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ORIGINAL ARTICLE

Temporal and spatial accumulation of heavy metals in the sediments at Paiva Castro Reservoir (São Paulo, Brazil)

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Abstract The analysis of heavy metals in sediments, associated with geochronology, can identify the historical accumulation of these contaminants that occurred over time as a result of anthropogenic activities. A study was conducted at Paiva Castro Reservoir, a tropical reservoir in Brazil, to (1) establish baseline values for the metals Cd, Cr, Cu, Ni, Pb, Zn, Mn, Al and Fe; (2) investigate the history of heavy metal accumulation through geochronology using ^{210}Pb; and (3) identify the main variables that differentiate the sampled regions. A gravity corer was released twice in three reservoir areas. Each core was sliced at intervals of 2 cm and stored in a sealed plastic bag. One core was used for the determination of metals and for dating using the ^{210}Pb technique. The other core was used for the determination of organic matter and particle size. The baseline values for heavy metals were calculated according to the mean bottommost samples of the three core analysed. In terms of the levels of heavy metals, the greatest impacts in the region occurred during periods prior to the period of reservoir operation. In surface sediments, Cu exceeded several times (97.0 mg kg^{-1}) the background (24.0 mg kg^{-1}). This result may be a consequence of the application of copper sulphate for controlling algal blooms. A canonical discriminant analysis indicated that the variables that significantly differentiated the three sampled areas were related to the elements Al, Fe, and Mn and to particle size. These data indicate that the main differences are due to lithological variations and to the dynamic operation of reservoirs that provide a larger particle size fraction in the area where the uptake of water for the public water supply is located and in the area upstream from Paiva Castro, where there is higher flow energy. Evidence of the degradation of Paiva Castro Reservoir is already being reflected in the sediments. It is necessary that public policies are actually applied to counteract the degradation of this important ecosystem; otherwise, the reservoir's 'good quality' will be at risk.

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Introduction

Sediments can act as an archive of environmental changes that occur over time and space in the drainage basin of a given water body (Xue et al. 2007). Among the many ecological indicators that can be analysed in sediments, heavy metals are a high priority for research. Heavy metals are recognised as toxic and, once deposited in the sediments, cannot be destroyed. The tendency of heavy metals

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to accumulate in sediments and the lack of a natural mechanism to remove them from this compartment makes these elements good markers of environmental change (Arnason and Fletcher 2003).

Thus, sediment profile analyses, together with sedimentary column dating, are able to predict the past conditions of the ecosystem, identifying, for example, accumulations of heavy metals that occur over time due to human activities such as mining, population growth and industrial development (Lokeshwari and Chandrappa 2007). Sedimentary column analysis can provide valuable information to managers, especially in areas where there is a lack of historical data, because it serves to establish how an environment is altered relative to the pristine condition and, as a result, to associate these changes with anthropogenic impacts (Van Metre and Callender 1997). As a consequence, the reference condition can be defined for the component analysed. These studies can also compensate for deficiencies in the analysis of data accumulated in different studies in a given region, e.g. changes in sampling points, the use of different methods and the use of different analytical detection limits, in addition to the data gaps for certain periods (Van Metre and Callender 1997; Bennion and Battarbee 2007).

Studies incorporating an approach aimed at environmental reconstitution have gained great interest, especially in the European Union, after the implementation of the Water Framework Directive, the European water resources management system (Räsänen et al. 2006; Kelly et al. 2008). This framework aims to achieve good chemical and ecological status in all water bodies of Europe. This goal requires that reference conditions be established, and the analysis of sediment profiles is a tool that can be used to meet this need.

The environmental reconstitution approach is widespread in lakes (Andersen et al. 2004) but can also be applied to reservoirs (Fávaro et al. 2007). Sediments in reservoirs are of high interest in terms of historical contamination because these water bodies tend to be located near urban centres or industrial areas and are therefore the focus of major impacts (Shotbolt et al. 2006). Additionally, the high sedimentation rates common in reservoirs indicate that reservoirs might represent a detailed archive of changes in the inputs of pollutants and nutrients during periods of decades to centuries (Shotbolt et al. 2006).

The purpose of this study is to establish baseline concentrations for Cd, Cr, Cu, Ni, Pb, Zn, Mn, Al and Fe for a tropical reservoir; to investigate the quality of the sediments through the historical accumulation of these metals, based on the enrichment factor; and to identify the main variables that differentiate the sampled areas in this water body.

Materials and methods

Study area

The Cantareira system is the major drinking water source in the metropolitan region of São Paulo. It is formed by five reservoirs connected by artificial underground tunnels, canals and pumps (Whately and Cunha 2007), with a total extent of 48 km (SABESP 2008). This artificial cascade system was developed in two principal stages. Three of these reservoirs, Paiva Castro, Atibainha and Cachoeira, began to operate in 1974, with a flow of 11 $m^3 s^{-1}$. In 1981, the second stage was finished with the inclusion of Jaguari and Jacareí Reservoirs, and the flow increased to 33 $m^3 s^{-1}$ (Whately and Cunha 2007).

Paiva Castro Reservoir is the last reservoir in this artificial cascade system. It is located in the Alto Tietê hydrographic basin and was formed by damming the Juquery River. Effluents from the sewage treatment plant of Mairiporã city are released in the area upstream from Paiva Castro. Paiva Castro has an altitude of 745 m, an area of 5.6 km^2, a drainage area of 314 km^2, a maximum depth of 16 m and a mean flow of 4.4 $m^3 s^{-1}$ (SABESP 2008).

The region of Paiva Castro Reservoir basin remained predominantly agricultural until the mid-twentieth century. Changes were mainly from the 1960s with the construction of the highway Fernão Dias. Such activity promoted changes in land use with the installation of industries and urban real estate speculation in the reservoir basin (Whately and Cunha 2007). Over time, without proper control of the use and occupation, the watershed of the Paiva Castro Reservoir became the most urbanised of the Cantareira system. Since then the population in the area of the reservoir has grown substantially (Whately and Cunha 2007), and an increase in the nutrient input to this reservoir has been recorded. To control algal blooms resulting from the nutrient inflow, regular applications of algicides such as copper sulphide and hydrogen peroxide have been performed. This practice is responsible for copper levels that are greater than the background values found in other reservoirs in the metropolitan region of São Paulo. However, no previous studies have examined the heavy metal levels in Paiva Castro's sediments. Despite the importance of the region, there is little information regarding the environmental quality of this reservoir. There is only one monitoring station in the Paiva Castro Reservoir belonging to the local environmental agency, CETESB (*Companhia de Tecnologia de Saneamento Ambiental*—Environmental Sanitation Technology Company), which does not evaluate the sedimentary compartment. Although SABESP (*Companhia de Saneamento Básico do Estado de São Paulo—*

Basic Sanitation Company of the State of São Paulo), the company responsible for the public water supply, does monitor the Paiva Castro Reservoir, it does not provide its environmental data set for the public. This way, with the exception of the CETESB reports and few scientific researches, there is little scientific information available regarding this reservoir.

Samples

Three cores were collected in three different areas of Paiva Castro Reservoir in March 2010. The choice of sampling stations was based on a previous study (Macedo 2011), which identified three areas of Paiva Castro Reservoir in terms of their trophic state: (a) the dam area, with a water flow of 1 $m^3 s^{-1}$ and with a depth of 16 m (station 1—SPdam, coordinates W0329356/S7418854), (b) the area from which water is taken for the public water supply, with a depth of 12 m (station 2—SPwts, coordinates W0329914/S7417199) and (c) the upstream area, near Mairiporã city and the effluent from the sewage treatment plant, with a depth of 9 m (station 3—SPriv, coordinates W0334152/S7419278) (Fig. 1). The sampling stations were georeferenced with a Garmin 72 GPS according to the UTM coordinate system, datum SAD69 and central meridian 45 °C.

A gravity corer was released twice in each of three areas of the reservoir. Each core was sliced at intervals of 2 cm and stored in a sealed plastic bag. The plastic bags were enclosed in thermal bags until the cores were analysed in the laboratory. The SPdam core, from a depth of 26 cm, was sliced in intervals of 1 cm. One core was used for the determination of heavy metals and dating using the ^{210}Pb

technique. The other core was used for the determination of organic matter and particle size. The core slices were numbered in ascending order from the top of the core to the bottom. Cores SPdam and SPwts had a total depth of 32 cm; core SPriv had a total depth of 38 cm. For grain size determination due to the insufficient amount of sediment for this analysis in the three cores collected, adjacent layers were combined.

Laboratory analyses

The grain size analysis used the Atterberg system and a beaker method proposed by Piper (1947) and modified by Meguro (2000). Organic matter (OM) was determined by ignition (Meguro 2000). Sediments dried at 45 °C were used for geochronology and metal analyses.

