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Statistical Approaches Link Sources of Sediment Contamination in Subtropical Reservoirs to Land Use: an Example from the Itupararanga Reservoir (Brazil)

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Abstract The identification and characterisation of diffuse pollutant sources in reservoirs remain a challenge due to the complexity of catchments with their variety of land use types. A sediment fingerprinting approach was used in this investigation for determining the sources of contaminants in sediments. By using this approach, we demonstrated how the effects of land use on pollution load of the subtropical Itupararanga Reservoir in Brazil can be de-convoluted. Sediments were collected at seven sampling sites (S1–S7) over the length of the reservoir. This was matched by eight sampling sites (P1–P8) of soils from different land use types (agriculture, urban and forest). Investigated parameters included grain size, total nitrogen (TN), total phosphorus (TP), total carbon (TC), organic matter by loss on ignition (OM), total sulphur (TS), and major ions and metals (Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, SO_4^{2-}, Cl^-, NO_3^-, As, Al, Ba, Cr, Cu, Fe, Mn, Ni and Zn). Our fingerprinting approach helped to outline horizontal spatial heterogeneities (categorised as riverine, transitional and lacustrine areas) that were attributed mainly to sand (>26.7%), Si (569 g kg^{-1}) and Cr (336 mg kg^{-1}) at S1 (riverine area). Moreover, fine particles of silt and clay leached from agricultural activities were enriched with OM, TP, TN, TC, As and Cr. These types of sediments were deposited into transitional and lacustrine areas. Furthermore, urban soils were a source of sand and phosphorus to sediments. The fingerprinting method reduced the number of relevant parameters for source identification and helped to identify non-point sources of sediments.

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1 Introduction

Diffuse pollution of freshwater systems is often related to anthropogenic inputs into catchments, such as agricultural activities, atmospheric deposition, and rainfall-runoff. Nutrients from agricultural activities, for example, can be mobilised via storm events or groundwater to lakes and reservoirs, thereby contributing to eutrophication (Kröger et al., 2007; Mockler et al., 2017; Ouyang et al., 2019). Metal concentrations are also affected by natural factors (e.g. soil properties along the catchment) and human activities (Ahmadi Doabi et al., 2019). Deforestation, for instance, may lead to increase the soil erosion and the transport of metals (e.g. Al and Fe) and nutrients to aquatic systems (Akerman et al., 2021; Melo et al., 2019a). Metals such as As, Cr, Cd and Pb can also accumulate in soils and waters as a result of increasing urbanisation, mining or expansion of agricultural areas (Acosta et al., 2011). The identification and characterisation of non-point pollutant sources remain a challenge because of the complexity of catchments and the variety of land use types that have different impacts on nutrient and metal inputs to freshwater systems (Acosta et al., 2011; Ouyang et al., 2019).

As an archive, sediments of lakes and reservoirs retain natural and anthropogenic compounds from the water column and thus record processes of the surrounding catchment. Hence, they can be source of contamination through remobilisation of metals and nutrients, causing chemical changes in the water column (Cardoso-Silva et al., 2018; de Oliveira Soares Silva Mizael et al., 2020; He et al., 2017; Sojka et al., 2018). Therefore, sediments of reservoirs and lakes can be used as good indicators of pollution from diffuse sources, especially if the contamination of the aquatic ecosystems is considered historically and land use related (Ouyang et al., 2019).

Tropical and subtropical areas are characterised by high rainfall rates that increase the load of sediments produced and transported into aquatic systems. Additionally, transport and deposition of eroded sediments can reduce storage capacities of surface reservoirs by sedimentation processes (Rahmani et al., 2018). Therefore, environmental quality monitoring of aquatic systems is important for their management and security (Chen et al., 2018; Pearce et al., 2017; Wang et al., 2018; Yang et al., 2018).

New monitoring approaches are required to quantify interactions between sediments and soils around reservoirs. Recent studies have shown advantages of integrating soil and water analyses (da Silva et al., 2015) and soil and suspended material investigations (Stutter et al., 2009) as well as soil and particulate sediment determinations (Tiecher et al., 2019). All these studies used a sediment fingerprinting approach as a tool to discriminate sources of pollution. Most of these studies focused on catchments (Didoné et al., 2014; Pulley et al., 2017; Tiecher et al., 2019), rivers (Patault et al., 2019), streams, groundwater (Long et al., 2018) and estuaries (Padalkar et al., 2019). However, only few investigations reported this approach to subtropical reservoirs (da Silva et al., 2018).

The sediment fingerprinting approach uses natural tracer technologies with a combination of field data collection, laboratory analyses of sediments and statistical modelling (Davis & Fox, 2009; Haddadchi et al., 2013; Koiter et al., 2013; Owens & Xu, 2011; Walling, 2013). Usually, it employs a combination of unique natural tracers collected from potential source areas. Tracers can include physical properties such as colour, particle size, fractal dimension or biogeochemical characteristics (Davis & Fox, 2009). Frequently, non-parametric statistical tests such as the Kruskal–Wallis H test or Mann–Whitney U test are employed to identify physicochemical properties that may serve as tracers of land use and source attributions. However, statistical fingerprinting studies need to adopt approaches that assume (Owens & Xu, 2011):

i) Direct connections between sources of sediments and sampling sites.
ii) Conservative behaviour of applied tracers.

The objective of this study was to investigate the effects of land use on sediment geochemistry of the Itupararanga Reservoir (São Paulo, Brazil) as a typical example for a subtropical climate zone. We followed this objective by application of multivariate statistics to show which parameters of land use were linked with sediment quality. Specific objectives were:

(i) To show how soils and surface sediments vary spatially according to catchment land use
(ii) To provide a link between land use and sediment quality status.
(iii) To determine which parameters might be linked to source of sediments.

To achieve these aims, our study examined spatial variations into soils from different land use classes together with reservoir sediment quality according to international indices. This investigation offers new insights to a growing area of sediment research by exploring observations of soil and surface sediment data across mixed land use spectra.

2 Materials and Methods

2.1 Study Area

The Itupararanga Reservoir is used for electricity and water supply and lies between 23.6209° and 23.6188°S and 47.3235° and 47.2741° W in the state of São Paulo (SP), Brazil. It is approximately 919 m above sea level and has slopes ranging from 0 to 53% of the catchment area (Simonetti et al., 2019). The Itupararanga Reservoir has a maximum depth of 21 m and a mean depth of 7.8 m. Its channel length is 26 km. The reservoir has a maximum storage volume of 286 million m^3 and an average surface area of 25 km^2. Its water residence time varies between 95 and 270 days (Melo et al., 2019a). The average daily precipitation in the reservoir from 2015 to 2017 was 7.2 ± 14.8 mm m^{-2} and 3.2 ± 11.4 mm m^{-2} during wet (October until March) and dry (April until September) seasons, respectively. Air temperatures range from 30 to 18 °C in the wet season and from 24 to 14 °C in the dry season (CBA-Itupararanga, http://www.aluminiocba.com.br/, accessed in 2019).

