core may reflect the release of P into the water column due to more reducing conditions observed from the 20–22 cm layer (~1993) (Fig. 4), as suggested by the statistically significant Pearson correlations between P contents and the Fe/

Mn ratio ($r = -0.66$). Hence, an elevation in Fe/Mn ratios, which may suggest the onset of anaerobic conditions (Davies et al. 2015) associated with declining phosphorus (P) levels, could be attributed to a release of P from sediments. Moreover, processes occurring in the river watershed, leading to a higher input of organic matter and/or phosphorus, could exacerbate eutrophication and create anoxic conditions at the sediment–water interface. The main activities contributing to increased P input into the reservoir are soil erosion and loss, as well as the use of phosphorus fertilizers in the agricultural and exotic forest plantations, likely complemented by local inputs of grey waters from a nearby touristic location (Meerhoff et al. 2018).

Main impacts in Maggiolo Reservoir as shown by the sediments

According to CONISS, the reservoir can be divided into two main zones: one before reservoir operation until around 1996, and the other from 1997 to 2017 (Fig. 5). Subsequently, a PCA was applied to better discuss the historical impacts. The PCA corroborates the data from the CONISS analysis and distinctly categorizes the reservoir

Fig. 5 A stratigraphically constrained cluster analysis (CONISS) in a sediment core sampled in the dam area of the Maggiolo reservoir (Minas-Uruguay). Color meanings: red = Zone I, before reservoir operation until around 1996 and blue = Zone II, from 1997 to 2017

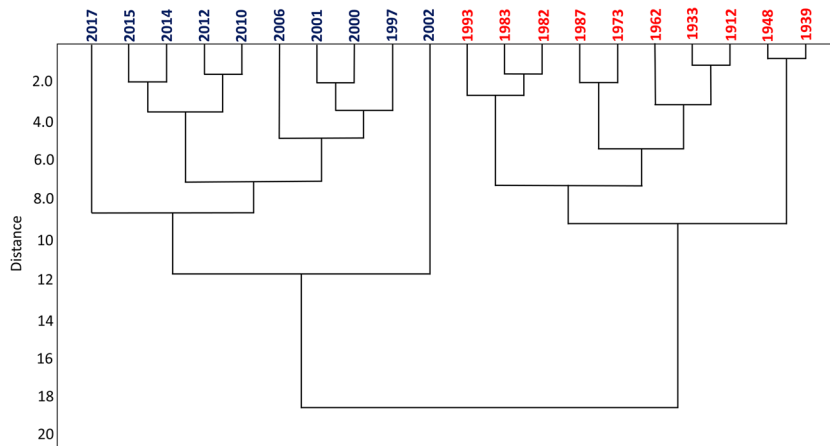
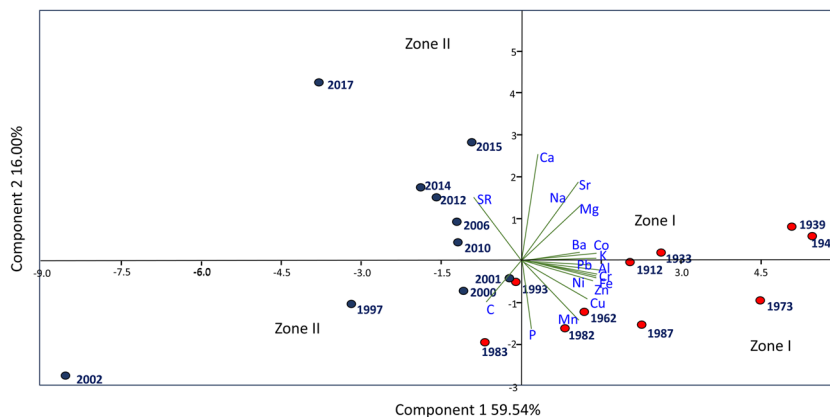


Fig. 6 PCA for metals, phosphorus, and carbon in a sediment core sampled in the dam area of the Maggiolo reservoir (Minas, Uruguay). Two main groups observed in a CONISS analysis are highlighted in red (~1933 to 1996- Zone I) and blue (~1997 to 2017- Zone II)



into two zones. These zones were influenced by the following variables (Tab. SM 2; Fig. 6).