For the determination of the radionuclides ^{210}Pb and ^{137}Cs, samples were analysed for 50,000 s in a spectrometer according to Figueira's (2000) recommendations. Samples were stored for at least 20 days to allow the ^{210}Pb to reach secular equilibrium with ^{222}Rn in the ^{238}U decay series. The counts of gamma emissions resulting from radioactive decay were made in a gamma spectrometer with a high counting efficiency and low background radiation (EG&G Ortec model GMX 25190P), with a mean resolution of 1.9 keV for ^{60}Co, as described in Figueira et al. (2007). Spectra were analysed with MAESTRO II software. The Concentration Initial Constant (CIC) model was adopted for dating and the calculation of sedimentation rates (Robbins and Edgington 1975).

The same dried sediment used for dating was subsequently prepared according to method 3050 B from US EPA series SW-846 (US EPA 1996) for heavy metal

Fig. 1 Paiva Castro Reservoir (**a**), located in São Paulo state, Brazil. **b** Localisation of the sampled cores on March 24, 2010
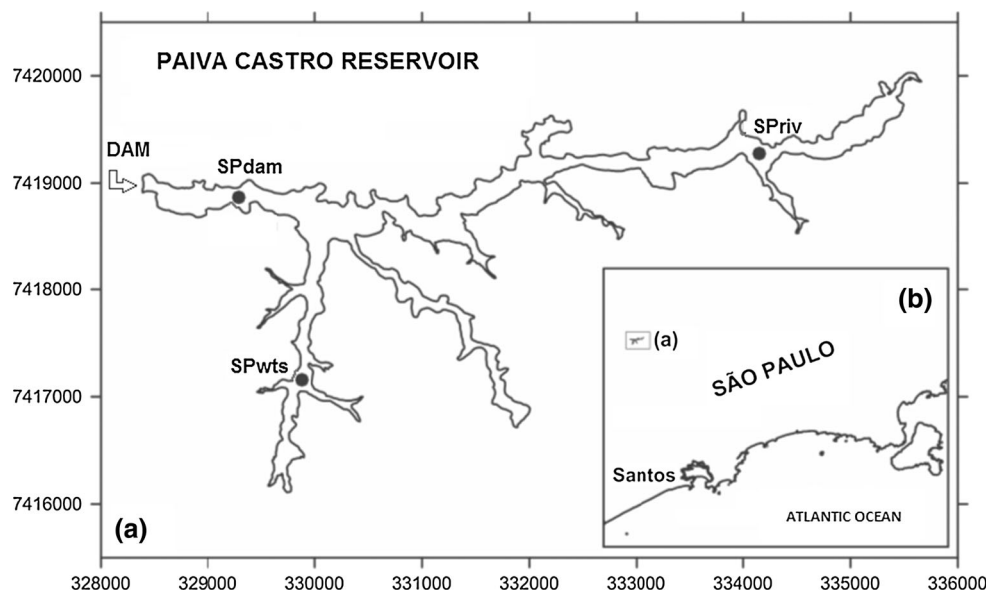
determination. Analytical-grade reagents were used (Merck and Sigma-Aldrich). Samples were analysed in replicate and stored at 4 °C until the analysis of the heavy metals. Zinc, copper, chromium, nickel, cadmium, lead and manganese were analysed with absorption atomic spectrometry (AAS) (Thermo Scientific Série S), and aluminium and iron were analysed with optical emission spectrometry with inductively coupled plasma (ICP OES).

The accuracy and precision of the data analysis were determined using SS1 certified reference material (soils from EnviroMAT™). The mean, standard deviation, precision and accuracy obtained for replicated analyses of the certified reference material are presented in Table 1.

Data analysis

In environmental studies, background values are usually defined as the values found in pre-industrial times (Tueros et al. 2008). In this study, the background values corresponded to the average concentrations of the elements in the three bottommost samples of the three analysed core, except for Pb. Pb background values were calculated only with the average of cores SPwts and SPriv. SPdam had a coefficient of variation of 40.74 %, and the bottommost samples of SPdam had Pb levels higher than those found in the uppermost samples, suggesting a possible past contamination of this element in the dam area.

Enrichment factors were also calculated. In combination with the geochronology, the enrichment factors can be used to determine whether enrichment of a metal has occurred and can suggest whether the source of the element is natural or related to human activity (Devesa-Rey et al. 2011). Enrichment factors are commonly used in geochemical and ecotoxicological evaluations (Hernández et al. 2009) and also aim to simplify the interpretation of normalisations. We calculated enrichment factors using the equation

$EF = (Me/El)/(Me_r/El_r)$, where EF is the enrichment factor, (Me/El) is the ratio of the metal analysed to the concentration of the conservative element in the sample and (Me_r/El_r) is the ratio of the background values for the metal to be analysed and for the conservative element. The enrichment factor varies between values that indicate geogenic and high levels of anthropogenic contamination for the analysed elements (Sutherland 2000) (Table 2).

The data were standardised for multivariate analyses with the ranging method. A multivariate canonical discriminant analysis was used to examine differences among the three cores examined. A tolerance value of 0.01 was used for the analyses. The computer programs PAST (Hammer 2001) and STATISTICA 7.0 were used to perform the calculations.

Results

Dating and sedimentation rates

The sedimentation rates are given in Table 3. Two different sedimentation rates were observed at SPdam and SPriv. From these data, it was possible to establish a dating scheme for the samples to describe the historical trends of heavy metal concentrations. The profiles for dating with ^{210}Pb are shown in Figs. 2, 3, 4, 5, 6 and 7.

Background at Paiva Castro Reservoir

The background values found in this study are similar to those found by Nascimento and Mozeto (2008) in the Alto Tietê Basin except for Pb and Cr, which were nearly two and one-half times lower at Paiva Castro Reservoir (Table 4). The cadmium levels were below the detection limit.

Table 1 Concentrations of Cd, Cr, Cu, Ni, Mn, Pb and Zn (in mg/kg) in standard reference materials (SS1)

Metal	SSI				n
	Certified concentration (mg/kg)	Measured concentration (mg/kg)	Precision (RSD) %	Accuracy (RE) %	
Cd	34	32.3 ± 2.4	6.3	5.9	3
Cr	64	82.1 ± 10.2	0.1	2.1	3
Cu	690	688.8 ± 7.6	1.1	0.2	3
Ni	231	234.1 ± 18.0	7.7	1.4	3
Mn	425	419.2 ± 7.4	1.8	1.4	3
Pb	233	241.3 ± 2.9	1.2	3.6	3
Zn	6775	6852.0 ± 45.5	0.7	1.1	6

Quality control through the evaluation of precision and accuracy of the methodology

Table 2 Enrichment factors (EFs) categorisation according to Sutherland (2000)

EF	Information
<2	Depletion of mineral enrichment
2–5	Moderate enrichment
5–20	Significant enrichment
20–40	Very high enrichment
>40	Extremely high enrichment

Table 3 Sedimentation accumulation rates (in cm year^{-1}) in the Paiva Castro Reservoir

Core	Sample	Sedimentation rate (cm year^{-1}) CIC	
		Mean	Error
SPdam	0–16	0.91	0.19
	16–32	0.26	0.05
SPwts	0–30	0.55	0.09
SPriv	0–14	0.63	0.11
	14–40	0.28	0.05

Values in mg kg^{-1} (dry weight)
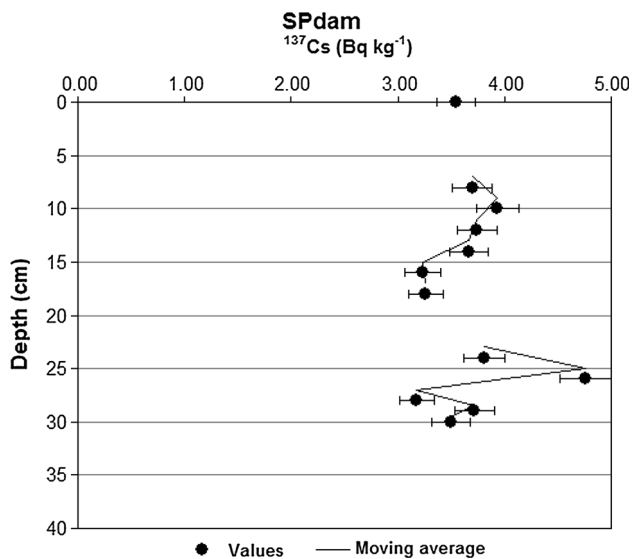
Fig. 2 ^{137}Cs vertical profile in the core SPdam