According to the Brazilian Agricultural Research Company (EMBRAPA), the major classes in the reservoir's catchment area are dystrophic red-yellow ultisols and cambisols Tb (PVAd9 code). The main characteristics of red-yellow ultisol are the presence of clays and hematite (Fe_2O_3) and goethite (FeOOH). The cambisol class occurs in hills, and it is characterised by variable fertility and the presence of clays with low cationic activity (Solos, 1997). The location of all sampling sites and the land use around the reservoir are shown in Fig. 1.

2.2 Sampling of Sediments and Soils

Sediment samples were collected at superficial depth (0–5 cm) with a dredge type lens (400 cm^2) in December 2016 at seven sampling locations (S1 to S7, Fig. 1). These locations were selected based on previous studies considering land use, horizontal compartmentalization and influence of inflows (Frascareli et al., 2015; Rosa et al., 2015). The surface layer of the sediments was chosen to observe a recent historical of surrounding activities on aquatic ecosystems (Zorzal-Almeida et al., 2018). The sediments were analysed for porosity (PW), dry weight (DW), organic matter (OM as a loss of ignition (LOI)) and particle size distribution. The latter was obtained by laser diffraction (CILAS 1190d; Quantachrome).

Soils were collected in June 2018 at two depths (0–20 cm and 20–50 cm ± 1.5 cm from the surface) at eight points around the reservoir (P1 to P8) for representing the different land use classes on the shoreline of the Itupararanga Reservoir. The collection of soil samples was carried out with a soil auger. The soil samples were afterwards stored in plastic bags. Each one of these sampling points was 20 m away from the shoreline. Although soils and sediments were collected in different periods, changes in land use were minimal as showed by Melo et al., (2019a). All samples were collected in random triplicates and homogenised at each sampling site.

2.3 Laboratory Analyses

The soil and sediment samples were dried at 60 °C until constant weight to determine dry weight (DW) and loss on ignition (LOI) in the laboratory. A portion of soil samples were sieved using a 2-mm sieve and were analysed in bulk for main and trace elements by X-ray fluorescence (XRF) as described in Morgenstern et al., (2001, 2004). Reference material was used (LKSD 1–4, STSD 1–4 and GBW

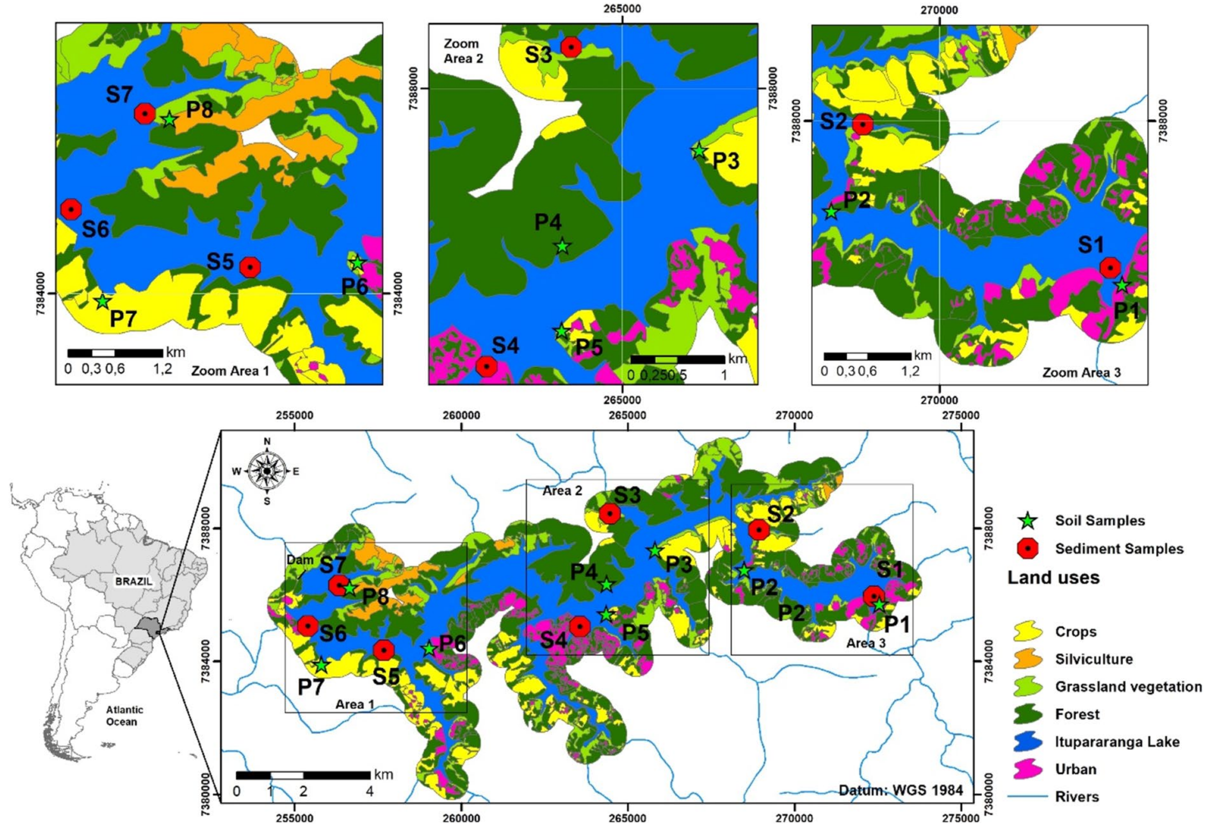

Fig. 1 Sampling sites and land use for the study area (figure created by D. Frascareli, author of this publication). P1 to P8 are soil samples related to the dominant land use types around Itupararanga Reservoir. P1, urban area; P2, natural forest cover mixed with an urban area; P3, grass/agriculture; P4, forest; P5, natural forest cover mixed with crops; P6, pasture and agriculture; P7, agriculture; and P8, silviculture (eucalyptus plantation). Sampling sites S1 to S7 are sediments samples collected in the reservoir. The map was created using RapidEye images (5-m spatial resolution from 17 July and 30 August 2014). All delineations were carried out using the software ArcGis 10.5 (ESRI, USA)

07,310), recovery of reference material was 95% and 105%, and quantification limit for trace elements is about 10 mg/kg (more details see Morgenstern et al., (2001). Total phosphorus (TP) was analysed photometrically (Skalar, The Netherlands) after digestion with hot HCl (German standard method DIN 38,414). Total organic carbon (TC), total nitrogen (TN) and total sulphate (TS) were quantified using a CNS analyser (DIMATOC, 2000, DIMATEC Analysentechnik GmbH, Germany); reproducibility and accuracy were better than 3%. Particle size distribution was obtained by laser diffraction (CILAS 1190d; Quantachrome). Chemical compositions in sediments and soils were expressed as Fe_2O_3, Al_2O_3, Na_2O, MgO, P_2O_5, SO_4, K_2O, CaO, and TiO_2; main nutrients (TP, TN, TS); carbon (TC); and grain size (GS).

