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Benthic fluxes in a subtropical reservoir estimated by pore-water diffusion calculation

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Abstract The internal load of metals and nutrients in reservoirs can be derived from fluxes at the sediment–water interface via pore water (PW) and may affect the water quality. The main goal of this study was to investigate the distribution and fluxes of nutrients and metals at SWI in a subtropical reservoir. Sediments cores were collected at five sites in Itupararanga Reservoir and sliced at 1-cm depth intervals (2-cm from 6 cm deep). PW was extracted and analysed by its dissolved cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) metals (Al, Ba, Cr, Cu, Fe, Mn, Ni e Zn), nutrient (total dissolved phosphorus, soluble reactive phosphorus-SRP; NO_3; NH_4^{+}) and C content. The sediments were analysed by porosity, particle size distribution and contents of C, N and P. Fluxes at SWI were calculated using Fick's law in one dimension. P was being released to the water column at Core 5, by the mineralisation of OM by oxic pathways and retained at Core 2. Although Core 4 had high P concentration on PW, no results of flux was possible due to lack on bottom water data. No concentration of SRP was detected in PW of Core 1 and 7. Release of Fe, Mn, Zn and Cr was also observed. SRP was absent at the most eutrophic site (Core 1). The contribution of 74.83 mg m^{-2} SRP day^{-1} at Core 2 was potentially harmful to water quality. This study showed the importance of investigating sediment interstitial water and expanded a discussion in sub-climatic environments on the release and contribution of sediments in the geochemistry of P in aquatic ecosystems.

Keywords Sediments · Subtropical environment · Phosphorus release · Metals

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1 Introduction

The sediment–water interface also known as benthic zone is an important compartment in aquatic ecosystems that is responsible for removal, transformations and cycling of elements such as carbon (C), nitrogen (N), phosphorus (P), iron (Fe) and manganese (Matos et al., 2022; Pan et al., 2017; Pearce et al, 2017; Zhang et al., 2014). It is a boundary between water and sediments where intense decomposition of organic matter (OM) by bacteria takes place. The gradients in density, solution composition, pH, redox potential and biological activity in this region are steep, and chemicals can be recycled several times before being buried (Santschi et al., 1990).

The pore water (PW) is the medium where the exchanges between the dissolved and particulate content will be carried out from the SWI. The forces driving this passage can be caused by pressure gradients which can be stimulated by various mechanisms in spatial and temporal intervals such as light intensity, temperature, bioturbulence, transport, flow and winds (movement of the water) (Bastakoti et al., 2018; Frogner-Kockum et al., 2016; He et al., 2017). The metal and flux nutrients estimation in the SWI is significantly important for assessing the biogeochemical cycle of elements, the sedimentary environment, water quality and the quality of ecosystems (Ni et al., 2017). Among the processes affecting this flow are bioturbation, desorption, PW advection and resuspension of particles (Santschi et al., 1990). Phosphorus is an important limiting nutrient in freshwater reservoirs. The loading of this element into these systems can be derived from both external (e.g., rivers and run off) and internal sources (from sediments via SWI). The role of the internal loading is greater in reservoirs of higher trophic levels, where P may be released from sediments at certain conditions, exceeding the sedimented amount originated from external loads. These conditions may involve for instance anaerobic and aerobic release of P, increase in pH and temperature (Perkins & Underwood, 2001).

The P released by sediments (usually as soluble reactive phosphorus—SRP) is normally bioavailable, turning it more important than external inputs (Burger et al., 2007; Nuernberg, 1985; Nürnberg & Peters, 1984; Peters, 1981). Traditionally, SRP released into interstitial water has been associated with anoxic environments (Hüpfer & Lewandowski, 2008). This assumption is based on the work of Einsele (1936) and Mortimer (1941) that attributed the P retaining in oxic sediments to iron oxy-hydroxides at the SWI. Under anoxic conditions, the "adsorbing influence of oxidised ferric complexes is destroyed" and the sorbed P is released together with Fe. High temperatures typical from subtropical environments associated with high rates of aerobic OM mineralisation accelerate this process of oxygen (O) consumption and P release (da Silva et al., 2020; A. Kleeberg & Dudel, 1997; Spears et al., 2006). However, alternative release mechanisms such a dissolution of calcium-bound P, decomposition of organic P under both, aerobic and anaerobic conditions, mineralisation of OM by bacteria activity are often more important than the redox-driven Fe-coupled P cycle (Caraco et al., 1989; Flower et al., 2022; Moura et al., 2020). Therefore, the classic model of anoxic release of P from sediments established by Eisenle (Einsele) and Mortimer (1942) should be used with caution and other processes and mechanisms need to be considered in order to better understand the P dynamics.

The release of P from the SWI has been the focus of several researchers worldwide because it is related to harmful algal blooming (Musong Chen et al., 2018; X. Chen et al., 2019). Vertical P movements are particularly important and can be measured by Fick's law equation. Studies applying Fick's law to SWI in subtropical environments are limited to estuaries (Zhao et al., 2021), lakes (Chiu et al., 2020), drowned valley bays (Zhang et al., 2020), and coastal lagoons (Pratihary et al., 2009). Brazilian subtropical reservoirs have few studies involving PW and even less estimating the flux and quantifying P release or retention from bottom sediments (e.g. Mozeto et al., 2001; Soares & Mozeto, 2006, Moura et al, 2020; Papera et al., 2021) by unit of area using Fick's law (e.g. Mozeto et al., 2001; Soares & Mozeto, 2006). Because of this, investigations that present data from pore water quality may promote environmental monitoring database enrichment (Benassi et al., 2021; Mozeto et al., 2001; Pierangeli et al., 2021; Soares & Mozeto, 2006).

High loads of phosphorus (P) are released daily into aquatic ecosystems via untreated sewage causing an increase in their primary productivity (Oliveira et al., 2022), especially in developing countries that are located in subtropical areas. Croos et al. (2005) state that this is a global trend and the use of fertilisers—a product closely correlated with the increase in aquatic trophic state—is increasing to meet demand for food and crop productivity, consequently intensifying the eutrophication that may lead to an increase of internal P loadings. This highlights the importance of studying internal P contributions to artificial reservoirs in subtropical areas where information about P fluxes at the SWI is few (Chalar & Tundisi, 2001; Gin & Gopalakrishnan, 2010; Han et al., 2014). In this investigation, Itupararanga Reservoir located in Brazil was used as subtropical reservoir model to study P fluxes as this reservoir has records of increasing tropic level and harmful cyanobacteria blooms. In this research, we identify the internal collaboration by unit of area in the release or trapping of P and some trace metals. We also propose an analysis of the sediment porewater and sediment parameters in order to: i) investigate the concentration and distribution of nutrients (P) and trace metals in sediment porewater; and ii) assess the nutrient and metal benthic fluxes. Some other studies were carried out focusing on nutrients dynamics on water (Frascareli et al., 2018; Simonetti et al., 2019) or sediments (Melo et al., 2019) in Itupararanga Reservoir. However, no one evaluated the nutrient dynamic in sediments and benthic flux in an integrated way.

2 Material and Methods

2.1 Study Area

The Itupararanga reservoir is located in the upper part of the Sorocaba River basin, in the state of São Paulo, Brazil (Fig. 1). It was built in 1912 for hydroelectric power generation and is currently used to supply drinking water to approximately one million people, for agricultural and recreational purposes (Melo et al., 2019). The reservoir has a maximum depth of 21 m, an average depth of 7.8 m, and its main channel is 26 km longer. The residence time varies between 95 and 270 days, and the reservoir has a maximum storage volume of 286 million m^3 (Frascareli et al., 2018; Ribeiro et al., 2014). The reservoir is formed by the Sorocabaçu, Sorocamirim and Una rivers as the main tributaries and numerous small streams (for instance, Paruru, Ressaca and Campo Verde) (Smith & Petrere, 2008).