Fig. 3 ^{137}Cs vertical profile in the core SPwts
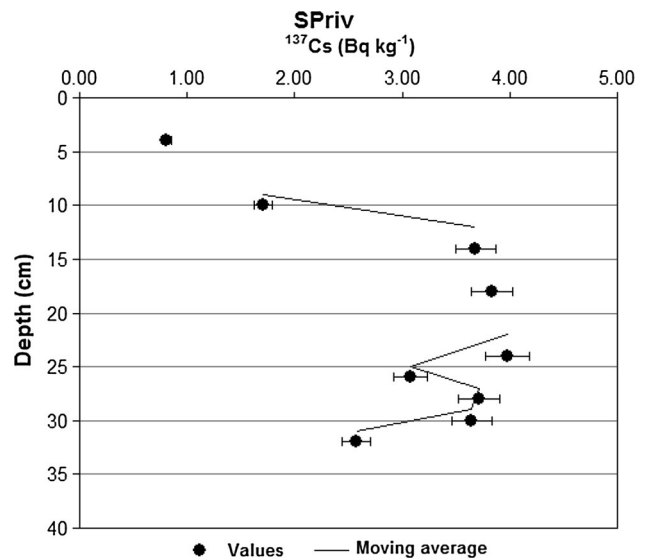
Fig. 4 ^{137}Cs vertical profile in the core SPriv

Grain size, organic matter and heavy metals

In the three cores, silt and clay were the predominant grain size fractions over time (Fig. 8). High proportions of sand were recorded before the beginning of reservoir operation in the dam area. The sediment in Paiva Castro Reservoir at all locations and times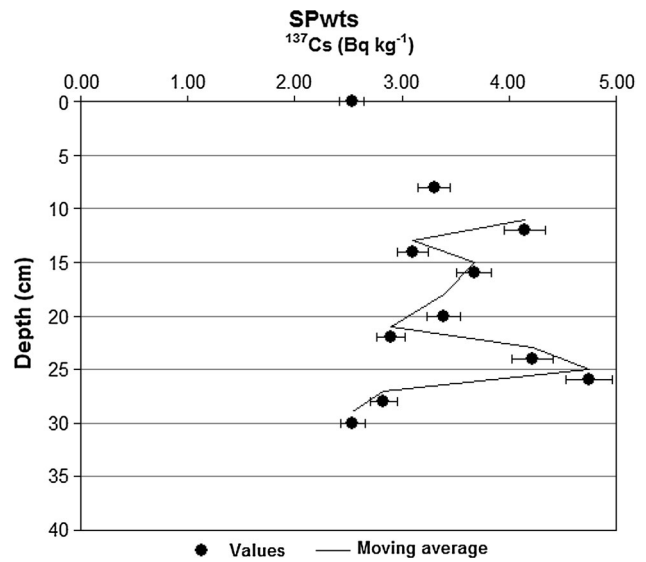 was considered inorganic. This determination was made because the percentage of organic matter in the sediments was less than 12 % of the dry weight (Esteves 2011). The range of variation of this percentage was 2.04–4.54 % in core SPriv, 2.05–6.67 % in core SPwts and 2.15–9.65 % in core SPdam.

The concentrations of Mn and Pb tended to be higher before the operation of Paiva Castro Reservoir began, tending to decrease from the bottom towards the top in cores SPdam and SPwts (Figs. 9, 10, 11, 12). In SPdam, Pb exceeded the reference value by approximately sixfold (142.6 mg kg^{-1} at a depth of 20–22 cm). In SPwts, Pb exceeded the reference value by approximately threefold
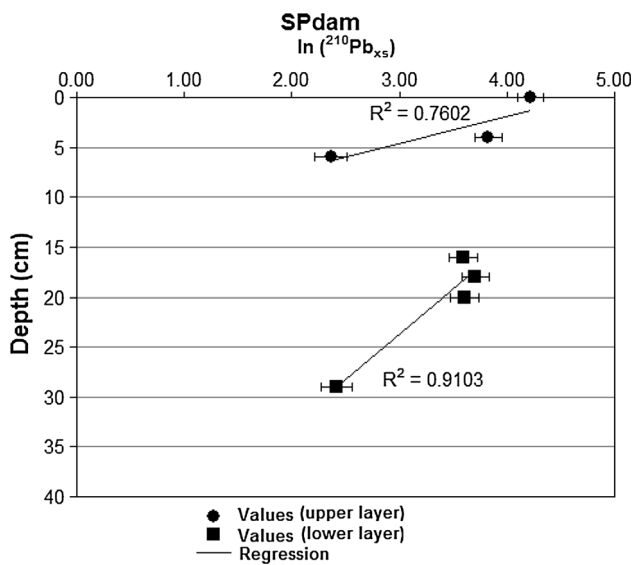
Fig. 5 Vertical profile of ln ($^{210}Pb_{xs}$) (unsupported) in core SPdam

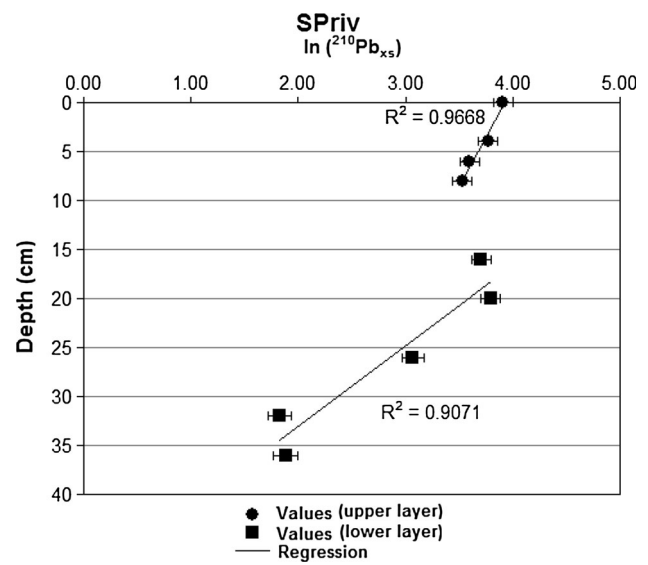**Fig. 7** Vertical profile of ln ($^{210}Pb_{xs}$) (unsupported) in core SPriv
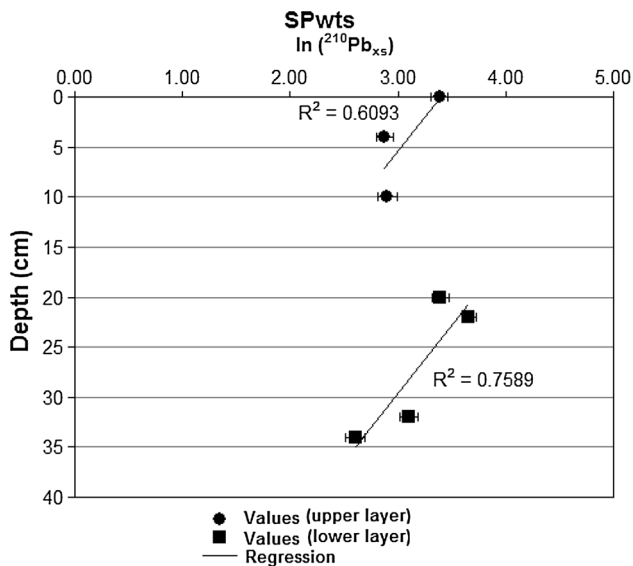
Fig. 6 Vertical profile of ln ($^{210}Pb_{xs}$) (unsupported) in core SPwts

Table 4 Proposed background values for the elements of interest (mean bottommost samples of the sampled cores) for the Paiva Castro Reservoir

Metal	Mean ± SD	BG Alto Tietê
Cr	26.52 ± 5.73	40
Cu	24.27 ± 13.15	25
Ni	32.63 ± 6.88	25
Pb	26.75 ± 12.37	61
Zn	69.51 ± 32.20	82
Mn	261.54 ± 154.77	–
Al	44,174.36 ± 13,144.74	–
Fe	46,810.52 ± 10,101.21	–

variations in the concentration of this heavy metal were considered small based on the coefficient of variation (15.51 %) (Table 5). Values for metals analysed in core SPriv are shown in Figs. 13 and 14.

Discussion

Sedimentation rate

The high sedimentation rates found in the limnetic area serve to explain the higher heavy metal accumulation rates observed in this area. In core SPdam, the change in sedimentation rate since 1994 may be due to the urban expansion occurring in the Juquery Basin during 1993–2002 (EMPLASA 2006). The rationale for this hypothesis is that changes in the sedimentation rate can be observed when there are changes in urbanisation around a

(97.54 mg kg^{-1}, 24–26 cm deep). In SPdam at a depth of 20–22 cm, high levels of Mn (720.8 mg kg^{-1}) and Zn (123.6 mg kg^{-1}) were also recorded (Fig. 10).