Zone I can be designated as follows:

- a) Prior to reservoir operation until ~ 1987: the metal contents, particularly those of terrigenous elements: Al (0.97), Ba (0.88), Fe (0.94) and K (0.94); as well as potentially toxic metals such as Cr (0.96), Zn (0.92), Ni (0.91), Pb (0.87), Cu (0.83), and Mg (0.73) significantly influenced the first principal component (PC 1) of the PCA (Tab. SM 3; Fig. 6). This period was characterized by mining activities in the watershed, including Pb mining activities from the 1930s onwards (Álvarez et al. 2015), which could partly account for the higher levels of metals. However, starting from the 1980s, these mining activities began to decline, decreasing the contribution of metals to the watershed. Despite the record of lead mining activity, and higher metal concentrations during this period, the enrichment for lead can be considered minimum ($EF < 2$). Another possible source of Pb is atmospheric, particularly from gasoline-powered vehicles. As previously discussed, the decrease in Pb levels coincides with the ban on the use of tetraethyl lead as a gasoline additive in the early 2000s (Renfrew 2011).

The reduction in Cu levels can be also linked to the suspension of the Cu_2SO_4 application as an algacide from the late 1980s onwards. Therefore, the first component is primarily associated with anthropogenic impacts such as mining activities and the application of Cu_2SO_4 .

- b) From the middle 1980s to the early 2000s: in this period, C and P (-0.581) concentrations (Tab. SM 3), significantly influenced the PC2 as one of the principal variables. Productive activities increasing in the watershed area during this period, such as P-demanding agriculture and afforestation, could explain the higher levels of P and C. Agriculture and afforestation account for 2.22% and 12.56% of the total watershed area, respectively. Agricultural areas are primarily located along the margins of the San Francisco stream, upstream of the Maggiolo reservoir (Pérez-Brum 2023). Hence, the second component is linked to variables related to the eutrophication process. Despite its increase over time, the current concentrations of P in the sediments are not high enough to classify the reservoir as polluted.

Zone II on the other hand is designated as follows:

- c) From the early 2000 to 2017: this period is characterized by higher sedimentation rates. This process is likely associated with erosion and weathering processes, estimated to occur especially in the agricultural areas of the watershed (Meerhoff et al. 2018). The increased loss of soil solely due to erosive processes and its subsequent input to the reservoir can reduce its useful life. As a

result, effective soil management policies seem required to prevent or minimize soil loss and ensure the sustainable use of the reservoir.

A PERMANOVA indicated significant differences ($p < 0.01$) between the two groups observed in the CONISS analysis. Pair-wise comparisons showed significant differences ($p < 0.01$) between zone II, characterized by increases in sedimentation rates, and zone I, mainly associated with mining activities and eutrophication. A summary of the main variables that showed changes over time is presented in Fig. 7.

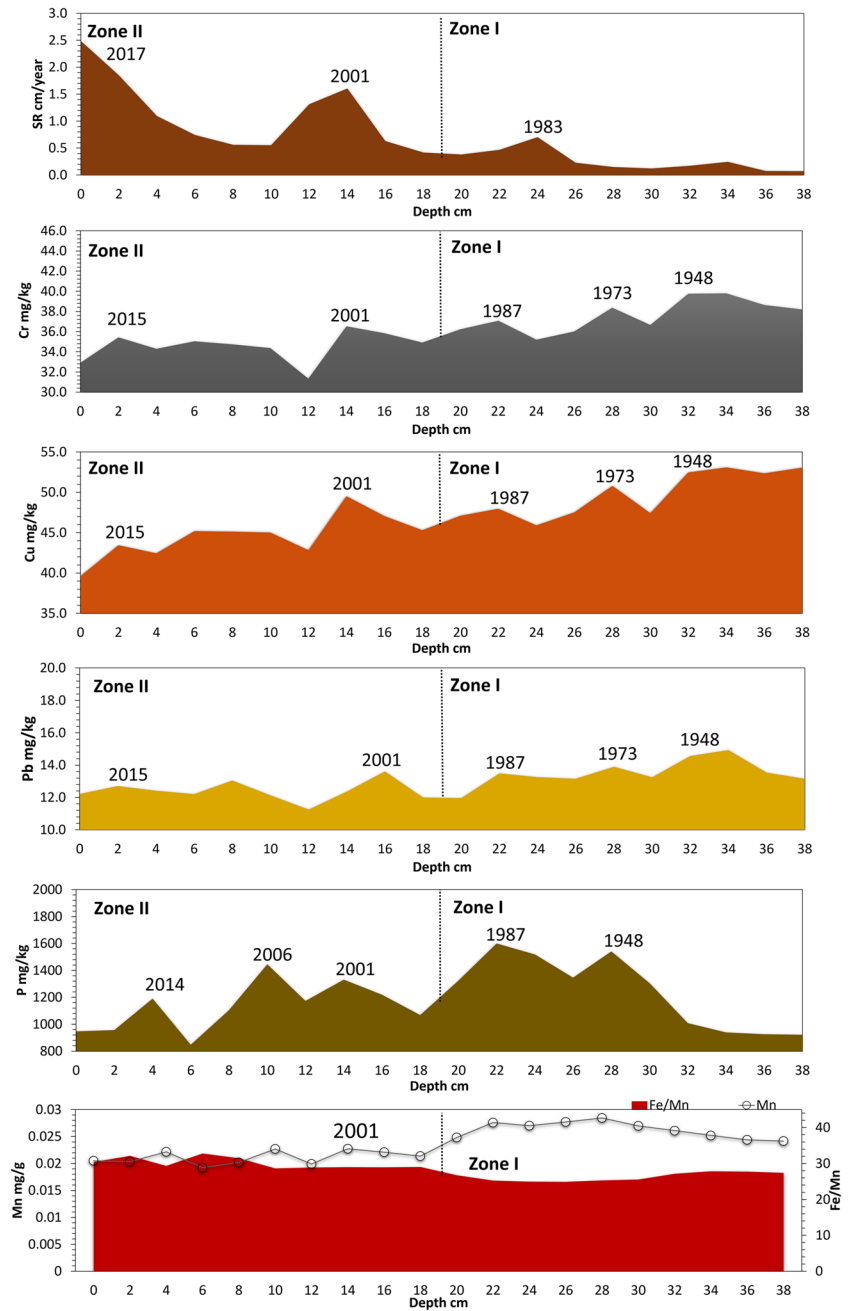
Surface sediments: general characteristics and reference conditions