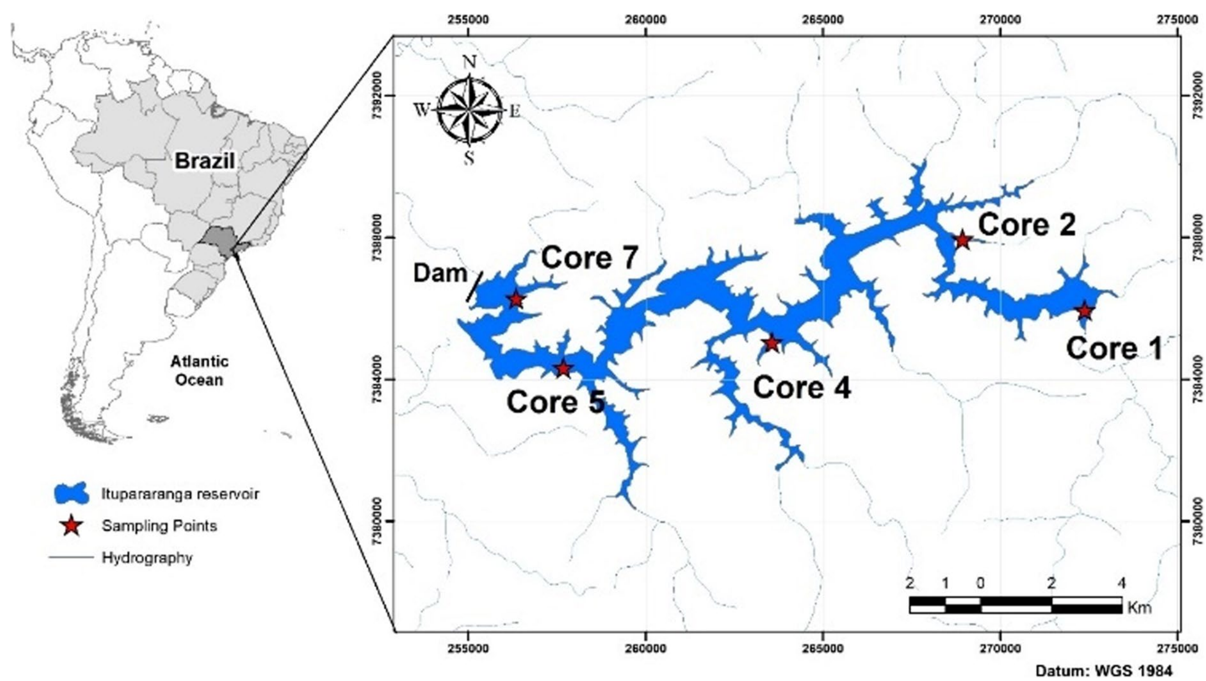

Fig. 1 Itupararanga Reservoir and its river network in the state of São Paulo, Brazil. Source: Present work

2.2 Sampling and characterisation of the sediment cores

Undisturbed cores of 30–40 cm length were collected at five sites (Core 1, Core 2, Core 4, Core 5 and Core 7) (Fig. 1) with a modified Kajak sampler (Bachmann et al., 2001). The sediment cores were sliced at the field site at 1-cm depth intervals to a depth of 6 cm and at 2-cm intervals to the bottom of the cores. Temperature, pH, and ORP were measured in each slice with specific electrodes (WTW, Germany) (Range and precisions, see Supplementary information -SI, Table 1). The material was stored in conical tubes and transported to laboratory where interstitial water was extracted by centrifugation (4 °C, 10 min, 4000 rpm) and filtered using 0.20-µm pore size syringe filters.

Dissolved cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and trace metals (Al, Ba, Cr, Cu, Fe, Mn, Ni e Zn) in the interstitial water were determined by inductively coupled plasma mass spectrometry (ICP-MS Agilent 7500c, Agilent, Germany). Calibration Standard: ICP Multi Element Standard Solution VI CertiPur (Merck). Reference Material: SRM 1640a (Trace Elements in Natural Water) from the NIST and TMDA-64.3 (Trace Element fortified Sample) from ECCC (Environment and Climate Change Canada). The limits of quantification (LQ) were calculated by dividing 10 times the standards deviation of 10 blank reading by the slopes of the calibration curves. Dissolved organic and inorganic carbon (DOC, DIC, respectively) were analysed by C-analyser (DIMATOC 2000; DIMATEC Analysentechnik GmbH, Germany). SRP, nitrate (NO_3^-), and ammonium (NH_4^+) were analysed according to Murphy and Riley (1962) by spectrophotometry (Herzsprung et al., 1998).

The sediment slices were analysed in the laboratory for porosity, dry weight (DW), organic matter (OM, loss on ignition-LOI) (550 °C, 2 h) and particle size distribution obtained by laser diffraction (CILAS 1190d; Quantachrome) (Range and precisions, see SI, Table 1). The geochemistry of the main and trace elements in the sediments was determined by X-ray fluorescence (XRF) as described in Morgenstern et al. (2001), Morgensternet al. (2004) and Frascareli et al. (in review, this volume). The relative repeatability precision of the measurements was better than 3% for the traces and better than 1% for the major components. Total organic carbon (TC) and total nitrogen (TN) were quantified by CN analyser (vario EL cube; Elementar Analysensysteme Hanau) (Range, precisions and limits, see SI, Table 1). Total phosphorus (TP) was determined by wet oxidation and subsequent spectrophotometry to Murphy and Riley (1962); reproducibility and accuracy was better than 3%. Phosphorus fractionation was carried using a sequential extraction method of modified by Psenner et al. (1984) and Hupfer et al. (1995) which separates the following P fractions: 1) NH_4Cl-phosphorus present in interstitial water; 2) BD-phosphates soluble under reducing conditions phosphates (Fe-hydroxides and Mn-bonds); 3) NaOH-SRP-phosphates bound to surfaces of metal oxides (Al, Fe); 4) NaOH NRP phosphorus in microorganisms and detritus-P and humic substance; 5) HCl TP carbonate fractions and apatite-P and 6) residual P-refractory organic phosphorus. The reproducibility and accuracy were better than 5%.

2.2.1 *Estimation of diffusional flow*

The vertical diffusional flux of dissolved nutrients and metals in the SWI was calculated from concentration gradients in PW (Δ C/Δ Z)z = 0 according to Fick's law in one dimension (De Vittor et al., 2012) represented by Eq. (1):

$$F = -\left(\frac{\phi \mathrm{Ds}}{\theta^2}\right)\left(\frac{\Delta C}{\Delta x}\right) \tag{1}$$

where F is the diffusive flow of the species (mg cm^{-2} $year^{-1}$) with concentration C at depth x, ϕ is the sediment porosity, θ is tortuosity, and Ds is the diffusion coefficient in the PW (mmol cm^{-2} day^{-1}). The diffusion coefficient (Ds) was estimated from the empirical relationship Ds = Do / F ϕ and F = θ^{-3} (Ullman & Aller, 1982), where Do is the diffusion coefficient in the infinite dilution defined by Burdige et al. (1992) and corrected by Strokes-Einstein (Meilian Chen et al., 2017; Yuan-Hui & Gregory, 1974).

2.2.2 *Hydrochemistry interactions (Aqion)*

The present study used Aqion (version 7.3.5) to determine the calcite carbonate in an open CO_2 system and equilibria with mineral phases. Aqion is a free software that calculates hydrochemistry interactions (www.aqion.de). Aqion uses the well-known United States Geological Survey (U.S.G.S.) software

PhreeqC (Parkhurst & Appelo, 1999) as an internal numerical solver and thermodynamical database *wateq4f* (Ball & Nordstrom, 1991).