The concentration of Cu was highest in the most recent layers of cores SPriv and SPdam. However, this pattern was not observed in core SPwts, most likely due to the lower sedimentation rates recorded in the area. In core SPriv (Fig. 13), the Cu levels showed higher values from 1991 to 1997, with a decreasing trend observed thereafter. In core SPdam, the Cu levels increased from the 2000s, with values exceeding the reference values up to fourfold (97.0 mg kg^{-1}) (Fig. 9). In core SPwts, the Cu concentration tended to decrease over time (Fig. 11), and the
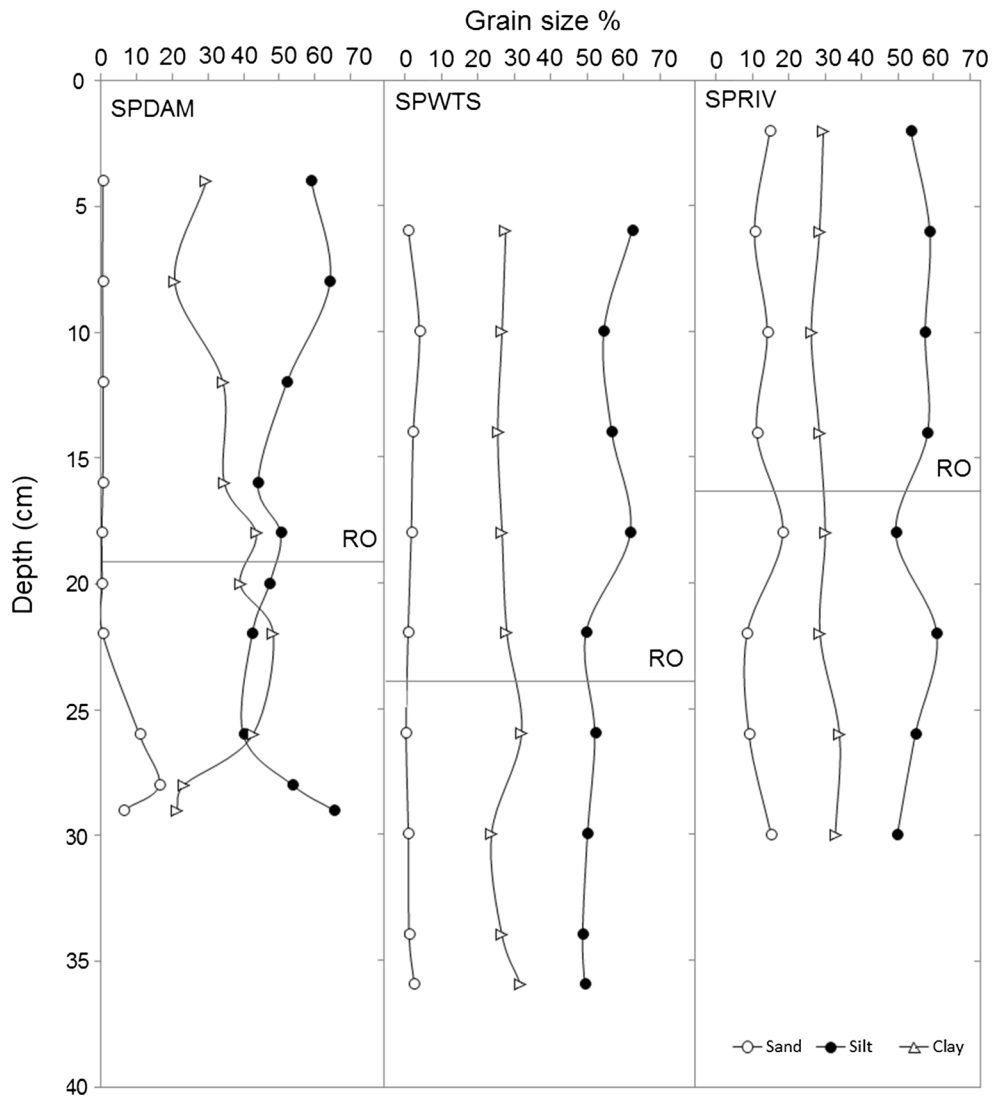
Fig. 8 Variation of grain size percentage in three cores (SPdam, SPwts and SPriv) from Paiva Castro Reservoir. *RO* reservoir operation

water body (Moreira et al. 2002). In core SPriv, changes in the sedimentation rates occurred in the same period during which Jaguari and Jacareí Reservoirs became part of the Cantareira system, a period when the system flow rate increased from 11 to 33 $m^3 s^{-1}$. In core SPwts, in the catchment area, the occurrence of a single sedimentation rate may reflect the extraction of water for the public water supply. This process would accelerate the flow of the water and, therefore, also produce a lower rate of sedimentation.

Binding of heavy metals to sediment

The predominance of the silt and clay size fractions, as observed at Paiva Castro Reservoir, indicates the prevalence of sedimentation processes (Fávaro et al. 2007). The silt fraction showed significant correlations with Cr, Mn, Ni, Pb, Zn and Fe, and the clay fraction showed a

significant correlation with Cu (Table 5). The reason for these results is that the sediment fraction less than 63 μm (silt and clay) has more active sites for adsorption of heavy metals (Förstner and Wittmann 1981; Rodríguez et al. 2006; Luoma and Rainbow 2008). Therefore, silt and clay soils retain more heavy metals by adsorption because the greater the surface area, the greater the likelihood that metals will be adsorbed (Huertos and Baena 2008; Devesa-Rey et al. 2011). Thus, the data suggest that these grain size fractions functioned as an important component of the binding of these contaminants to the sediment in Paiva Castro Reservoir.

Organic matter also acts as a binding site for heavy metals (Huertos and Baena 2008). It has been observed that in many water bodies, more than 50 % of the heavy metals present are associated with organic matter (Förstner and Wittmann 1981). However, the data from this study suggest

Fig. 9 Cr, Cu, Ni and Pb vertical profiles (**a**) and enrichment factors (**b**) for the past ~45 years (EF > 2 indicate moderate enrichment) for the SPdam core (limnetic area of the Paiva Castro Reservoir). *BG* background, *RO* reservoir operation
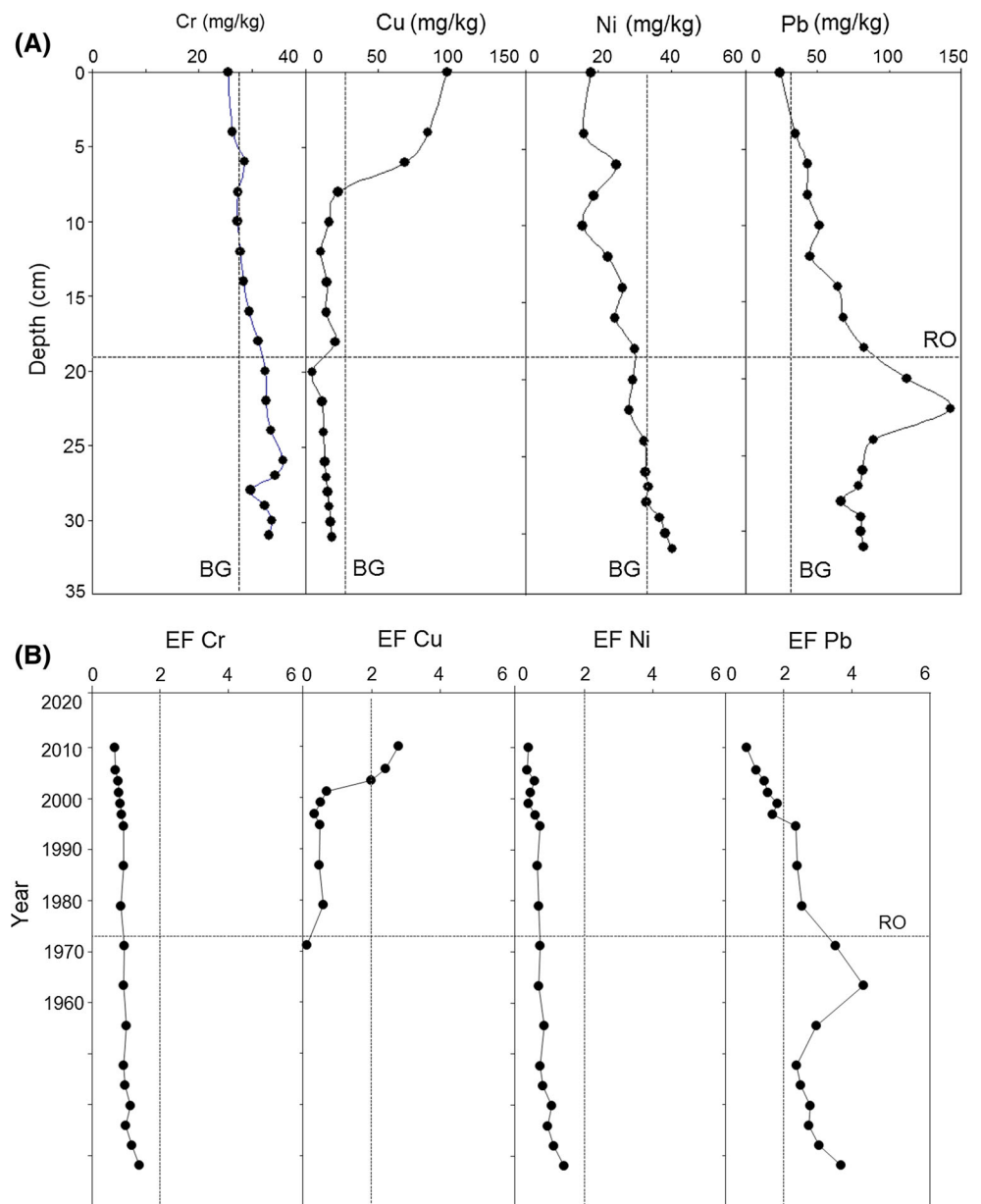