2.4 Data Analysis

2.4.1 *Metal Contamination: Evaluation Using Background Data, Enrichment Factors (EF), Ecological Risk Index (RI), and Pollution Load Index Approach*

Metal sediment data from each point were gathered and then compared with correspondent background values determined in the three last slices of a sediment core from the reservoir by Cardoso-Silva et al., (2021) using ^{210}Pb chronology (SI, Table A2). This helped to assess the level of metal contamination against a common reference. The application of the EF, RI and PLI has been widely used to identify whether the origin of a trace metal in the sediment is anthropic or geogenic. The description of how the metal contamination was evaluated is available within the supplementary information (SI, Eqs. 10 to 13), and EF, RI and PLI classification categories are listed in SI, Table A3.

2.4.2 Determination of Sources: Statistical Fingerprinting Approach

Firstly, the soil data were grouped according to their similarities by cluster correlation distance analysis (SI, Fig. A1). All data were standardised using z-scores transformation before the analysis (Gotelli & Ellison, 2016). Afterwards, the land use category was tested by non-parametric Kruskal–Wallis H variance test (KW-H) to assess which parameters can discriminate between different soil sources. Variables that had discrimination potential were selected and used in further tests. KW-H tests were performed with 95% of confidence level ($\alpha = 0.05$). A null hypothesis ($P > 0.05$) that assumed that sources belong to the same population was formulated. The KW-H test for land use (forest, urban, agricultural) indicates that these classes are significantly different from each other ($P < 0.05$) (see SI, Table A1).

During the stepwise discriminant function analysis (DFA) selection, the initial screening data set (SI, Table A1) applied to select the optimum composite fingerprints confirmed the discriminatory feature of the fingerprint method via the reduction of Wilks' Lambda variable (Collins et al., 1997). A particle size correction factor Z is incorporated into the optimised mixing model (Minella et al., 2009). The distance of Mahalanobis allowed the discrimination between the sources, groups variability and the ratio of correctly classified samples (Minella et al., 2008).

Finally, a linear model proposed by Yu & Oldfield (1989) was applied for the mathematical determination of the relative contribution of each source through a multivariate mixing model. This model deals with the fact that sediments are a mixture of sources and that the comparison between the concentration of source elements (soil types) and sediment elements can define the contribution of each source. The solution is found through an iterative process proposed by Walling and Woodward, (1995). According to Minella et al., (2008), the model is suitable for identifying sources if the average relative mean error (RME) is less than 17%. This indicates that the optimised mixing model is able to provide an acceptable prediction of the fingerprint property concentrations associated with sediment samples (Minella et al., 2008). The results describe the relationship between source proportions (P_s) and sediment mixing parameters. The equations of the fingerprinting method are presented in detail within the SI (Eqs. 1 to 9).

The data treatment was performed using RStudio software version 1.2.5033, Past 2.7 (Hammer et al., 2001) and Microsoft Excel. The FingerPro package was used (Lizaga et al., 2019) with some adaptations for fingerprinting.

3 Results

3.1 Sediment Pollution Assessment

Lower concentrations of TC (10.9 g kg^{-1}), LOI (3.9%), TP (0.5 g kg^{-1}) and TN (1.1 g kg^{-1}) were found in surface sediments from riverine area (S1) when compared to the sampling sites of transitional and lacustrine areas of the reservoir (S4 to S7) (Table 1). The fine fraction (<63 µm) in the sediments was predominant in samples S2, S3, S4, S5, S6 and S7.

The fine fraction was predominant in all soil samples. Natural forest areas presented the highest silt contents (78.8%), while urban soils had the highest clay contents (12.5%). Sand contents with grain size larger than 63 µm were higher in urban and agricultural areas, where they reached maximum values of 26.7% and 19.8%, respectively (Table 1). Dry weight (DW) was higher in forest soils with values up to 22.8%, followed by silviculture and agriculture areas that reached up to 22.0%. LOI values were always higher than 21% and indicated higher organic composition of soil samples when compared to sediments. Specifically organic matter contents in agricultural soils presented higher C:N and C:P ratios, up to 15.6 and 886.8, respectively. In contrast, sediments of the reservoir had lower C:N and C:P of 9.9 and 101.4, respectively (Table 1).

Table 1 Data set from surface sediments and soils (classified by land use). Legend: *SD*, standard deviation; *DW*, dry weight; *LOI*, loss by ignition; *TS*, total sulphur; *TC*, total carbon; *TN*, total nitrogen; *TP*, total phosphorus; *C:N*, molar ratio carbon/nitrogen; and *C:P*, molar ratio carbon/phosphorus

Sampling site		Clay	Silt	Sand	DW	LOI	TS	TC	TN	TP	C:N	C:P
Units		%	%	%	%	%	g kg^{-1}					
Sediment	MEAN	8.5	82.6	8.9	32.1	12.8	1.4	26.3	3.1	0.7	9.9	101.4
	SD	3.7	18.2	20.5	12.2	4.2	0.3	7.2	0.9	0.1	0.8	20.0
Urban-soil	MEAN	12.5	60.8	26.7	17.5	21.1	0.5	13	1.4	0.4	11.3	140.1
	SD	5.6	8.4	9.9	2.8	2.8	0.3	1.9	0.3	0.3	2.2	92.2
Forest-soil	MEAN	11.9	78.8	9.3	22.8	22.4	0.5	17.3	1.9	0.2	10.8	189.8
	SD	1.5	7.4	8.5	3.8	4.1	0	3.4	0.4	0	0.4	16.2
Agriculture-soil	MEAN	11.4	68.8	19.8	22	27.9	0.6	24.4	1.8	0.1	15.6	886.8
	SD	1.2	4.8	5	1.3	1.6	0	5.2	0.3	0.1	1.8	646.8

3.2 Metal Contamination

The presence of clay minerals in the sediment composition was indicated by high content of Al, Fe and Mg (up to 30% percent by weight) and the predominance of fine fraction (Landajo et al., 2004) that also showed increasing trends towards the dam (Table 2). The agriculture soil in the surrounding area of the reservoir presented high contents of these elements (e.g. 291,055, 96,745 and 2543 mg kg^{-1} of Al_2O_3, Fe_2O_3 and MgO).

Values up to 336 mg kg^{-1} were found for Cr in the reservoir at site S1. Maximum As values of 36 and 25 mg kg^{-1} were found at sites S5 and S6, respectively. The EF indicated that As was moderately enrichment at S5 and S6, and Cr was considerably enrichment at S1 (Table 3).

3.3 Identification of Sediment Sources by Fingerprint Analysis

Cluster correlation distance analysis of soil data (SI, Fig.A1) indicated similarities between the following land use types: forest and forest/crops (P4 and P5), crops and silviculture (P3, P6, P7 and P8) and urban (P1 and P2). The samples P2, P3, P5 and P6 that were derived from mixed land use areas and were re-classified according to the dominant land use type based on this cluster analysis. For instance, P2 that is located in a private area with holiday houses (urban land use) mixed with forest fragments was re-classified as urban area according to the cluster analysis (see in SI, Fig. A1). Similarly, all sampling sites were re-classified according to the dominant land use (urban/agricultural/forest).