3 Results and Discussion

3.1 Sediment–water interface geochemistry.

The sediments were composed mainly by silt and clay at all sampling sites (average of clay, silt and sand were respectively, at Core 1 10.5, 83 and 6.5%; Core 2 7.7, 88 and 4.3%; Core 4 7.9, 91.4 and 0.77%; Core 5 9.7, 82.3 and 8.0%, and, Core 7 11.0%, 78.2% and 10.7%). Porosity ranged from 0.8 to 0.9 in all sampling sites. The PW presented pH values more neutral (pH 7.0 ± 0.2) than the hypolimnetic water, which had values slightly acidic (pH 6.8 ± 0.83) in most of sediment cores. However, the ORP presented larger differences between PW and the hypolimnetic water. The PW values were lower (46 ± 30 mV) than hypolimnetic water (387 ± 68 mV), indicating an environment with less oxidative tendencies. ORP ranged between 27 ± 12 mV (Core 2) and 85 ± 7 mV (Core 4) in the sediment cores. Despite this ORP variation, the pH did not change significantly with a variation coefficient of less than 3%. The distribution of pH and ORP in the PW and hypolimnetic water is shown in Fig. 2.

An increase of SRP, SO_4^{2-}, NH_4^+, Ca^{2+}, Mg^{2+}, K^+, DIC, Si, Fe and Mn in the PW was registered from the bottom towards the sediment surface. High concentrations of these ions were detected in depths from 0 to 8 cm (Figs. 1 and 2, Supplementary information- SI), indicating the presence of a sub-oxic layer (Froelich et al., 1978). The highest concentrations may be associated with: 1) a greater dissolution of carbonated minerals such as calcite and dolomite; 2) cation exchange and aluminium weathering; 3) iron and silicate oxide hydroxides (Smolders et al., 2006). In the layers below 8 cm, there was a reduction of these ions concentration, suggesting an increase in their particulate forms. The concentration decrease may be attributed for example to the ions adherence to organic matter, sulphur forms or in the sediment grains (Keshavarzifard et al., 2019; Miranda et al., 2022; Xia et al., 2020). This compartmentalisation between surface and bottom sediment core can be observed by the high variability within the groups presented by PCA analysis (Fig. 3).

The two main axes from PCA explained 76% of total data variation, PC1 elucidated 43,6%, while PC2 23,4% of data variation. The PC1 was mainly influenced by Fe (0,98), Si (0,92), NH4 (0,82), DIC (0,81), ORP (-0,91) and SRP (-0,76). In the PC2, the variables that influenced the arrangement were K (0,97) e DOC (0,88) and Mn (-0,60). Cores 4 and 7 had

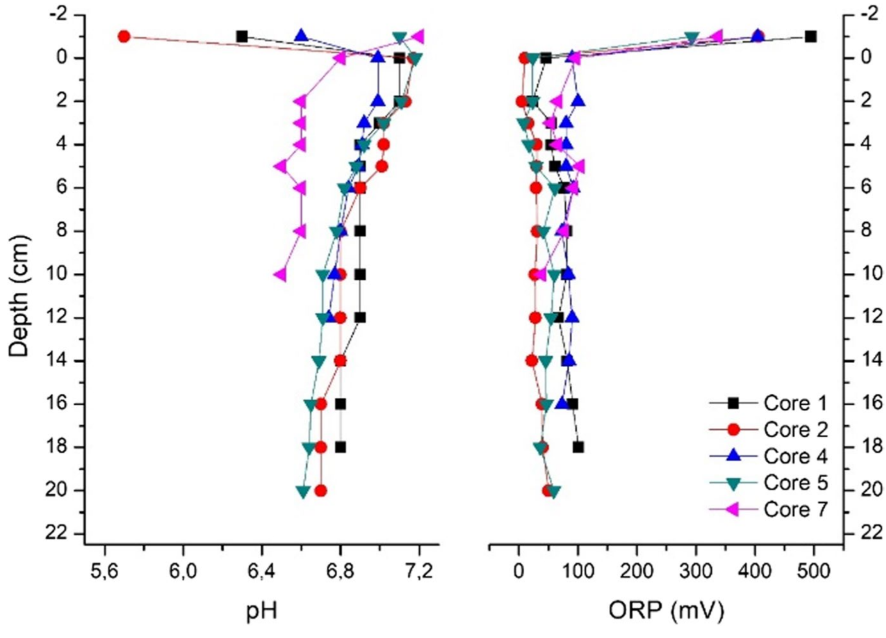

Fig. 2 pH and ORP determined in the interstitial and hypolimnetic water

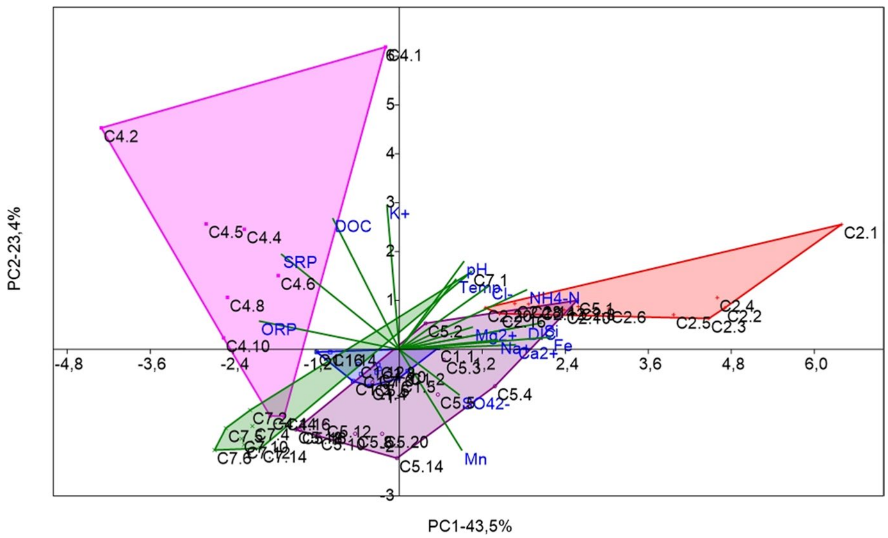

Fig. 3 PCA with PW data

lower concentrations of Fe and Mn in PW since the ORP values were higher. According to Wetzel (2001): "… a change in pH of one unit is accompanied by a change in redox potential of 58 mV." Also, the presence of microorganisms that catalyse the oxidation of H_2 coupled to the reductions of NO_3^-, Mn (IV), Fe (III), sulphate or CO_2 can affect ORP variations (Wetzel, 2001). These microorganisms can maintain lower pH levels as observed. In core 4 and 7, we also observed low values for total Fe contents, which implies lower Fe concentrations in its different forms. Of the many reducing compounds that contribute to the reduction in ORP, ferrous iron of the sediments is the most important (Wetzel, 2001). Therefore, in these cores (4 and 7), the highest level for the ORP can be associated with these lower Fe concentrations and confirmed by PCA.

Regarding the trace-metals, Cr, Ni and Pb suggest uncertain toxic effects to biota (> threshold effect level, TEL, CCME, 1999). On the other hand, in Core 5, Cr exceeded the probable effect level (PEL), and the adverse toxic effects are likely to occur (Table 2, see SI). Actually, toxic effects depend on several factors as geochemical characteristics, species, exposure routes and condition of the biota. Therefore, to be sure about the toxicity we suggest future ecotoxicological investigations conducted in laboratory as well as in natural conditions considering organism, population and community levels. The release of metals trapped in sediment into water column can occur for several factors already mentioned. These changes occur mainly by vertical movements of the column water (Lewis, 2000). As reported by Melo et al.,(2019), Itupararanga Reservoir presents stratification in the water column during warmer season (November to March) and it is totally mixed in the colder season (July to August). Therefore, the variations of ORP visualised in the sedimentary samples, especially at sites 2 and 5, can also be the result of oxygen stratification periods and vertical mixing of the water column that may lead to the release of compounds trapped in the sediment.