that organic matter was not an important participant in the binding of the heavy metals, as the concentration of organic matter tended to be low. Studies performed by this research group have shown that over time, organic matter, nitrogen and phosphorus are low in Paiva Castro's sediments. An increase in these constituents was found during the filling of the reservoir due to the natural decomposition of organic matter present in the flooded area. With the exception of the upstream area of the reservoir, the organic matter present at the sampled stations tends to be of autochthonous origin. Low levels of organic matter indicate that the region does not show significant impacts resulting from population growth in the occupation of the Paiva Castro Basin.

Significant correlations were observed between Mn and Cu, Cr, Ni, Pb and Zn and between Fe and Cu, Cr, and Pb (Table 5). The reason for these findings is, most likely, because Mn and Fe oxides are important binding sites for these heavy metals (Chapman et al. 1999).

Historical trends in heavy metal contamination

The enrichment factor categorised the sediments in periods prior to the operation of the reservoir as moderately enriched for Mn in the SPdam core and as moderately enriched for Pb in the SPwts and SPriv cores (Figs. 9, 11). These findings may be related to the construction of the reservoir, which began in 1963.

Fig. 10 Zn, Mn, Al and Fe vertical profiles (**a**) and enrichment factors (**b**) for the past $\sim$45 years (EF > 2 indicate moderate enrichment) for the SPdam core (limnetic area of the Paiva Castro Reservoir). *BG* background, *RO* reservoir operation
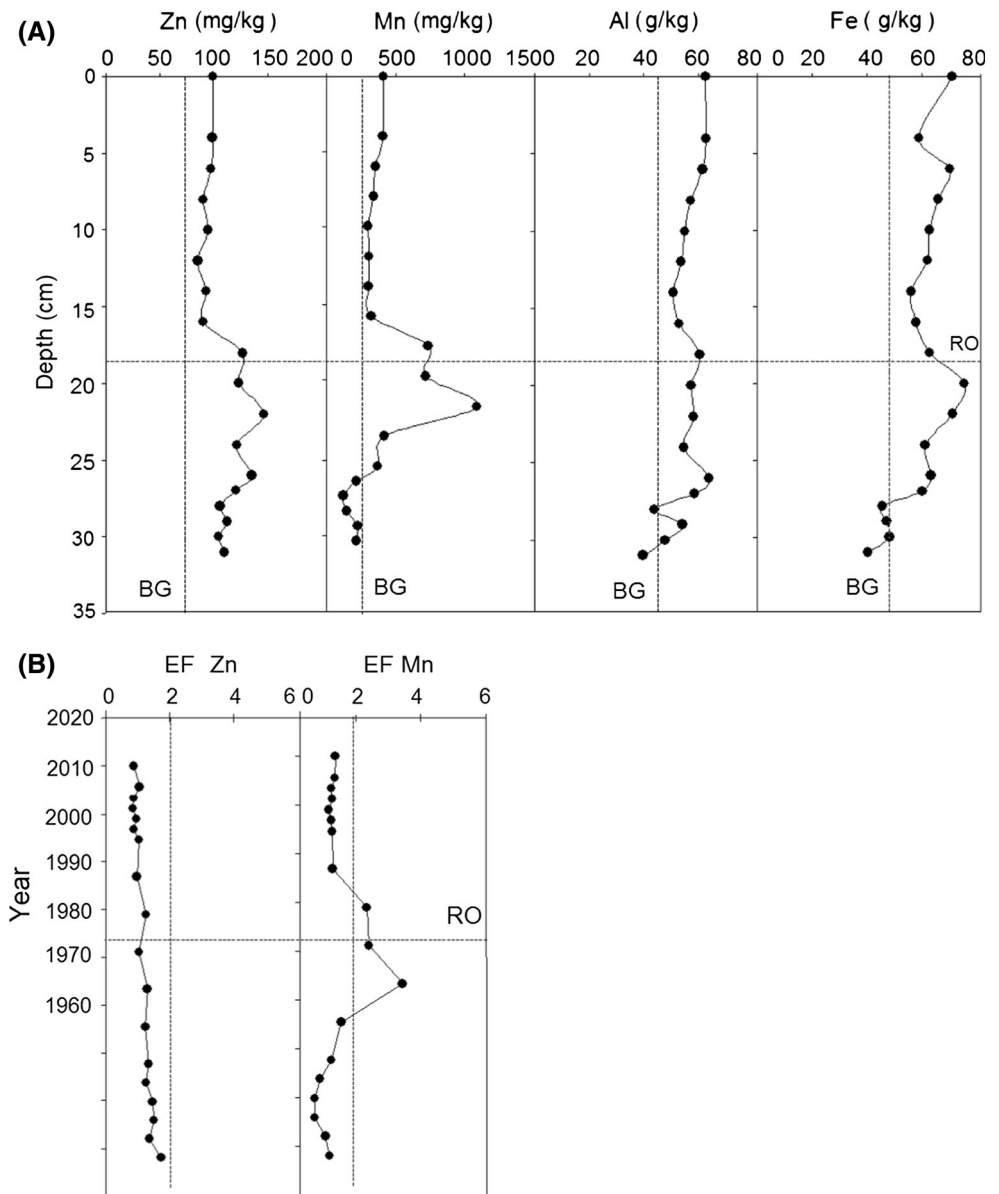
For Pb, another factor that may have contributed to the high levels of this heavy metal could be the use of lead arsenate as a pesticide. Lead arsenate is a pesticide that was widely used in grape culture until the mid-1950s (Wolz et al. 2003). In the period prior to reservoir construction, the Paiva Castro watershed was a site in which grapes were cultivated in subsistence agriculture. Accordingly, the possible use of lead arsenate for crop protection could have contributed to the high levels recorded for this element.

High levels of lead can also be produced as a result of the use of tetraethyl lead as an additive in gasoline. Several studies (Pienitz et al. 2006; Chalmers et al. 2007; Michelutti et al. 2009) have observed a decrease in lead in cores from the time that the use of tetraethyl lead as an additive in gasoline was banned. The Paiva Castro Basin region showed an increase in automobile traffic beginning primarily in the 1960s with the construction of the Fernão Dias Highway, a period prior to reservoir construction and coinciding with the time at which the peak levels of Pb were recorded.

Although the use of tetraethyl lead may have contributed to the higher concentrations of lead in Paiva Castro Reservoir, this observation does not explain the peak in the concentration of this heavy metal. The decrease in the levels of lead does not coincide with the period in which the use of tetraethyl lead in Brazil began to be reduced, in 1993. Part of the increase in lead may also be a result of natural lithological variations, as increased levels also occurred for zinc. These heavy metals were significantly correlated (Table 5) and are usually found associated in

nature, primarily in the form of lead sulphide (galena) (Allaby 2008).

For manganese, in addition to the peak found in the limnetic area, which may have resulted from reservoir construction, high levels were also recorded in SPriv in the topmost core layers. The enrichment factor categorised these topmost layers as moderately enriched (Fig. 11). The increase in this element observed in the most recent layers in SPriv may be due to the effluent from the nearby wastewater treatment station. Manganese is commonly found in municipal wastewater. However, it is normally present in domestic wastewater at concentrations that do not pose any environmental risks (Vymazal and Švehla 2013). The results for manganese may also be due to natural lithological variations because the peak in the concentration of this heavy metal was found in the deeper layers of the sediment, representing periods prior to the occurrence of significant anthropogenic activities in the region.