The Kruskal–Wallis *H* test revealed that out of 28 chemical elements analysed, 9 can discriminate sources by distinguishing among the different land use compartments. The variables that had discriminating capacity ($H_{critical} = 5.99$, at 5% significance level and 2 degrees of freedom) were silt, LOI, TOC, MgO, Al_2O_3, SiO_2, P_2O_3, K_2O and Pb (SI, Fig. A2). These variables best indicated the differences between the land uses around the reservoir.

The selection of the best set of tracers was carried out by minimising Wilks' Lambda. In this stage, four

Table 2 Average mass concentrations of main elements within sediments and soils classified by land use. *Units*, mg kg^{-1}; *SD*, standard deviation; *CV*, coefficient of variation

Sampling site		Fe_2O_3	Al_2O_3	SiO_2	Na_2O	MgO	P_2O_5	SO_4	K_2O	CaO	TiO_2	MnO
Sediment	Mean	85659	249275	859	459558	2653	1922	3986	17520	1417	11273	489
	SD	25624	70217	473	146929	748	487	988	5261	247	2352	129
Urban Soil	Mean	77267	216012	542852	< 300	1014	2211	< 300	1512	494	15663	275
	SD	26543	11148	36122	< 300	516	986	< 301	405	205	6175	167
Forest Soil	Mean	67964	219365	548557	1177	4899	785	< 302	26,134	301	10729	181
	SD	6510	15098	8231	242	493	91	< 303	9053	49	1072	10
Agriculture Soil	Mean	96745	291055	380362	1384	2543	1372	993	7907	871	17914	187
	SD	10344	7957	18203	652	992	111	60	6079	478	1411	64

Table 3 Results of enrichment factor (EF), potential ecological risk index (RI) and pollution load index. The highlighted values correspond to contamination present or absent or the levels of contamination (EF and RI)

	Cr	Ni	Cu	Zn	As	Pb	RI	PLI
	EF							
S1	**12.3**	1.7	0.4	1.1	< LD	1.02	34.6	1.3
S2	1.3	1.6	1.0	0.7	1.7	0.59	70.4	**2.1**
S3	0.9	1.1	0.7	0.6	0.7	0.81	43.7	1.6
S4	0.7	0.9	0.7	0.7	0.5	0.73	47.1	1.7
S5	1.2	0.9	1.0	0.5	**4.4**	0.39	**159.4**	**2.7**
S6	1.2	1.0	0.8	0.5	**3.3**	0.50	119.3	**2.4**
S7	0.6	0.8	0.5	0.5	1.4	0.66	67.5	1.9

LD: Limit of Detection

tracers were selected (MgO, SiO_2, P_2O_5 and Pb) using boxplot (SI, Fig. A3), discriminant function analysis (DFA) map (SI, Fig. A4) and PCA map (Fig. 2). This selected set simplified all the correlations observed between the variables determined by Kruskal-W Test (SI, Table A4). However, the variables determined by Kruskal-W test were considered to have high importance for the evaluation of sediment mixtures because they are suppressed in the DFA but still belong to the group of discriminators.

In the sediment and soil PCA, the first two principal components (PC1 and PC2) explained over 65.7% of the total data variance (Fig. 2). PC1 was responsible for 39.2% of the variance and indicated that the sediments were spatially heterogeneous distributed. The sampling points S1, S2, S3, S4 and S7 were divided mainly above PC1, showing high rankings for SiO_2 (0.71) and Pb (0.74) at PC2. The sampling points S5 and S6 in the lower portion of the chart (below PC1) indicated little influence by SiO_2 and Pb. Urban areas influenced the points that were above PC1, while the points in the lower portion were related to agriculture source. The urban source is well defined by the absence of MgO and K_2O, whereas agriculture and urban sources are also indicated by high concentrations of P_2O_5 and organic material (LOI) (Table 2).

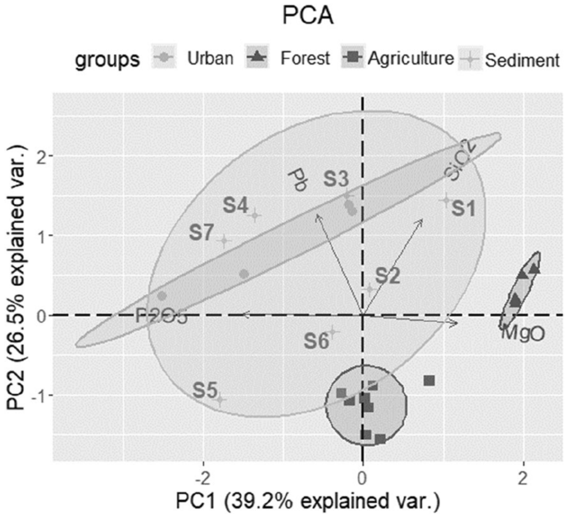

Fig. 2 Principal component analysis (PCA) of soil (urban, forest and agriculture) and sediment data with the variables with discriminant potential determined by the Kruskal-W and DFA-tests (biplot of the first two principal components, PC1 versus PC2)

From the uncertainties associated with the ability to discriminate among sources, the calculation of Mahalanobis' distance provided results for the correct classification of sources. Distances between urban and forest and between urban and agriculture sources are greater than between agriculture and forest (Table 4). This does not mean that agriculture and forest samples are the same, but rather that they are less different from each other. Urban formation has the greatest distinction between the other sources. Analysing the samples and the source groups, all samples were classified as belonging to the groups of origin (except point 16, SI, Table A5).

Table 4 Mahalanobis distance between sources

	Forest	Agriculture
Urban	144.5	90.6
Agriculture	53.1	-

For all surface sediment samples, the contribution from each source (urban, agriculture and forest) was calculated as described below. Apart from S2, S5 and S6, the sampling points received a large contribution of sediment from urban sources (Fig. 3). Sediments from S1, S3, S4 and S7 showed the same order of source contribution, having an urban contribution, followed by forest and agriculture sources. The points S2, S3 and S6 indicated an overlapping of urban and forest sources, which make it difficult to identify the amount of each origin. Agriculture source showed relatively low contribution to the sediments of the riverine compartment of the reservoir (S1, S2). However, apart from S5 where the contribution of agriculture and urban sources cannot be well differentiated, the sampling points had very distinct sources. Nevertheless, both sources (urban and agriculture) showed high contribution to the sediment composition at S5. All the RME values were less than 2%, indicating that fingerprinting model is suitable for identifying sources.