3.1.1 Phosphorus release

Although essential to phytoplankton growth, excess of P (SRP) may cause potentially harmful algal blooms such as the ones caused by cyanobacteria (de Souza Beghelli et al., 2016). High SRP concentrations were observed in the interstitial water in the cores 2, 4 and 5 (Fig. 4). Maassen et al. (2005) determined that the concentration of SRP found in the interstitial water of the sediments is a good indicator of the surface waters trophic status. In fact, paleolimnological studies in sediment cores indicate that aquatic organic production contributes to the organic enrichment of the sediments (de Oliveira Soares Silva Mizael et al., 2020). However, SRP was not detected in the PW at sampling Core 1 that is located in the most eutrophic area of the reservoir (Melo et al., 2019). The results from the sites 2, 4 and 5, in the contrary are in accordance with Maassen et al., (2005) observations.

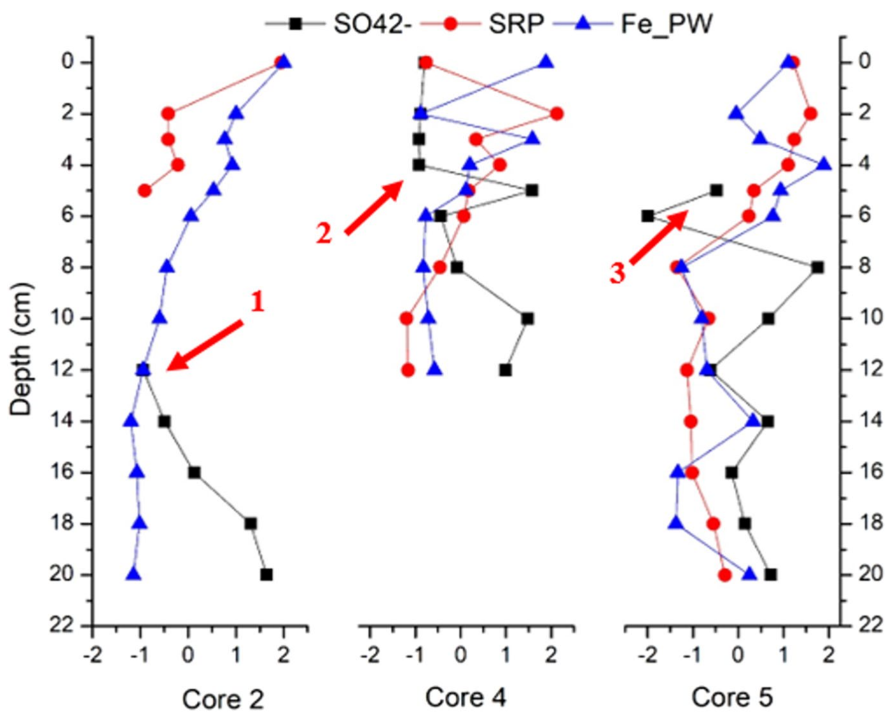

Fig. 4 Normalised concentrations by z-score method (x-axis) of SO4, Fe and SRP in interstitial water of cores 2, 4 and 5

The absence of SRP in the PW water from Core 1 in contrast to the observations of (Maassen et al., 2005) opens the opportunity to explore how the spatial heterogeneity in subtropical reservoirs may influence sedimentary P dynamics (Thornton, 1990).

The Itupararanga Reservoir inlet is the shallowest site and has the lowest light incidence (Melo et al., 2019). This is because it has higher flow velocity that can be confirmed by the presence of high particulate matter content (Melo et al., 2019). Burger et al. (2007) found no difference in SRP releases between light and dark exposed benthic chambers, suggesting that primary productivity at the water–sediment interface may not have an important influence on nutrient fluxes in shallow regions. The authors explain that convective transport and disturbance of sediments do not allow significant accumulation of periphytic material (Burger, 2006; Burger et al., 2007; Dodds, 2003).

A possible explanation for the absence of SRP in Core 1 may be its precipitation with inorganic material. High Ca^{2+} concentrations (> 15 mg L^{-1}) for instance favour precipitation and deposition of P with calcite in the sediments (Flower et al., 2022). Supersaturation of calcite ($CaCO_3$) was confirmed by Aqion in Core 1.

In the PW, a relationship was observed between reduction or absence of SO_4^{2-} as there was an increase in Fe and SRP concentrations (Figs. 3, 4 and 5). ORP compartmentalisation at Core 2 and Core 5 can be observed on cluster analysis (Fig. 5). Through the analysis, we observed surface sediment core was split from bottom sediment core in both samples (Core 2 and 5); in contrast, we observe Core 4 was not influenced by ORP and remained in the group where they had higher SRP and Fe concentrations and lower ORP concentrations.

Two variations in the ORP values were recorded in the Core 2: the first one at depth of 5 cm, where an ORP reduction was observed (30 to 5 mV) with the appearance of phosphate and ferrous species in PW (Fig. 6a). Furthermore, reduction of Fe in the solid portion of the sediment occurred (Fig. 6b). The second ORP variation took place in the layer from 14 to 20 cm, where we recorded total reduction of the SO_4^{2-} as there was an increase in Fe, DIC, DOC, NH_4^+ species in PW (Fig. 6b and c). At Core 5, the surface sediment (0–5 cm—dashed line – Fig. 7) from Core 5, the decrease of SO_4^{2-} and increase of Fe and SRP in the interstitial water.

In fact, the increase in SRP may be derived from the release of Fe oxyhydroxide phases into the