The enrichment factor for Cu categorised the topmost layers from cores SPriv and SPdam as moderately enriched, suggesting anthropogenic contamination. In the dam area, the increase in Cu started in the 1990s and was observed in core SPriv at the beginning of 2000, a period of great urban expansion in the Paiva Castro watershed. Between 1989 and 2003, urban water use had an increase of 33.5 % at the Paiva Castro basin while areas with natural vegetation decreased by about 12.4 % (Whately and Cunha 2007).

The increased copper levels in the dam core (SPdam) and in the core sampled at the upper part of the dam (SPriv)

Fig. 11 Cr, Cu, Ni and Pb vertical profiles (a) and enrichment factors (b) for the past ~45 years (EF > 2 indicate moderate enrichment) for the SPwts core (water supply area of the Paiva Castro Reservoir). BG background, RO reservoir operation

Fig. 12 Zn, Mn, Fe and Al vertical profiles (**a**) and enrichment factors (**b**) for the past ∼45 years (EF > 2 indicate moderate enrichment) for the SPwts core (water supply area of the Paiva Castro Reservoir). *BG* background, *RO* reservoir operation
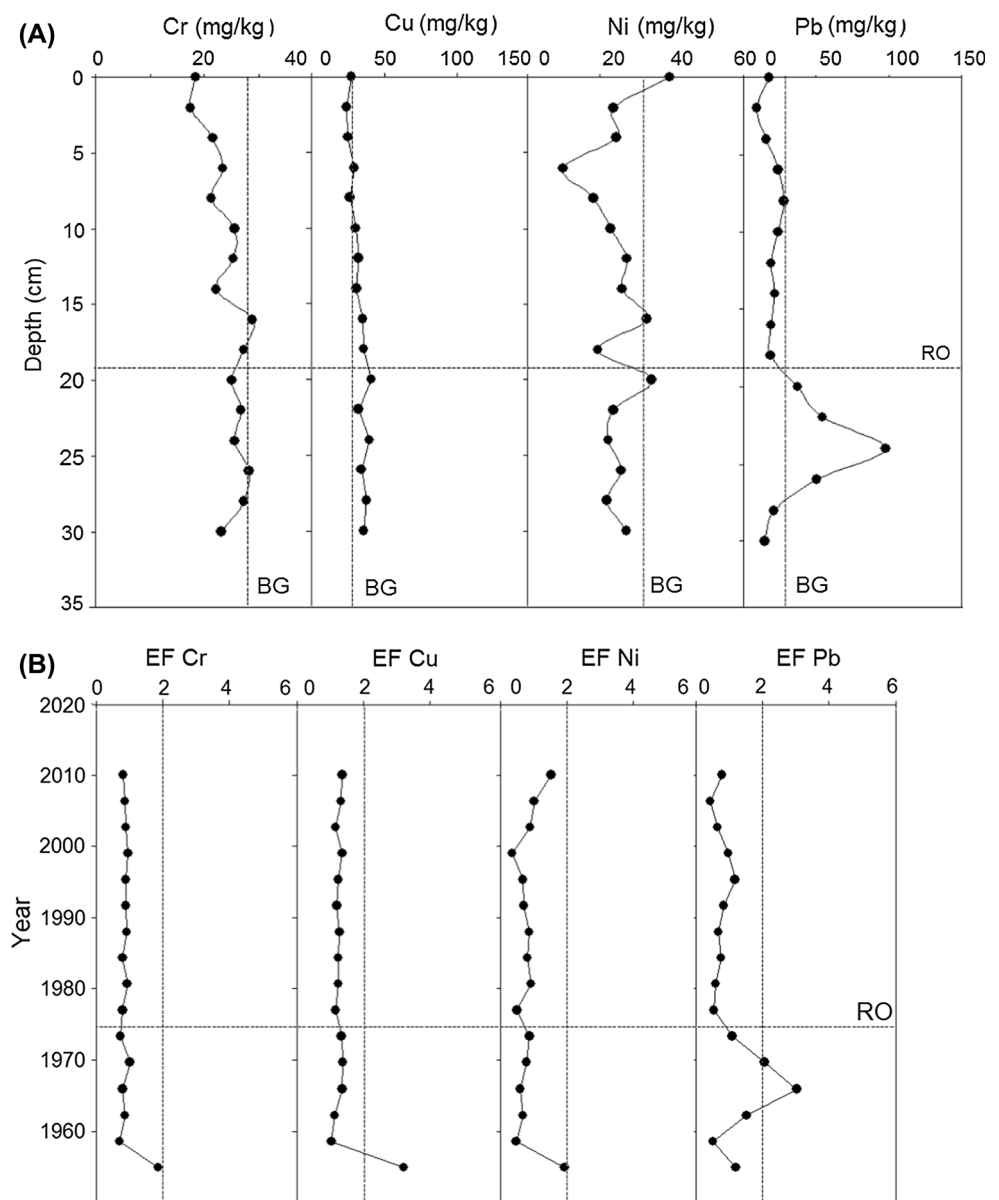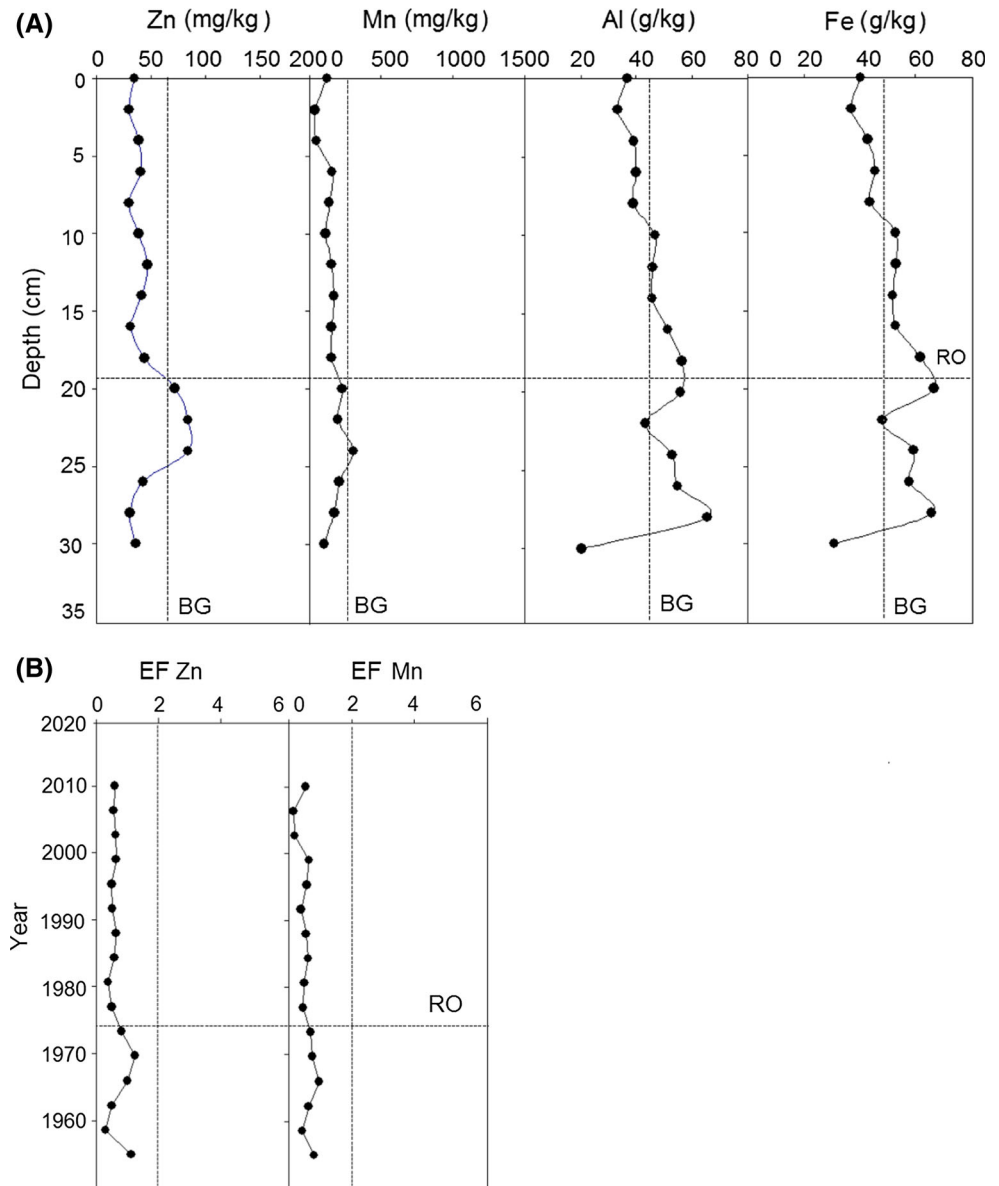

showed a strong and significant ($\alpha = 0.05$) linear correlation with data from population growth ($r^2 = 0.86 - \mathrm{SPdam}$, $r^2 = 0.60 - \mathrm{SPriv}$, $p < 0.05$) and agricultural production ($r^2 = 0.88 - \mathrm{SPdam}$, $r^2 = 0.78 - \mathrm{SPriv}$, $p < 0.05$) in the Paiva Castro watershed.