Sediments along the reservoir showed organic matter contents of $15.28 \pm 2.76\%$ being categorized as organic following Ungemach classification (1960) (Tab 2). Sediments were not considered polluted by P (0.68 ± 0.19 mg/g DW), according to the Ontario Sediment Quality Guidelines that establish the threshold value of 2 mg/g DW. Values for the metalloid As were below the Quantification limit (QL) and there were no significant variations for most metals according to the coefficient of variation along the reservoir (Table 2) implying a homogeneous distribution. The range and the mean values for metals indicated that toxicity is unlikely to occur, except for Ni, as values suggesting toxicity are classified as e uncertain to occur (Table 1). However, Ni has a geological source according to the EF. Significant Pearson correlations between metals ($r > 0.6$) suggested a similar origin of these elements (Tab. SM 3). All elements exhibited a significant linear correlation with Al ($r > 0.5$) and a low associated error (Fig. SM 2; Table 3), suggesting a low level or absent contamination.

Enrichment factors (EF) were calculated using both the reference values established by the bottommost core samples and by the PI and regression statistic technique (Table 4). For both techniques, values were below 2, indicating enrichment was absent or very low. Also, a *t*-test ($p < 0.05$) indicated there was no statistically significant difference using one or another background value, corroborating the efficiency of the PI and regression analysis technique. The PI regression technique is advantageous compared to the core bottom sediment values because usually core sediments are sampled in few areas and therefore do not consider the natural spatial heterogeneity in metals. Our background values seem more appropriate to be used in the monitoring and management of similar systems in the region than the global average shale obtained from Turekian and Wedepohl (1961), which does not consider regional characteristics.

According to our results, toxicity was unlikely to occur for the main elements of ecotoxicological interest, namely As, Cr, Pb, and Zn. The mean values of Cu and Ni contents

Fig. 7 Summary of the main variables that showed changes over time in a sediment core sampled in the dam area of the Maggiolo reservoir (Minas, Uruguay)



ranged between the ISQG and PEL, however, these values were close to the background. In such situations, the SQGs must be replaced by background values (Chapman et al. 1999), indicating toxicity for these metals is unlikely to occur in these sediments. SQGs are useful tools for areas where metal concentrations are not very high (Chapman et al. 1999; Hübner et al. 2009). Considering that this is the first study evaluating the metal concentrations in the sediments of Maggiolo Reservoir, the SQGs seem very useful in pinpointing the ecological risk associated with these potentially toxic elements. Despite some agricultural and mining activities in the watershed that could lead to a great input of

metals into the Maggiolo reservoir, we did not find evidence of contamination and potential toxicity in surface sediments as suggested by the SQGs. Therefore, at present, the reservoir exhibits favorable conditions concerning metal content.