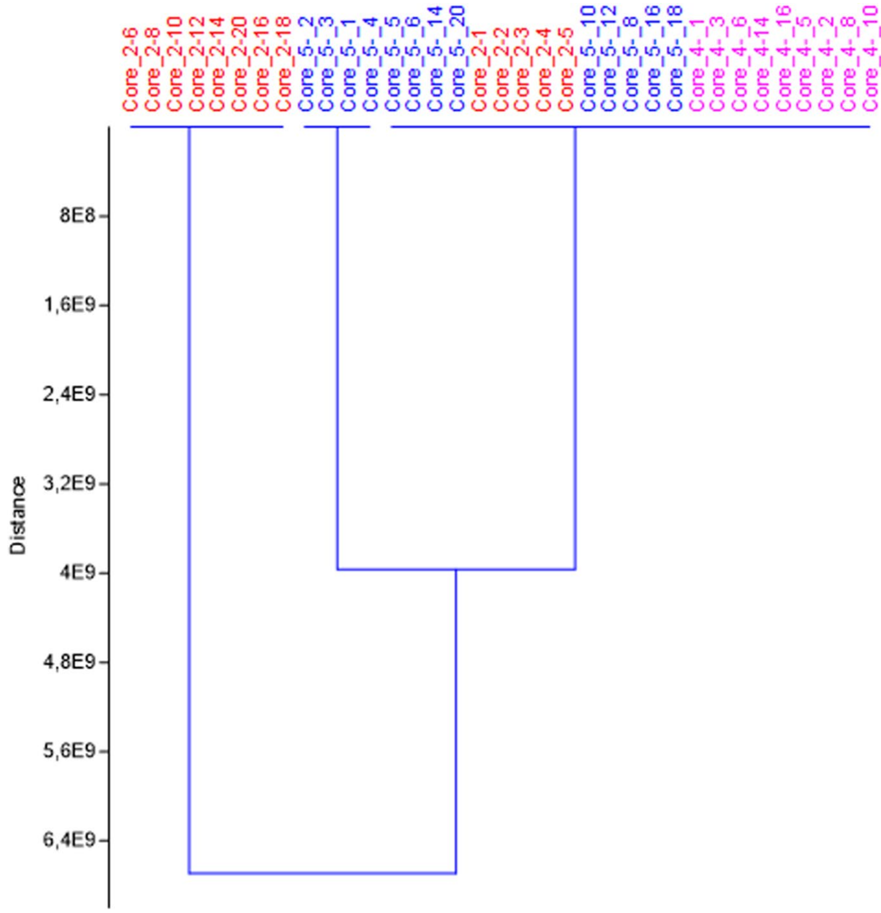

Fig. 5 Cluster analysis using ward's method distance

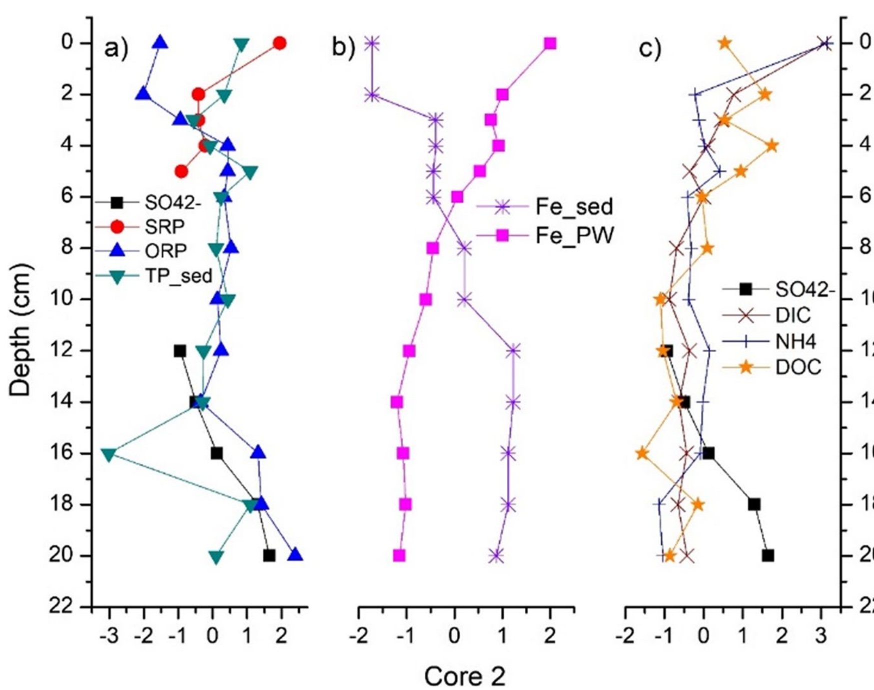

Fig. 6 Normalised concentrations by z-score method (x-axis) of SRP, Fe and SO4 and variation of ORP in interstitial water and TP in sediments from the core 2

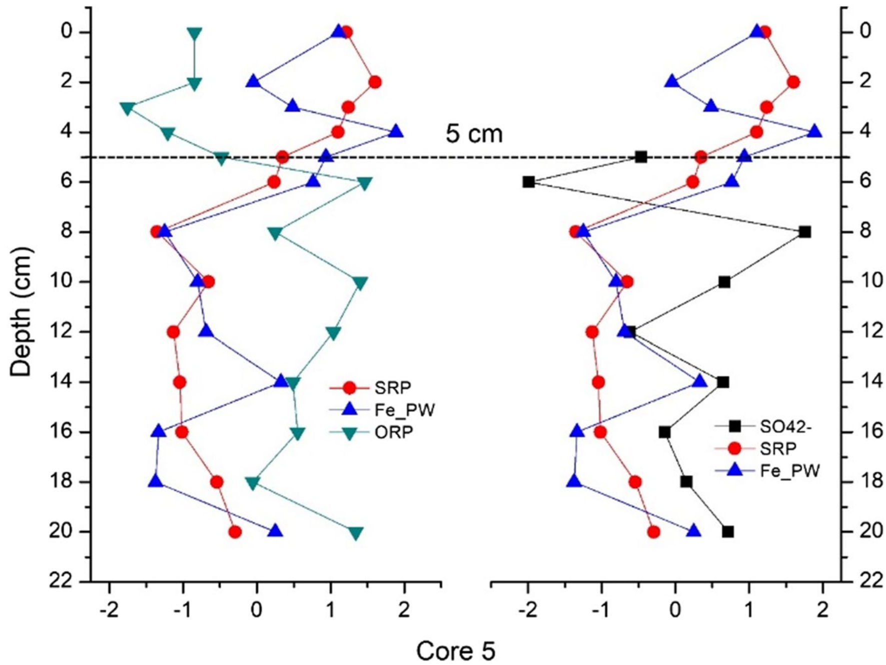

Fig. 7 Normalised concentrations by z-score method (x-axis) of Fe, SO4 and SRP in the interstitial water of sediment core 5

interstitial water (Froehlich et al., 1978; Li et al., 2016). As nitrate was not found in any of the studied sites, it was probably completely consumed by the microbial respiration processes (Konovalov et al., 2007). Although the SRP release rates are generally much higher during column anoxia (Nowlin et al., 2005), there are evidence of high release rates under aerobic conditions in sediment core incubations (Krivtsov et al., 2001). The authors explain that the rapid decomposition utilises oxygen and nitrate creating a localised reductive condition that leads to P desorption from metal complexes (Andreas Kleeberg, 1997; Krivtsov et al., 2001). As well as Froelich et al., (1978), the present investigation eliminated the possibility of phosphate release by anoxic diagenesis and indicated the mineralisation of OM through oxic pathways.

Related to contamination limits, values above of 4.8 mg N g^{-1} were observed and indicated contamination of sediments according to the Ontario and Canadian Sediment Quality Guidelines (Canadian Council of Ministers of the Environment; CCME, 1999; Persaud et al., 1993) and current local legislation (Brazilian National Environment Council, CONAMA, resolution 454/2012). Conversely, P presented constant values and low coefficient of variation over time (Table 3, SI). Furthermore, no contamination according to CCME and CONAMA 454/2012 for P in sediments was observed (values below 2 mg g^{-1}).

3.2 Diffusional flow into sediment–water interface

According to the two-dimensional flow calculations (Table 1), P was being released to the water column at Core 5 while retention at Core 2. The contribution of 2.42 mmol m^{-2} SRP day^{-1} which corresponds to 74.83 mg m^{-2} SRP day^{-1} at Core 2 could

Table 1 Two-dimensional fluxes of DIC, DOC, NH_4, Fe, Mn, and SRP at the SWI (in mmol L^{-1} m^{-2} d^{-1}). Negative values: release to reservoir water Positive values: retention to sediment.

	Core 1	Core 2	Core 4	Core 5	Core 7
Unit	mmol L^{-1} m^{-2} day^{-1}				
DIC	-11.33	-35.88	-14.07	6.42	-24.60
DOC	-0.44	-1.32	-11.32	-0.03	-2.19
NH4	-12.19	-39.68	-28.83	-18.82	36.43
SRP	NA	2.42	NA	-0.02	NA
Fe	-9.98	-24.93	-8.19	-18.71	-14.61
Mn	-0.36	-0.52	-0.23	-0.79	-0.56

NA: not available.

be considered a substantial concentration to promote harmful effects on the quality of surface water. This concentration would classify the reservoirs as eutrophic (P between 52 to 120 mg L^{-1}) according to the Environmental Company of the State of São Paulo (CETESB, 2008). Although the concentration found in Core 2 is trapping, the opposite direction could occur, resulting in the release of P from sediment. This phenomenon can lead to increase of eutrophication process in this meso-eutrophic reservoir due to sediment flux activity. We need to highlight Core 4 had the highest concentration of SRP on PW; however, no concentration in bottom column water was verified to proceed with Diffusional Flow calculation. We believe core 4 had the capacity to release/retain due to the SRP concentration found at PW, but we cannot confirm that for lack of data.