Moreover, between 1989 and 2003, an increase in phosphorus levels was recorded in the sediments of the area. This increase can be associated not only with the rising population and agricultural activities, but also with the fact that there is no full urban sewage coverage, collection and treatment at Mairiporã. By 2012, the sewage collection network served only 36 % of the population and only 27 % of the sewage generated was treated (PMM 2012) in the city. Therefore, the growing urban activities and phosphorus levels in sediments at the Paiva Castro

Reservoir can explain the use of algicides such as copper sulphate to control algal blooms, thus resulting in higher levels of Cu in the sediments.

The situation deserves attention because Cu persists in the environment and is highly toxic to aquatic communities. It is included in the list of bioaccumulative toxic pollutants of the Environmental Protection Agency of the United States (US EPA 1999). The application of algicides is a palliative practice that is also performed in other reservoirs in the metropolitan region of São Paulo. For example, the sediments in Guarapiranga Reservoir had a Cu level of 1157 mg kg^{-1}, a value 64 times higher than the regional reference (Pompêo et al. 2013). In the Rio Grande Reservoir (Billings Complex), Cu values of 3582 mg Cu kg^{-1} were recorded, approximately 143 times the regional reference

value (Mariani and Pompêo 2008). Despite the increases in Cu in Paiva Castro Reservoir, the values did not reach the same magnitude recorded for Billings and Guarapiranga. However, attention is needed to halt the degradation at Paiva Castro. Otherwise, the same level of contamination found in Guarapiranga and Billings will result.

Although it is considered an effective algicide, copper sulphate can be toxic to aquatic communities (Hanson and Stefan 1984; Hawkins and Griffiths 1987). The use of copper sulphate as an algicide has been banned in countries such as Great Britain since the mid-1960s. Within the European Union, the use of this algicide is being banned because of its accumulation in sediments and its toxic

effects on aquatic communities (Galbreath-O'leary 2009). There is a need to adopt measures to reduce nutrient loads in water bodies. Examples of such measures include the effective control of the development of the basin area and investments in sewage collection and treatment. If such measures are taken, algal blooms will be less frequent, and consequently, the use of algicides will be unnecessary.

For the other heavy metals analysed, the enrichment factor showed that Paiva Castro sediments were depleted or showed minimum enrichment (Figs. 9, 10, 11). The finding that Cd levels were below the detection limit is a sign that the area has not been significantly affected by this contaminant.

Fig. 13 Cr, Cu, Ni and Pb vertical profiles (**a**) and enrichment factors (**b**) for the past ~45 years (EF > 2 indicate moderate enrichment) for the SPriv core (upstream area of the Paiva Castro Reservoir). *BG* background, *RO* reservoir operation

Fig. 14 Zn, Mn, Al and Fe vertical profiles (**a**) and enrichment factors (**b**) for the past ~45 years (EF > 2 indicate moderate enrichment) for the SPriv core (upstream area of the Paiva Castro Reservoir). *BG* background, *RO* reservoir operation
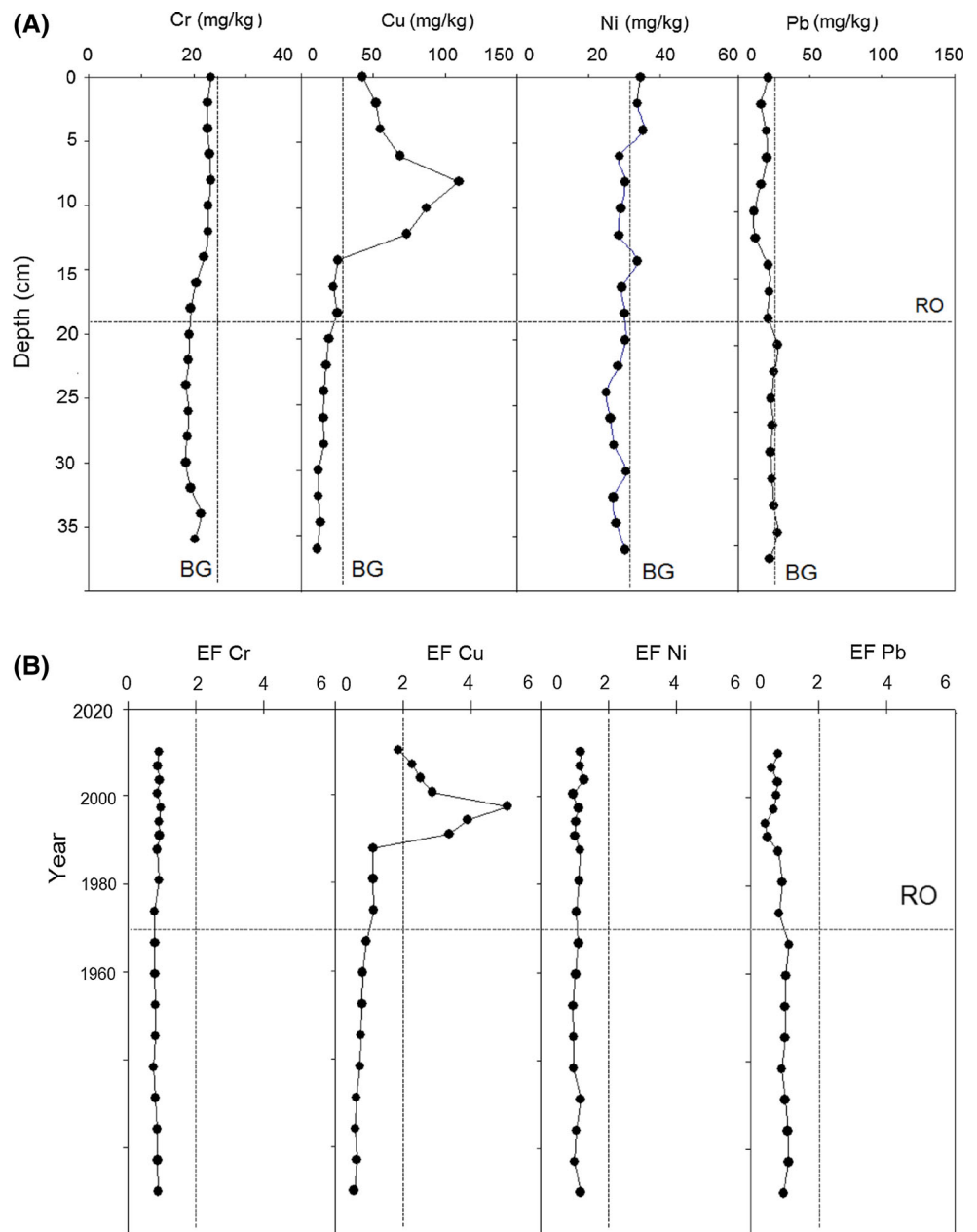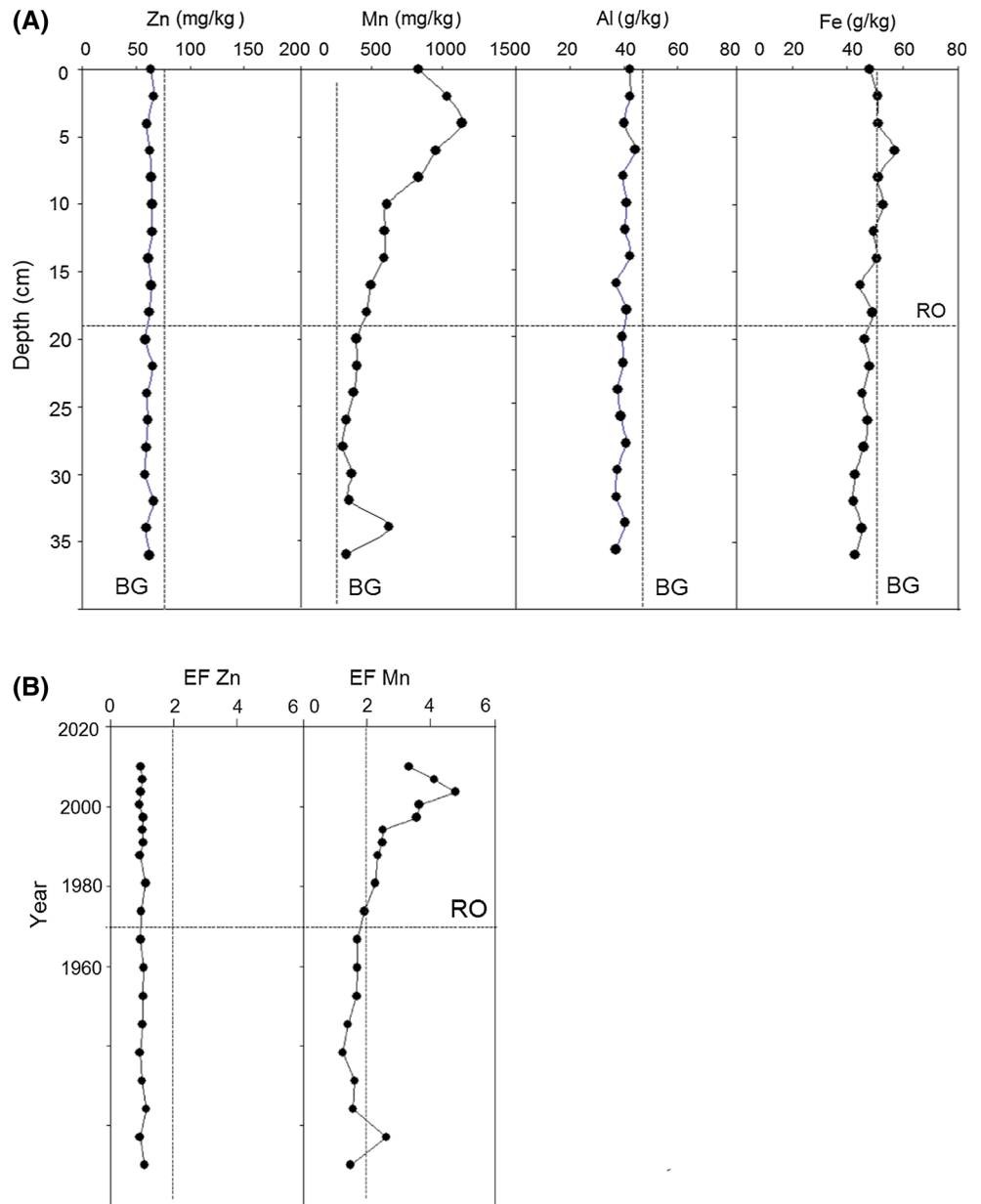