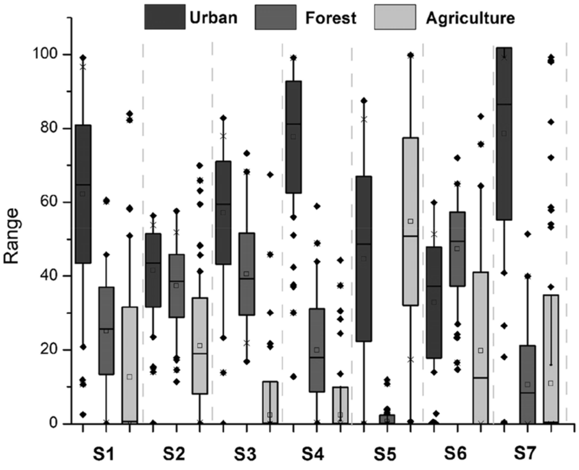

Fig. 3 Relative contribution of each source to the surface sediment composition

4 Discussion

4.1 Land Uses as a Source of Contamination in Surface Sediments

Small size reservoirs (<50 km^2) are considered important sinks for C, N and P. Changes in the amount of these elements in their sediments are sensitive to the land use around them (Harrison et al., 2009). Vanni et al. (2011) observed in a historical perspective that the C:N:P fractions decrease with the increase of agricultural activities. In this study, high concentration and low spatial variability were found to C:N values that presented coefficient of variation (CV) of 7.6% for surface sediment samples (Table 1). Conversely, a lower P concentration and higher CV were observed for C:P (19.7%) and N:P (21.45%). The analysed soils from all land use types presented higher CV: 21.6% to C:N; 111.2% to C:P and 96.11% to N:P. This higher variability occurred mainly due to spatial horizontal heterogeneity that occurs in the surface sediment or the influence of land use surrounding of the reservoir (Thornton, 1990) or release of dissolved P from sediments (Perkins & Underwood, 2001). Concerning the P release in anoxic conditions, the Itupararanga Reservoir presents stratification of the water column in the warmer season (November to March), according to Melo et al., (2019b), indicating the occurrence of anoxia. However, investigations that determine the Fe-bounded P can help to understand the aquatic geochemistry of P-release from sediments.

This study indicated that the P from soils was an important parameter in the fingerprinting analysis. It was shown that urban soils had higher P content, suggesting that urban areas may contribute to most of the P loading into the Itupararanga Reservoir. This is supported by previous investigations in reservoirs (Jones et al., 2004; Knoll et al., 2003, 2014). The average P concentrations in the surface sediments (0.65 ± 0.11 mg g^{-1}) were similar to the ones from reservoirs that have catchment dominated by agriculture (e.g. Ohio Reservoir sediment average = 1.0 mg g^{-1}; Knoll et al., 2014). In fact, Silva et al., (2015) indicated that familiar farming activities around Itupararanga catchment have the potential to contaminate soils, water and then sediments by excess of fertilisers. Although the riverine area (mainly S1) of the Itupararanga Reservoir has a record of organic contamination (Frascareli et al., 2015), only low concentrations for N, P and C were found in its surface sediments because of the higher amounts of sand. Nevertheless, the levels of P, clay and silt increased from sampling site S2 towards the dam in the reservoir. This was associated with the increase of mixes of land uses, mainly, mixing of agricultural and urban activities, also observed in other studies (Lindfors et al., 2020).

The high content of Al, Fe and Mg in the sediments is generally associated with high precipitation followed by intense erosion of tropical soils (generally rich in Al and Fe) from surrounding catchments (de Oliveira Soares Silva Mizael et al., 2020; Fonseca et al., 2011). de Oliveira Soares Silva Mizael et al. (2020), for instance, detected high amounts of Al and Fe (50,968 and 52,411 mg Kg^{-1} in average, respectively) in the Broa Reservoir (Brazil). The Três Marias and Tucuruí (Brazil) reservoirs also presented high concentrations of Al (ca. 25% Al_2O_3) and Fe (ca. 10% Fe_2O_3) and predominance of silt and clay (Fonseca et al., 2011). The transport of clay minerals from the reservoir surroundings by runoff may increase the contamination of water and sediments from the reservoir. This occurs because clay minerals have the largest capacity to adsorb trace metals and nutrients (Uddin, 2017).

The high concentrations of CaO in agricultural soil samples can be explained by liming practice to neutralise the acidity of tropical soils (Pöttker & Ben, 1998). Low to absent CaO values in the forested areas can be considered as natural background levels which may serve as an indirect indication that such liming actions have only been carried out in other land use types than forests. The application of $CaCO_3$ enriches the soil with Ca^{2+}, Mg^{2+} and $SO_4{}^{2-}$ (Braga et al., 1995; Pavan, 1986). This explains the elevated concentrations of $SO_4{}^{2-}$, K_2O and CaO in agricultural soils. Elevated K_2O concentrations in the deepest layer of forest soils may be related to the recycling of nutrients and downwards mobility of K_2O (Pavan, 1986). Dominance of clays and silts in agricultural and urban soils can exceed 90% and with their affinity for fine fractions may explain the increase of K^+ and Ca^{2+} in sediments from transitional to lacustrine areas by the erosion of such soils. Similar observations were made by Lal, (2003) and Liu et al., (2019). Negative correlations between Al_2O_3 and SiO_2 may be explained by a more intense weathering followed by leaching of Si, K and Mg than their less soluble counterparts Al_2O_3 and Fe_2O_3 present in tropical soils (Santos et al., 2006) (SI, Fig. A5).

According to RI index, metal concentrations detected in sediments were moderate at S5 and low in the other sampling points. The Cr values at S1 were much higher than other tropical reservoirs in Brazil. Pompêo et al., (2013), for instance, reported 59.6 ± 50.8 mg kg^{-1} in the sediments of Guarapiranga Reservoir. In Rio Grande Reservoir, Mariani & Pompêo, (2008) found 56.7 ± 27.0 mg kg^{-1} of Cr. Values of Cr and As were higher than the reference values established by the Brazilian National Environment Council (Resolution CONAMA n°454, 2012) and the background values for Itupararanga Reservoir estimated by Cardoso-Silva et al., (2021). Apart from Ni, Cu, Zn, As and Pb at S1, all analysed metals were above the background values established by Cardoso-Silva et al., (2021).

Fingerprinting analysis with the support of descriptive analysis indicated an enrichment of the riverine area with sand, P and Cr from urban and agricultural sources. The lacustrine area was characterised by higher concentrations of TC, Al, TS, silt and Pb mainly derived from agricultural activities. Moreover, K_2O and MgO were considered typical markers of the transition area, and they were related to forest areas. A summary of the parameters that contributed to the spatiality in the reservoir is presented (Table 5).