Regarding the metals, the calculation of flux indicated release of Fe, Mn, Zn and Cr from sediment to the hypolimnetic water (negative values). The results of NH_4^+ (Core 7) and DIC (Core 5) indicated retention in the sediment (positive values) (Table 1).

In order to understand the potential of the sediment to release P observed in Core 5, a sequential extraction of P was performed, which is considered the most important factor to explain the mobility of phosphorus in sediments (Kwak et al., 2018; Min et al., 2014). The predominant fractions determined in the sediments were NaOH-NRP (56%) > NH_4Cl (26%) > BD-P (10%) > P-rest (4%) > NaOH-SRP (3%) (Fig. 8) (Table 4 – At SI). According to Cardoso-Silva et al. (2021), the Itupararanga sedimentation rate in the lentic area is 0.55 cm $year^{-1}$. Therefore, the sediment cores in present study managed to reach, on average, the period between 1978 (bottom core) and 2018 (surface sediments).

The fractions NaOH-NRP (56%) > NH_4Cl (26%) > BD-P (10%) > (4%) P-rest > NaOH-SRP (3%) were predominant in sediment. In summary, NH4Cl fraction is the phosphorus present in interstitial water; BD fraction phosphorus soluble under reducing conditions phosphates (Fe-hydroxides and Mn-bonds); the NaOH-SRP fraction bound to surfaces of metal oxides (Al, Fe); NaOH-NRP the phosphorus in microorganisms, detritus and humic substance; and residual P-refractory organic phosphorus. The results of P-fractionation indicated that the concentration of P in the sediments was adhered to microorganisms and detritus, P bound to humic materials (NaOH-NRP) followed with phosphate in the interstitial water (NH_4Cl). Both predominant fractions confirm that the release of P is being controlled in Core 5 by the degradation of labile organic material. Together with the C:N ratio, the results confirmed that the sedimentary OM is mostly of autochthone origin (data in SI)(Finlay & Kendall, 2007). In contrast, recent investigation

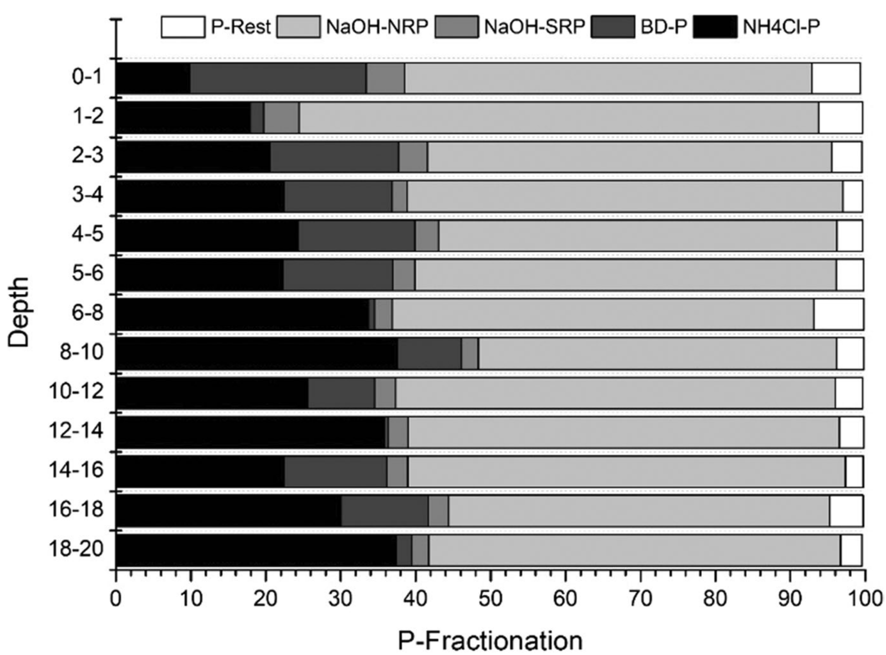

Fig. 8 Sequential extraction of phosphorus in the sedimentary core 5. 1) NH4Cl-phosphorus present in interstitial water; 2) BD-phosphates soluble under reducing conditions phosphates (Fe-hydroxides and Mn-bonds); 3) NaOH-SRP-phosphates bound to surfaces of metal oxides (Al, Fe); 4) NaOH NRP phosphorus in microorganisms and detritus-P and humic substance; 5) Residual P-refractory organic phosphorus

of the sedimentary OM (humic substances) from surface sediments revealed that allochthonous sources are predominant across Itupararanga Reservoir, although the authors detected an increase in autochthonous originated material towards the dam area (the C/N decrease over the reservoir) (Gontijo et al., 2021). Cronological variation in Core 5 could be observed since the coefficient of variation was more than 30% to NH4Cl, NaOH-SRP and P-rest and more than 60% to BD-P (SI-Table 4). This means that the variations in BD-P concentrations demonstrated that re-oxygenation by water circulation is affecting the release of P in SWI.

4 Conclusions

The characterisation of the PW of Itupararanga Reservoir was useful to understand the dynamics of P and metals between the water column and sediments. We observed different behaviours in different areas of the reservoir: in core 5, an area with high trophic levels, we observed SRP release (core 5) from sediments, meanwhile core 2, in an upper reaches area tended to retain SRP. We suggested that the release of SRP in interstitial water was caused by the mineralisation of OM by oxic pathways. Furthermore, temporal seasonality could be a factor influencing SRP release into the water column through oxygenation/deoxygenation of the hypolimnion that induces the reactions of release of P adhered to Fe oxi-hydroxides as supported in the P-fractionation results of Core 5.

Among the methods used in this study, the two-dimensional diffusional flow helped to understand the importance of how sediments can act as important sources of pollution for the aquatic environment and how this compartment should be monitored to avoid damage to the multiple uses of these ecosystems. In addition, sequential extraction was a tool to understand the structural dynamics of its release into the waters. Therefore, we suggest that both methods can be applied to better understand the dynamics of P in reservoirs.

Finally, this study showed the importance of investigating sediment interstitial water and expanded a discussion in sub-climatic environments on the release and contribution of sediments in the geochemistry of P in aquatic ecosystems. Although no contamination according to CCME and CONAMA 454/2012 for P in sediments was observed, increases in population and land use and occupation without adequate public policies can increase the inputs of P and other contaminants. We suggested that the inputs of P need to be reduced and/or they should be extinguished to avoid possible future negative impacts to water quality. Otherwise, the reservoir multiple uses will be compromised.

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Data Availability (1) The datasets generated during and/or analysed during the current study are available in the UNESP repository, [https://repositorio.unesp.br/handle/11449/205095].

Declarations

Conflicts of Interest There are no conflicts to declare.

References

Bachmann, T. M., Friese, K., & Zachmann, D. W. (2001). Redox and pH conditions in the water column and in the sediments of an acidic mining lake. *Journal of Geochemical Exploration, 73*(2), 75–86.

Ball, J. W., & Nordstrom, D. K. (1991). User's manual for wateo4f, wtth revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters.

Bastakoti, U., Robertson, J., & Alfaro, A. C. (2018). Spatial variation of heavy metals in sediments within a temperate mangrove ecosystem in northern New Zealand. *Marine Pollution Bulletin, 135*, 790–800. https://doi.org/10.1016/j.marpolbul.2018.08.012

Benassi, R. F., de Jesus, T. A., Coelho, L. H. G., Hanisch, W. S., Domingues, M. R., Taniwaki, R. H., . . . Mitsch, W. J. (2021). Eutrophication effects on CH 4 and CO 2 fluxes in a highly urbanized tropical reservoir (Southeast, Brazil). *Environmental Science and Pollution Research*, 1–14.