Although searching for reference conditions is a promising measure in resource management, it is not a common practice in Uruguay and South America. Several factors explain the low use of this tool, such as the lack of monitoring data due to insufficient investment in the sector, the low availability of specific equipment, and the shortage of trained personnel in many areas and countries of the region. Water resource management in some countries may

Table 2 Basic descriptive statistics for the contents of metals and phosphorus (mg/kg dw) and organic matter (LOI%) in surface sediments of the Maggiolo reservoir (Minas-Uruguay). ISQG (Interim Sediment Quality Guideline) and PEL (Probable Effect Level) values established by CCME (2001)

	n=29	Range		Mean	Standard deviation	Coefficient of variation	ISQG	PEL
Al		19×10^{-3}	34×10^{-3}	29×10^{-3}	3081.53	10.43	–	–
Cr		22.24	36.44	32.69	2.85	8.71	37.3	90
Cu		27.82	48.72	40.79	4.02	9.85	35.7	197
Fe		23×10^{-3}	39×10^{-3}	31×10^{-3}	3207.6	10.31	–	–
Ni		15.89	24.14	22.3	1.62	7.25	18	36
P		441.6	1252.3	682.53	188.65	27.64	–	–
Pb		7.68	14.01	11.52	1.2	10.45	35	91.3
Zn		59.39	96.98	88.13	8.01	90.13	123	315
LOI%		8.38	24.54	15.28	2.76	18.10	–	–

Values between ISQG and PEL are indicated in bold

Table 3 Background equations with Pearson correlation (r^2) and associated errors for metals with toxicological potential. Following Kim et al. (2017) recommendations, to calculate the background equation, all values located outside the prediction interval curve from each element were removed, and the regression curve was adjusted to the new values. Each element then presented an error defined by the prediction interval

Metal	Equation ($\hat{Y} = b1 + b0 \times x0$)
Cr	$\hat{Y} = 0.0008x + 9.0565$ ($r^2 = 0.934; p < 0.05$) [Cr]bg = $\hat{Y} \pm 0.86$
Cu	$\hat{Y} = 0.0012x + 4.4817$ ($r^2 = 0.8731; p < 0.05$) [Cu]bg = $\hat{Y} \pm 2.53$
Ni	$\hat{Y} = 0.0005x + 7.8996$ ($r^2 = 0.8619; p < 0.05$) [Ni]bg = $\hat{Y} \pm 1.03$
Pb	$\hat{Y} = 0.0002x + 4.0618$ ($r^2 = 0.5439; p < 0.05$) [Pb]bg = $\hat{Y} \pm 1.23$
Zn	$\hat{Y} = 0.0024x + 16.782$ ($r^2 = 0.8616; p < 0.05$) [Zn]bg = $\hat{Y} \pm 5.13$

be fragmented across different levels of government and agencies, complicating the implementation of uniform and effective monitoring policies. Furthermore, existing publications are insufficient to provide reference condition data due to both the lack of financial investment in the sector and the diversity of geological, climatic, and ecological characteristics, especially in large countries like Brazil.

Despite the region’s low applicability of reference values, some scientific research could be used as auxiliary tools in water management processes. Examples include studies on metals in Argentina (Nassini et al. 2023), Brazil (Nascimento and Mozeto 2008; Cardoso-Silva et al. 2021; Moulatlet et al. 2023), Bolivia (Tapia et al. 2012; Moulatlet et al. 2023), Chile (Correa-Burrows et al. 2021; Valdés et al. 2023), Colombia (Alonso et al. 2020; Moulatlet et al. 2023), Ecuador (Moulatlet et al. 2023), Peru (Biamont-Rojas et al. 2023; Moulatlet et al. 2023), and Venezuela (Mogallon et al. 1996).

The techniques applied in these studies vary from the use of paleolimnological approaches (Cardoso-Silva et al. 2021; Biamont-Rojas et al. 2023) or the reference site approach (Nascimento and Mozeto 2008) to statistical techniques (Mogallon et al. 1996; Correa-Burrows et al. 2021; Nassini et al. 2023). None of the cited studies used a combined analysis of paleolimnological data and Prediction Interval measurement through chemometric techniques as presented in this research. To advance the management of metals in water resources in Uruguay and South America, a coordinated effort is necessary. This should include increased funding for research and monitoring, technicians and managers training, the strengthening of environmental legislation, and the promotion of awareness about the importance of water quality.