Table 5 Summary of results from compartmentalisation and land uses categories for main parameters contributing to the spatial analysis (*GS*, grain size)

Compartment	Lacustrine	Transitional	Riverine
Land use	Agriculture, silviculture, urban	Agriculture, forest	Agriculture, urban
Sampling site (sediments)	S5, S6, S7	S3, S4	S1, S2
Sampling site (soils)	P6, P7, P8	P4, P5	P1, P2, P3
Contribution			
High contents	GS (clay), Al, TN, TC, TS, TP, As, Ti	GS (clay), Ti, Al, TS, TC, K, Mg	GS (sand), P, Si, Ni, Cr, Co
Low contents	Si	GS (silt), Pb	TC, LOI, TP, TN

5 Conclusions

Our study was able to determine relationships between land use and sediment geochemistry using statistical approaches that related riverine, transitional and lacustrine reservoir compartments to each other. The spatial heterogeneity within the reservoir was derived from the higher proportions of sand, Si and Cr in the riverine than in the lacustrine zone. Although it was expected that the main river inflow would mobilise larger particles (> 63 µm) to the reservoir, our study demonstrated that sand particles were also derived from urban areas. Transitional and lacustrine areas presented high proportions of fine particles (silt and clay) associated with organic compounds (TP, TN, TC) and specific elements (As, Al).

The results for As and Cr exceeded the limits set by the Brazilian legislation and—for comparison—those by the Canadian Environment Quality Guidelines. Enrichment factors rated As as “moderate level” at S5 and S6 and Cr as “considerable level” at the S1 sampling site. Metal levels in riverine (S2) and lacustrine areas (S5 and S6) indicated leaching processes of contaminated material that probably derived from agricultural soils.

The statistical analysis indicated enrichment of riverine area with sand and P from urban and agricultural activities. Silt, TC, TS, Al and Pb within the lacustrine area may be related to agricultural sources, whereas K_2O and MgO in the transitional area can be attributed to forest soil sources. Our approach also reduced the number of parameters of the soil sampling sites from 26 to 4 without losing quality in the characterisation of the environmental conditions. However, this procedure cannot be only based on statistical tests but also on the expert knowledge.

This work is a contribution to the sediment geochemistry of reservoirs, which are so far hardly explored for subtropical systems. Given the increasing number of water bodies affected by urbanisation and agriculture, we state that the findings of this work can also help to assist recovery and management of reservoirs. The statistical fingerprinting approach applied here can be transferred to other studies and serves as a valuable tool for monitoring of water ecosystems and engineered structures.

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Data Availability The data sets generated during and/or analysed during the current study are available in the UNESP repository, [https://repositorio.unesp.br/handle/11449/205095].

Declarations

Conflict of Interest The authors declare no competing interests.

References

Acosta, J. A., Faz, A., Martínez-Martínez, S., & Arocena, J. M. (2011). Enrichment of metals in soils subjected to different land uses in a typical Mediterranean environment (Murcia City, southeast Spain). *Applied Geochemistry, 26*(3), 405–414. https://doi.org/10.1016/j.apgeochem.2011.01.023

Ahmadi Doabi, S., Karami, M., & Afyuni, M. (2019). Heavy metal pollution assessment in agricultural soils of Kermanshah province. *Iran. Environmental Earth Sciences, 78*(3), 70. https://doi.org/10.1007/s12665-019-8093-7

Akerman, A., Oliva, P., Poitrasson, F., Boaventura, G. R., da Silva Souza, V., & Seyler, P. (2021). Impact of deforestation on soil iron chemistry and isotope signatures in Amazonia. *Chemical Geology, 577*, 120048. https://doi.org/10.1016/j.chemgeo.2020.120048

Braga, F. D. A., Vale, F. R., & Muniz, J. A. (1995). Movimentação de nutrientes no solo, crescimento e nutrição mineral do eucalipto, em função de doses de gesso e níveis de irrigação. *Bras Ci Solo, 19*, 69–77.

Cardoso-Silva, S., Ferreira, P. A. D. L., Figueira, R. C. L., da Silva, D. C. V. R., Moschini-Carlos, V., & Pompêo, M. L. M. (2018). Factors that control the spatial and temporal distributions of phosphorus, nitrogen, and carbon in the sediments of a tropical reservoir. *Environmental Science and Pollution Research, 25*(31), 31776–31789. https://doi.org/10.1007/s11356-018-2923-0

Cardoso-Silva, S., Oliveira Soares Silva Mizael, J., Frascareli, D., Alves de Lima Ferreira, P., Henrique Rosa, A., Vicente, E., . . . Moschini-Carlos, V. (2021). Paleolimnological evidence of environmental changes in seven subtropical reservoirs based on metals, nutrients, and sedimentation rates. *CATENA*, *206*, 105432. https://doi.org/10.1016/j.catena.2021.105432

Chen, N., Mo, Q., Kuo, Y.-M., Su, Y., & Zhong, Y. (2018). Hydrochemical controls on reservoir nutrient and phytoplankton dynamics under storms. *Science of the Total Environment, 619–620*, 301–310. https://doi.org/10.1016/j.scitotenv.2017.09.216

Collins, A. L., Walling, D. E., & Leeks, G. J. L. (1997). Source type ascription for fluvial suspended sediment based on a quantitative composite fingerprinting technique. *CATENA, 29*(1), 1–27.

CONSELHO NACIONAL DO MEIO AMBIENTE (CONAMA) (2012). Resolution n 454, of November 1, 2012. Establishes the general guidelines and referential procedures for the management of material to be dredged in waters under national jurisdiction. Available at: https://www.ibama.gov.br/component/legislacao/?view=legislacao&legislacao=128537. Accessed 1 Apr 2022.

da Silva, A. M., Manfre, L. A., Urban, R. C., Silva, V. H. O., Manzatto, M. P., & Norton, L. D. (2015). Organic farm does not improve neither soil, or water quality in rural watersheds from southeastern Brazil. *Ecological Indicators, 48*, 132–146.

da Silva, E. M. R., Medeiros, P., Araújo, J. C., & d. (2018). Applicability of fingerprinting for identification of sediment sources in a mesoscale semiarid catchment. *Engenharia Agrícola, 38*(4), 553–562.

Davis, C. M., & Fox, J. F. (2009). Sediment fingerprinting: Review of the method and future improvements for allocating nonpoint source pollution. *Journal of Environmental Engineering, 135*(7), 490–504.

de Oliveira Soares Silva Mizael, J., Cardoso-Silva, S., Frascareli, D., Pompêo, M. L. M., & Moschini-Carlos, V. (2020). Ecosystem history of a tropical reservoir revealed by metals, nutrients and photosynthetic pigments preserved in sediments. *CATENA, 184*, 104242. https://doi.org/10.1016/j.catena.2019.104242

Didoné, E. J., Minella, J. P. G., Reichert, J. M., Merten, G. H., Dalbianco, L., de Barrros, C. A. P., & Ramon, R. (2014). Impact of no-tillage agricultural systems on sediment yield in two large catchments in Southern Brazil. *Journal of Soils and Sediments, 14*(7), 1287–1297.