Burdige, D. J., Alperin, M. J., Homstead, J., & Martens, C. S. (1992). The Role of Benthic Fluxes of Dissolved Organic Carbon in Oceanic and Sedimentary Carbon Cycling. *Geophysical Research Letters, 19*(18), 1851–1854. https://doi.org/10.1029/92GL02159

Burger, D. F. (2006). Benthic-pelagic coupling of nutrients in Lake Rotorua.
Burger, D. F., Hamilton, D. P., Pilditch, C. A., & Gibbs, M. M. (2007). Benthic nutrient fluxes in a eutrophic, polymictic lake *Shallow lakes in a changing world* (pp. 13–25): Springer.
Canadian Council of Ministers of the Environment. (1999). *Canadian environmental quality guidelines* (Vol. 2). Canadian Council of Ministers of the Environment.
Caraco, N. F., Cole, J. J., & Likens, G. E. (1989). Evidence for sulphate-controlled phosphorus release from sediments of aquatic systems. *Nature, 341*(6240), 316.
Cardoso-Silva, S Oliveira, Mizael, Soares Silva, Frascareli, J., Alves, D., 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
CETESB–COMPANHIA, D. T. D. S. (2008). *AMBIENTAL. Relatório de qualidade das águas interiores do estado de São Paulo*. São Paulo: Governo do Estado de São Paulo, Secretaria do Meio Ambiente.
Chalar, G., & Tundisi, J. G. (2001). Phosphorus Fractions and Fluxes in the Water Column and Sediments of a Tropical Reservoir (Lobo-Broa–SP). *International Review of Hydrobiology: A Journal Covering All Aspects of Limnology and Marine Biology, 86*(2), 183–194.
Chen, M., Ding, S., Chen, X., Sun, Q., Fan, X., Lin, J., & Zhang, C. (2018). Mechanisms driving phosphorus release during algal blooms based on hourly changes in iron and phosphorus concentrations in sediments. *Water Research, 133*, 153–164.
Chen, M., Kim, S.-H., Jung, H.-J., Hyun, J.-H., Choi, J. H., Lee, H.-J., & Hur, J. (2017). Dynamics of dissolved organic matter in riverine sediments affected by weir impoundments: Production, benthic flux, and environmental implications. *Water Research, 121*, 150–161.
Chen, X., Wang, J., Cukrov, N., & Du, J. (2019). Porewater-derived nutrient fluxes in a coastal aquifer (Shengsi Island, China) and its implication. *Estuarine, Coastal and Shelf Science, 218*, 204–211. https://doi.org/10.1016/j.ecss.2018.12.019
Chiu, C.-Y., Jones, J. R., Rusak, J. A., Lin, H.-C., Nakayama, K., Kratz, T. K., & Tsai, J.-W. (2020). Terrestrial loads of dissolved organic matter drive inter-annual carbon flux in subtropical lakes during times of drought. *Science of The Total Environment, 717*, 137052.
Cross, W. F., Benstead, J. P., Frost, P. C., & Thomas, S. A. (2005). Ecological stoichiometry in freshwater benthic systems: Recent progress and perspectives. *Freshwater Biology, 50*(11), 1895–1912. https://doi.org/10.1111/j.1365-2427.2005.01458.x
de Oliveira Soares, J., Cardoso Mizael-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
de Souza Beghelli, F. G., Frascareli, D., Pompêo, M. L. M., & Moschini-Carlos, V. (2016). Trophic State Evolution over 15 Years in a Tropical Reservoir with Low Nitrogen Concentrations and Cyanobacteria Predominance. *Water, Air, & Soil Pollution, 227*(3), 95. https://doi.org/10.1007/s11270-016-2795-1
De Vittor, C., Faganeli, J., Emili, A., Covelli, S., Predonzani, S., & Acquavita, A. (2012). Benthic fluxes of oxygen, carbon and nutrients in the Marano and Grado Lagoon (northern Adriatic Sea, Italy). *Estuarine, Coastal and Shelf Science, 113*, 57–70. https://doi.org/10.1016/j.ecss.2012.03.031
Dodds, W. K. (2003). The role of periphyton in phosphorus retention in shallow freshwater aquatic systems. *Journal of Phycology, 39*(5), 840–849.
Einsele, W. (1936). Über die Beziehungen des Eisenkreislaufs zum Phosphatkreislauf im eutrophen See. *Archiv Für Hydrobiologie, 29*, 664–686.
Finlay, J. C., & Kendall, C. (2007). Stable isotope tracing of temporal and spatial variability in organic matter sources to freshwater ecosystems. *Stable Isotopes in Ecology and Environmental Science, 2*, 283–333.
Flower, H., Rains, M., Taşcı, Y., Zhang, J.-Z., Trout, K., Lewis, D., & Dalton, R. (2022). Why is calcite a strong phosphorus sink in freshwater? Investigating the adsorption mechanism using batch experiments and surface complexation modeling. *Chemosphere, 286*, 131596.
Frascareli, D., Cardoso-Silva, S., de Oliveira Soares-Silva Mizael, J., Rosa, A. H., Pompêo, M. L. M., López-Doval, J. C., & Moschini-Carlos, V. (2018). Spatial distribution, bioavailability, and toxicity of metals in surface sediments of tropical reservoirs. *Brazil. Environmental monitoring and assessment, 190*(4), 199. https://doi.org/10.1007/s10661-018-6515-8
Froehlich, C. G., Arcifa-Zago, M. S., & de Carvalho, M. A. J. (1978). Temperature and oxygen stratification in Americana Reservoir, State of São Paulo, Brazil: With 11 figures and 2 tables in the text. *Internationale Vereinigung Für Theoretische Und Angewandte Limnologie: Verhandlungen, 20*(3), 1710–1719.
Frogner-Kockum, P., Göransson, P., Åslund, H., Ländell, M., Stevens, R., Tengberg, A., & Ohlsson, Y. (2016). Metal contaminant fluxes across the sediment water interface. *Marine Pollution Bulletin, 111*(1–2), 321–329.
Gin, K.Y.-H., & Gopalakrishnan, A. P. (2010). Sediment oxygen demand and nutrient fluxes for a tropical reservoir in Singapore. *Journal of Environmental Engineering, 136*(1), 78–85.
Gontijo, E. S. J., Herzsprung, P., Lechtenfeld, O. J., de Castro Bueno, C. A. C., Barth, J., Rosa, A. H., & Friese, K. (2021). Multi-proxy approach involving ultrahigh resolution mass spectrometry and self-organising maps to investigate the origin and quality of sedimentary organic matter across a subtropical reservoir. *Organic Geochemistry, 151*, 104165. https://doi.org/10.1016/j.orggeochem.2020.104165
Han, H., Lu, X., Burger, D. F., Joshi, U. M., & Zhang, L. (2014). Nitrogen dynamics at the sediment–water interface in a tropical reservoir. *Ecological Engineering, 73*, 146–153.
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
Herzsprung, P., Friese, K., Packroff, G., Schimmele, M., Wendt-Potthoff, K., & Winkler, M. (1998). Vertical and annual distribution of ferric and ferrous iron in acidic mining lakes. *Acta Hydrochimica Et Hydrobiologica, 26*(5), 253–262.
Hupfer, M., Gächter, R., & Giovanoli, R. (1995). Transformation of phosphorus species in settling seston and during early sediment diagenesis. *Aquatic Sciences, 57*(4), 305–324.
Hupfer, M., & Lewandowski, J. (2008). *Oxygen controls the phosphorus release from Lake Sediments–a long-lasting paradigm in limnology*. *International Review of Hydrobiology, 93*(4–5), 415–432.
Keshavarzifard, M., Moore, F., & Sharifi, R. (2019). The influence of physicochemical parameters on bioavailability and bioaccessibility of heavy metals in sediments of the intertidal zone of Asaluyeh region, Persian Gulf. *Iran. Geochemistry, 79*(1), 178–187.
Kleeberg, A. (1997). Interactions between benthic phosphorus release and sulfur cycling in Lake Scharmützelsee (Germany). *Water, Air, and Soil Pollution, 99*(1–4), 391–399.
Kleeberg, A., & Dudel, G. E. (1997). Changes in extent of phosphorus release in a shallow lake (Lake Großer Müggelsee; Germany, Berlin) due to climatic factors and load. *Marine Geology, 139*(1–4), 61–75.
Konovalov, S. K., Luther Iii, G. W., & Yücel, M. (2007). Porewater redox species and processes in the Black Sea sediments. *Chemical Geology, 245*(3–4), 254–274.
Krivtsov, V., Sigee, D. C., Bellinger, E. G., & Porteous, G. (2001). Determination of P release from Rostherne Mere sediment cores. *Acta Hydrochimica Et Hydrobiologica, 29*(2–3), 111–117.
Kwak, D.-H., Jeon, Y.-T., & Duck Hur, Y. (2018). Phosphorus fractionation and release characteristics of sediment in the Saemangeum Reservoir for seasonal change. *International Journal of Sediment Research, 33*(3), 250–261. https://doi.org/10.1016/j.ijsrc.2018.04.008
Lewis, W. M., Jr. (2000). Basis for the protection and management of tropical lakes. *Lakes & Reservoirs: Science, Policy and Management for Sustainable Use, 5*(1), 35–48. https://doi.org/10.1046/j.1440-1770.2000.00091.x
Li, Z., Sheng, Y., Yang, J., & Burton, E. D. (2016). Phosphorus release from coastal sediments: Impacts of the oxidation-reduction potential and sulfide. *Marine Pollution Bulletin, 113*(1–2), 176–181.
Maassen, S., Uhlmann, D., & Röske, I. (2005). Sediment and pore water composition as a basis for the trophic evaluation of standing waters. *Hydrobiologia, 543*(1), 55–70.
Matos, C. R. L., Berrêdo, J. F., Machado, W., Metzger, E., Sanders, C. J., Faial, K. C. F., & Cohen, M. C. L. (2022). Seasonal changes in metal and nutrient fluxes across the sediment-water interface in tropical mangrove creeks in the Amazon region. *Applied Geochemistry*, 105217.
Melo, D. S., Gontijo, E. S. J., Frascareli, D., Simonetti, V. C., Machado, L. S., Barth, J. A. C.,Friese, K. (2019). 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/10.1029/2019WR025991
Min, C., Jiang, T., Qi, Y.-Z., Dong, H.-P., Teng, D.-Q., & Lu, S.-H. (2014). Phosphorus forms and distribution in Zhejiang coastal sediment in the East China Sea. *International Journal of Sediment Research, 29*(2), 278–284.
Miranda, L. S., Ayoko, G. A., Egodawatta, P., & Goonetilleke, A. (2022). Adsorption-desorption behavior of heavy metals in aquatic environments: Influence of sediment, water and metal ionic properties. *Journal of Hazardous Materials, 421*, 126743.
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.
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.
Mortimer, C. H. (1941). The exchange of dissolved substances between mud and water in lakes. *Journal of Ecology, 29*(2), 280–329.
Mortimer, C. H. (1942). The exchange of dissolved substances between mud and water in lakes. *Journal of Ecology, 30,* 147–201.
Moura, D. S., Neto, I. E. L., Clemente, A., Oliveira, S., Pestana, C. J., de Melo, M. A., & Capelo-Neto, J. (2020). Modeling phosphorus exchange between bottom sediment and water in tropical semiarid reservoirs. *Chemosphere, 246*, 125686.
Mozeto, A. A., Silvério, Pcf, & Soares, A. (2001). Estimates of benthic fluxes of nutrients across the sediment–water interface (Guarapiranga reservoir, São Paulo, Brazil). *Science of The Total Environment, 266*(1–3), 135–142.
Murphy, J., & Riley, J. P. (1962). A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta, 27*, 31–36.
Ni, Z., Zhang, L., Yu, S., Jiang, Z., Zhang, J., Wu, Y., & Huang, X. (2017). The porewater nutrient and heavy metal characteristics in sediment cores and their benthic fluxes in Daya Bay. *South China. Marine Pollution Bulletin, 124*(1), 547–554.
Nowlin, W. H., Everts, J. L., & Vanni, M. J. (2005). Release rates and potential fates of nitrogen and phosphorus from sediments in a eutrophic reservoir. *Freshwater Biology, 50*(2), 301–322. https://doi.org/10.1111/j.1365-2427.2004.01316.x
Nuernberg, G. K. (1985). Availability of phosphorus upwelling from iron-rich anoxic hypolimnia. *Archiv Fur Hydrobiologie. Stuttgart, 104*(4), 459–476.
Nürnberg, G., & Peters, R. H. (1984). Biological availability of soluble reactive phosphorus in anoxic and oxic freshwaters. *Canadian Journal of Fisheries and Aquatic Sciences, 41*(5), 757–765.
Oliveira, A. FBd., Gomes, B. R. S., França, R. S., Moraes, A. S., Bataglion, G. A., & Santos, J. M. (2022). Assessment of Urban Contamination by Sewage in Sediments from Ipojuca River in Caruaru City, Pernambuco, Brazil. *Journal of the Brazilian Chemical Society, 33*, 163–172.
Pan, F., Liu, H., Guo, Z., Li, Z., Wang, B., & Gao, A. (2017). Geochemical behavior of phosphorus and iron in porewater in a mangrove tidal flat and associated phosphorus