Table 5 Pearson's correlations ($p < 0.05$, $\alpha = 0.05$) between Cd, Cu, Ni, Pb, Zn, Mn, Fe and Al concentrations, organic matter (OM) and grain size levels (Cl—clay and Sil—silt) in the Paiva Castro's sediments

Core dam

Mn/Zn	0.60	Pb/Sil	−0.52	Pb/Zn	0.82	Fe/Sil	−0.47	Fe/Al	0.79	Fe/Mn	0.66
Mn/Pb	0.58								

Core wts

Cu/Mn	0.76	Cu/Fe	0.69	Mn/Pb	0.83	Mn/Al	0.60	Zn/Sil	0.46	Fe/Al	0.97
Cu/Cl	0.55	Mn/Zn	0.72	Mn/Fe	0.68	Mn/Cr	0.59	Zn/Pb	0.80	Fe/Cr	0.70

Core riv

Cu/Mn	0.67	Mn/Sil	0.71	Mn/Fe	0.71	Zn/Pb	−0.53	Sil/Fe	0.49	Al/Fe	0.83
Cu/Fe	0.76	Mn/Pb	−0.47	Mn/Al	0.65	Sil/Pb	−0.53	Pb/Fe	−0.60	
Mn/Ni	0.67	Mn/Cr	0.84	Ni/Sil	0.69	Sil/Cr	0.70	Cr/Fe	0.71	

Spatial differentiation of sediments

The objective of the discriminant analysis was to identify the variables that significantly differentiated the three analysed cores. Only the values during the time that the reservoir was in operation were used for this analysis. All variables were selected at the 0.01 tolerance level. Table 6 shows that the Wilks' λ test was significant for the independent variables Al, Mn, sand and silt. This test result shows that the differences among the means of the three groups were significant for the variables mentioned. The smallest value of Wilks' λ indicates the most important variable in the discriminant analysis. In the present study, the most important variables according to this test were silt and Al.

Table 7 shows the eigenvalues for the analysis. Larger eigenvalues correspond to better explanations by the discriminant function. In this case, the largest eigenvalue was 24.92, representing the first discriminant function. The independent variables with the highest correlations with the first discriminant function were fine sand and silt; the independent variables with the highest correlations with the second discriminant function were Al and Mn.

Particle size and the levels of conservative elements such as Al significantly differentiated the cores analysed over time and space. The highest levels of fine sand were recorded in the area where the uptake of water for the public water supply is located and in the area upstream from Paiva Castro, whereas a higher clay content was recorded in the dam area. The predominance of sand fractions in the catchment area is due, in part, to the increased flow of water in the region due to the withdrawal

Table 6 Discriminant analysis

	Wilks' lambda	F	P	Toler.
Fe	0.004	1.749	0.208	0.166
Al	**0.006**	**4.199**	**0.036**	**0.122**
Cu	0.004	0.474	0.631	0.264
Mn	**0.007**	**7.280**	**0.006**	**0.529**
Ni	0.004	0.114	0.893	0.655
Zn	0.004	0.866	0.441	0.292
Pb	0.004	1.777	0.203	0.241
Cr	0.004	0.329	0.725	0.358
OM	0.004	0.182	0.835	0.688
CS	0.004	0.362	0.702	0.364
FS	**0.007**	**7.692**	**0.005**	**0.275**
Silt	**0.006**	**5.021**	**0.021**	**0.269**
Clay	0.005	2.159	0.150	0.232

Test of equality among the group means. The significant independent variables are highlighted. *OM* organic matter, *CS* coarse sand, *FS* fine sand

Table 7 Matrix structure and eigenvalues for the discriminant functions

	Function 1	Function 2
Fe	0.77	0.79
Al	−1.07	**−1.43**
Cu	0.34	−0.36
Mn	−0.49	**0.88**
Ni	−0.03	0.15
Zn	−0.31	0.54
Pb	0.59	−0.71
Cr	−0.34	0.08
OM	0.16	0.10
CS	−0.23	−0.29
FS	**1.23**	0.65
Silt	**1.26**	0.02
Clay	0.87	−0.51
Eigenvalues	24.92	9.84
Variation %	0.72	0.28
Cumulative %	0.72	1.00

The significant independent variables are highlighted. *OM* organic matter, *CS* coarse sand, *FS* fine sand

of water for the public water supply; as previously discussed, larger particles tend to occur in areas of higher flow energy (He et al. 2011). On the contrary, the highest clay levels were found in the dam area. This finding is a result of the characteristics of this zone, which is an area of low energy with a predominance of sedimentation processes (Thorton 1990), favouring the accumulation of smaller particles.

Differences in Al levels can be associated with lithological variations, as this metal is not usually associated with anthropogenic sources (Din 1992). The Mn concentrations also contributed to explain the difference between the sampled cores. As previously discussed, the high levels of Mn may be due to lithological variations as well as the presence of effluents (Vymazal and Švehla 2013) from the waste water treatment station located in the upstream area of the reservoir. Despite the recent increase in the Cu levels in the topmost layers of two sampled cores, the concentrations of this heavy metal did significantly differentiate the three cores analysed.

Conclusions and considerations

The sampled cores allowed the establishment of baseline concentrations for heavy metals in Paiva Castro Reservoir and indicated the impacts of these potential contaminants prior to the beginning of the operation of the reservoir. At present, only the high Cu content suggests anthropogenic

contamination. This result indicates that it is necessary to control human impacts on the basins forming the Cantareira System and to make investments in the sanitation sector. These measures would end the application of algicides such as copper sulphate to control algal blooms, thus minimising the risk to aquatic communities. It is recommended that toxicity tests be performed in the limnetic area and in the upstream reservoir area because both regions showed a moderate enrichment for Cu. Although it is still considered a protected reservoir, evidence of the degradation of Paiva Castro Reservoir has already been reflected in sediments. It is now necessary to have public policies that prevent the degradation of this important ecosystem; otherwise, the reservoir's 'good quality' will be at risk.

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