Fonseca, R., Canário, T., Morais, M., & Barriga, F. J. A. S. (2011). Phosphorus sequestration in Fe-rich sediments from two Brazilian tropical reservoirs. *Applied Geochemistry, 26*(9), 1607–1622. https://doi.org/10.1016/j.apgeochem.2011.04.017

Frascareli, D., Beghelli, F. G. D. S., Silva, S. C. D., & Carlos, V. M. (2015). Heterogeneidade espacial e temporal de variáveis limnológicas no reservatório de Itupararanga associadas com o uso do solo na Bacia do Alto Sorocaba-SP. *Revista Ambiente & Água, 10*, 770–781. https://doi.org/10.4136/ambi-agua.1715

Gotelli, N. J., & Ellison, A. M. (2016). *Princípios de estatística em ecologia*. ARTMED editora.

Haddadchi, A., Ryder, D. S., Evrard, O., & Olley, J. (2013). Sediment fingerprinting in fluvial systems: Review of tracers, sediment sources and mixing models. *International Journal of Sediment Research, 28*(4), 560–578.

Hammer, O., Harper, D. A. T., & Ryan, P. D. (2001). PAST: Paleontological statistic software package for education and data analysis. *Paleontologia Eletronica, 4*(1), 1–9.

Harrison, J. A., Maranger, R. J., Alexanderm, R. B., Giblin, A. E., Jacinthe, P. A., Mayorga, E., Seitzinger, S. P., Sobota, D. J. & Wollheim, W. M. (2009). The regional and global significance of nitrogen removal in lakes and reservoirs. *Biogeochemistry, 93*, 143–157.

He, Y., Men, B., Yang, X., Li, Y., Xu, H., & Wang, D. (2017). Investigation of heavy metals release from sediment with bioturbation/bioirrigation. *Chemosphere, 184*, 235–243. https://doi.org/10.1016/j.chemosphere.2017.05.177

Jones, J. R., Knowlton, M. F., Obrecht, D. V., & Cook, E. A. (2004). Importance of landscape variables and morphology on nutrients in Missouri reservoirs. *Canadian Journal of Fisheries and Aquatic Sciences, 61*(8), 1503–1512.

Knoll, L. B., Vanni, M. J., & Renwick, W. H. (2003). Phytoplankton primary production and photosynthetic parameters in reservoirs along a gradient of watershed land use. *Limnology and Oceanography, 48*(2), 608–617.

Knoll, L. B., Vanni, M. J., Renwick, W. H., & Kollie, S. (2014). Burial rates and stoichiometry of sedimentary carbon, nitrogen and phosphorus in M idwestern US reservoirs. *Freshwater Biology, 59*(11), 2342–2353.

Koiter, A. J., Owens, P. N., Petticrew, E. L., & Lobb, D. A. (2013). The behavioural characteristics of sediment properties and their implications for sediment fingerprinting as an approach for identifying sediment sources in river basins. *Earth-Science Reviews, 125*, 24–42.

Kröger, R., Holland, M. M., Moore, M. T., & Cooper, C. M. (2007). Plant senescence: A mechanism for nutrient release in temperate agricultural wetlands. *Environmental Pollution, 146*(1), 114–119. https://doi.org/10.1016/j.envpol.2006.06.005

Lal, R. (2003). Soil erosion and the global carbon budget. *Environment International, 29*(4), 437–450.

Landajo, A., Arana, G., de Diego, A., Etxebarria, N., Zuloaga, O., & Amouroux, D. (2004). Analysis of heavy metal distribution in superficial estuarine sediments (estuary of Bilbao, Basque Country) by open-focused microwave-assisted extraction and ICP-OES. *Chemosphere, 56*(11), 1033–1041.

Lindfors, S., Österlund, H., Lundy, L., & Viklander, M. (2020). Metal size distribution in rainfall and snowmelt-induced runoff from three urban catchments. *Science of the Total Environment, 743,* 140813.

Liu, J.-J., Diao, Z.-H., Xu, X.-R., & Xie, Q. (2019). Effects of dissolved oxygen, salinity, nitrogen and phosphorus on the release of heavy metals from coastal sediments. *Science of the Total Environment, 666*, 894–901.

Lizaga, I., Latorre, B., Gaspar, L., & Navas, A. (2019). fingerPro: An R package for sediment source tracing. In.

Long, D. T., Pearson, A. L., Voice, T. C., Polanco-Rodríguez, A. G., Sanchez-Rodríguez, E. C., Xagoraraki, I., . . . Rzotkiewicz, A. T. (2018). Influence of rainy season and land use on drinking water quality in a karst landscape, State of Yucatán, Mexico. *Applied Geochemistry*, *98*, 265-277.

Mariani, C. F., & Pompêo, M. L. M. (2008). Potentially bioavailable metals in sediment from a tropical polymictic environment—Rio Grande Reservoir. *Brazil. Journal of Soils and Sediments, 8*(5), 284. https://doi.org/10.1007/s11368-008-0018-0

Melo, D. S., Gontijo, E. S. J., Frascareli, D., Simonetti, V. C., Machado, L. S., Barth, J. A. C., . . . Friese, K. (2019a). Self-organizing maps for evaluation of biogeochemical processes and temporal variations in water quality of subtropical reservoirs. *Water Resources Research*, *55*(12), 10268-10281. https://doi.org/10.1029/2019wr025991

Melo, D. S., Gontijo, E. S. J., Frascareli, D., Simonetti, V. C., Machado, L. S., Barth, J. A. C., . . . Friese, K. (2019b). Self-organizing maps for evaluation of biogeochemical processes and temporal variations in water quality of subtropical reservoirs. *Water Resources Research*, *n/a*(n/a). https://doi.org/10.1029/2019bWR02599

Minella, J. P. G., Merten, G. H., & Clarke, R. T. (2009). Método" fingerprinting" para identificação de fontes de sedimentos em bacia hidrográfica rural. *Revista Brasileira De Engenharia Agrícola e Ambiental, 13*(5), 633–638.

Minella, J. P. G., Walling, D. E., & Merten, G. H. (2008). Combining sediment source tracing techniques with traditional monitoring to assess the impact of improved land management on catchment sediment yields. *Journal of Hydrology, 348*(3–4), 546–563.

Mockler, E. M., Deakin, J., Archbold, M., Gill, L., Daly, D., & Bruen, M. (2017). Sources of nitrogen and phosphorus emissions to Irish rivers and coastal waters: Estimates from a nutrient load apportionment framework. *Science of the Total Environment, 601–602*, 326–339. https://doi.org/10.1016/j.scitotenv.2017.05.186

Morgenstern, P., Friese, K., Wendt-Potthoff, K., & Wennrich, R. (2001). Bulk chemistry analysis of sediments from acid mine lakes by means of wavelength dispersive X-ray fluorescence. *Mine Water and the Environment, 20*(3), 105–113.

Morgenstern, P., Brüggemann, L., & Wennrich, R. (2004). Validation of an X-ray methodology with environmental concern. *Spectrochimica Acta Part B: Atomic Spectroscopy, 59*(2), 185–197.