Table 4 Background values calculated through two techniques: core bottom-most mean values and Predicted Interval. Enrichment Factor (EF) calculated with the bottom core mean values and the Predicted Interval (Mean values- X and Standard deviation -SD). N=29

	Core bottom mean values		Predicted interval		EF			
	X	SD	Lower limit	Upper limit	Core bottom values		Predicted interval	
					X	SD	X	SD
Cr	35.79	4.91	23.74	37.32	0.95	0.03	0.94	0.03
Cu	43.77	6.32	25.75	48.99	0.97	0.04	0.89	0.03
Ni	24.48	3.52	16.29	25.55	0.95	0.05	0.94	0.05
Pb	12.20	1.87	7.63	13.75	0.98	0.08	0.90	0.08
Zn	94.64	13.56	94.34	174.80	0.97	0.04	0.54	0.02

Recommendations

The increase in sedimentation rates in the recent period, which may reduce the reservoir's lifespan, has emerged as the primary challenge to be addressed in managing this water body. Internationally, various methods have been employed to restore the useful volume of reservoirs and could be implemented in the Maggiolo reservoir. These methods include reducing sediment inflow from the watershed by maintaining and restoring riparian zones, which act as a mechanical buffer over watercourses (Zaimes et al. 2021; Mykrä et al. 2023); constructing small dams upstream to control the sediments deposited into the reservoir (Moridi and Yazdi 2017); and implementing sediment extraction techniques such as dredging, mechanical extraction, and flushing (Moridi and Yazdi 2017; Petkovsek et al. 2020).

Each technique has its own set of advantages and disadvantages that should be carefully evaluated, considering the available resources and the potential environmental consequences of each measure. For instance, constructing small dams upstream may create areas clogged with sediments, leading to instabilities and potentially high maintenance costs (Kondolf et al. 2014). Dredging, on the other hand, is often employed to remove sediment in specific areas near water intakes (Palmieri et al. 2003; Shrestha et al. 2021) due to the heavy economic costs particularly for sediment transport and deposition (Junakova and Junak 2017; Shrestha et al. 2021). Sediment flushing should be considered carefully (Moridi and Yazdi 2017), as its application can affect downstream wildlife, water quality, and other ecosystem services.

This study offers a broad perspective on some of the primary impacts that have left their mark in the region surrounding the reservoir dam. Future studies could concentrate on additional contaminants such as pesticides, explore other sections of the reservoir, and delve into the spatial–temporal variations within the area, topics that were not covered in this research. To gain a deeper understanding of eutrophication in the reservoir, additional biological proxies such as photosynthetic pigments and diatoms could be employed.

Conclusions

The PI chemometric technique and regression analysis were used to determine reference conditions for metals, encompassing all elements of ecotoxicological interest. This technique has demonstrated its effectiveness in freshwater environments and can be applicable in other areas of interest. The values obtained can also serve as guiding benchmarks for future research conducted in the region. Although the VGQS TEL/ISQG and PEL criteria suggested that the toxicity of Cr, Cu, and Ni was uncertain in some periods and locations,

these data were consistent with background values, except for three core samples (Cr 39.8 mg/kg ~ 1939 and 1948—32–36 cm depth and Cu 53.1 mg/kg ~ 1939—32–34 cm). Therefore, no signs of recent metal contamination were observed. While the enrichment for the analyzed metals was minimal, higher metal concentrations were observed during periods of more intense mining activities in the watershed (Zone I 1934–1986). However, our results thus suggest that the contributions of metals from mining in the watershed did not significantly affect the sediment quality in the reservoir.

The higher impacts were observed mainly after the early 2000 with the higher sedimentation rates predominantly associated with soil losses in the watershed, which can compromise the reservoir's useful life, given its role as a drinking water supply. This is particularly relevant considering the process of deterioration of freshwater quality in Uruguay (Goyenola et al. 2021) and increasing regional climate variability in the region (Rusticucci and Renom 2008). As a management measure, considering only metal concentrations, sediment extraction, at least to a depth of 30 cm, is expected to produce safe material suitable for various subsequent uses. Considering the absence of similar research in Uruguayan freshwater ecosystems, particularly in terms of establishing baseline values, our study makes a significant contribution to monitoring and management efforts.

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Author contribution All authors contributed to the study conception and design as follows: Sheila Cardoso-Silva: conceptualization, writing original draft, formal analysis, and investigation; Bianca Sung Mi Kim: formal analysis and writing review; Paulo Alves de Lima Ferreira: formal analysis, investigation, and writing review; Beatriz Benedetti: formal analysis and writing review; Guillermo Goyenola: writing review; Carlos Iglesias: writing review; Rubens Cesar Lopes Figueira: formal analysis and writing review; Anahí López-Rodríguez: investigation and writing review; Viviane Moschini-Carlos: writing review, supervision, funding acquisition, and project administration; Franco Teixeira de Mello: writing review, investigation, and project administration; Mariana Meerhoff: writing review, supervision, investigation, funding acquisition, and project administration; Marcelo L. M. Pompêo: supervision, funding acquisition, and project administration. All authors commented, read, and approved the final manuscript.

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Data availability The data that support the findings of this study are available from the authors upon reasonable request.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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