Ouyang, W., Hao, X., Wang, L., Xu, Y., Tysklind, M., Gao, X., & Lin, C. (2019). Watershed diffuse pollution dynamics and response to land development assessment with riverine sediments. *Science of the Total Environment, 659*, 283–292. https://doi.org/10.1016/j.scitotenv.2018.12.367

Owens, P. N., & Xu, Z. (2011). Recent advances and future directions in soils and sediments research. In: Springer.

Padalkar, P. P., Chakraborty, P., Chennuri, K., Jayachandran, S., Sitlhou, L., Nanajkar, M., . . . Singh, K. (2019). Molecular characteristics of sedimentary organic matter in controlling mercury (Hg) and elemental mercury (Hg0) distribution in tropical estuarine sediments. *Science of the total environment*, *668*, 592-601

Patault, E., Alary, C., Franke, C., & Abriak, N.-E. (2019). Quantification of tributaries contributions using a confluence-based sediment fingerprinting approach in the Canche river watershed (France). *Science of the Total Environment, 668*, 457–469.

Pavan, M. A. (1986). Comportamento do gesso nos solos ácidos das regiões tropicais e subtropicais. *Piracicaba, POTAFOS-Associação Brasileira para Pesquisa da Potassa e do Fosfato*.

Pearce, A. R., Chambers, L. G., & Hasenmueller, E. A. (2017). Characterizing nutrient distributions and fluxes in a eutrophic reservoir, Midwestern United States. *Science of the Total Environment, 581–582*, 589–600. https://doi.org/10.1016/j.scitotenv.2016.12.168

Perkins, R. G., & Underwood, G. J. C. (2001). The potential for phosphorus release across the sediment–water interface in an eutrophic reservoir dosed with ferric sulphate. *Water Research, 35*(6), 1399–1406.

Pompêo, M., Padial, P. R., Mariani, C. F., Cardoso-Silva, S., Moschini-Carlos, V., Silva, D. C. V. R. D., . . . Brandimarte, A. L. (2013). Biodisponibilidade de metais no sedimento de um reservatório tropical urbano (reservatório Guarapiranga – São Paulo (SP), Brasil): há toxicidade potencial e heterogeneidade espacial? *Geochimica Brasiliensis*, *27*(2), 104. https://doi.org/10.21715/gb.v27i2.364

Pöttker, D., & Ben, J. R. (1998). Calagem para uma rotação de culturas no sistema plantio direto. *Revista Brasileira De Ciência Do Solo, 22*(4), 675–684.

Pulley, S., Foster, I., & Collins, A. L. (2017). The impact of catchment source group classification on the accuracy of sediment fingerprinting outputs. *Journal of Environmental Management, 194*, 16–26.

Rahmani, V., Kastens, H. J., DeNoyelles, F., Jakubauskas, E. M., Martinko, A. E., Huggins, H. D., . . . Blackwood, J. A. (2018). Examining Storage Capacity Loss and Sedimentation Rate of Large Reservoirs in the Central U.S. Great Plains. *Water*, *10*(2). https://doi.org/10.3390/w10020190

Rosa, A. H., Silva, Â. A. M. J., Melo, C. d. A., Moschini, V., Carlos, M., Guandique, E. G., . . . Lourenço, R. W. (2015).

Diagnóstico ambiental e avaliação de uso e ocupação do solo visando a sustentabilidade da represa de Itupararanga, importante área da bacia do médio Tietê. In *Ecologia de reservatórios e interfaces* (pp. 213–231). Instituto de Biociências da Universidade de São Paulo.

Santos, M. D. C., Varajão, A. F. D. C., & Yvon, J. (2006). Geochemistry of a sedimentary lateritic kaolin deposit in Quadrilátero Ferrífero. *Brazil. Journal of Geochemical Exploration, 88*(1–3), 318–320.

Simonetti, V. C., da Cunha, D. C., & Rosa, A. H. (2019). Proposta metodológica para identificação de riscos associados ao relevo e antropização em áreas marginais aos recursos hídricos. *Scientia Plena*, *15*(2).

Sojka, M., Jaskuła, J., & Siepak, M. (2018). Heavy metals in bottom sediments of reservoirs in the lowland area of western Poland: Concentrations, distribution, sources and ecological risk. *Water*, *11*(1). https://doi.org/10.3390/w11010056

Solos, E. (1997). *Manual de métodos de análise de solos*. Centro Nacional de Pesquisa de Solos.

Stutter, M. I., Langan, S. J., Lumsdon, D. G., & Clark, L. M. (2009). Multi-element signatures of stream sediments and sources under moderate to low flow conditions. *Applied Geochemistry, 24*(5), 800–809.

Thornton, K. W. (1990). Perspectives on reservoir limnology. IN: *Reservoir Limnology: Ecological Perspectives*. John Wiley & Sons, New York. 1990. p 1–13, 10 fig, 1 tab, 20 ref.

Tiecher, T., Ramon, R., Laceby, J. P., Evrard, O., & Minella, J. P. G. (2019). Potential of phosphorus fractions to trace sediment sources in a rural catchment of Southern Brazil: Comparison with the conventional approach based on elemental geochemistry. *Geoderma, 337*, 1067–1076.

Uddin, M. K. (2017). A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. *Chemical Engineering Journal, 308*, 438–462.

Vanni, M. J., Renwick, W. H., Bowling, A. M., Horgan, M. J., & Christian, A. D. (2011). Nutrient stoichiometry of linked catchment-lake systems along a gradient of land use. *Freshwater Biology, 56*(5), 791–811.

Walling, D. E. (2013). The evolution of sediment source fingerprinting investigations in fluvial systems. *Journal of Soils and Sediments, 13*(10), 1658–1675.

Walling, D. E., & Woodward, J. C. (1995). Tracing sources of suspended sediment in river basins: A case study of the River Culm, Devon. *UK. Marine and Freshwater Research, 46*(1), 327–336.

Wang, X., Zhang, L., Zhao, Z., & Cai, Y. (2018). Heavy metal pollution in reservoirs in the hilly area of southern China: Distribution, source apportionment and health risk assessment. *Science of the Total Environment, 634*, 158–169. https://doi.org/10.1016/j.scitotenv.2018.03.340

Yang, Z., Cheng, B., Xu, Y., Liu, D., Ma, J., & Ji, D. (2018). Stable isotopes in water indicate sources of nutrients that drive algal blooms in the tributary bay of a subtropical reservoir. *Science of the Total Environment, 634*, 205–213. https://doi.org/10.1016/j.scitotenv.2018.03.266

Yu, L. I. Z. H. O. N. G., & Oldfield, F. (1989). A multivariate mixing model foridentifying sediment source from magnetic measurements. *Quaternary Research, 32*(2), 168–181.

Zorzal-Almeida, S., Salim, A., Andrade, M. R. M., Nascimento, M. D. N., Bini, L. M., & Bicudo, D. C. (2018). Effects of land use and spatial processes in water and surface sediment of tropical reservoirs at local and regional scales. *Science of the Total Environment, 644*, 237–246. https://doi.org/10.1016/j.scitotenv.2018.06.361