input into the ocean. *Continental Shelf Research, 150*, 65–75. https://doi.org/10.1016/j.csr.2017.09.012

Papera, J., Araújo, F., & Becker, V. (2021). Sediment phosphorus fractionation and flux in a tropical shallow lake. *Acta Limnologica Brasiliensia, 33*.

Parkhurst, D. L., & Appelo, C. A. J. (1999). User's guide to PHREEQC (Version 2): A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. *Water-Resources Investigations Report, 99*(4259), 312.

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.

Persaud, D., Jaagumagi, R., & Hayton, A. (1993). *Guidelines for the protection and management of aquatic sediment in Ontario*.

Peters, R. H. (1981). Phosphorus availability in Lake Memphremagog and its tributaries 1. *Limnology and Oceanography, 26*(6), 1150–1161.

Pierangeli, G. M. F., Domingues, M. R., De Jesus, T. A., Coelho, L. H. G., Hanisch, W. S., Pompêo, M. L. M., Benassi, R. F. (2021). Higher Abundance of Sediment Methanogens and Methanotrophs Do Not Predict the Atmospheric Methane and Carbon Dioxide Flows in Eutrophic Tropical Freshwater Reservoirs. *Frontiers in Microbiology, 12*.

Pratihary, A. K., Naqvi, S. W. A., Naik, H., Thorat, B. R., Narvenkar, G., Manjunatha, B. R., & Rao, V. P. (2009). Benthic fluxes in a tropical estuary and their role in the ecosystem. *Estuarine, Coastal and Shelf Science, 85*(3), 387–398.

Psenner, Rv., & PucskoSager, R. M. (1984). Die Fraktionierung organischer und anorganischer Phosphorverbindungen von Sedimenten-Versuch einer Definition ökologisch wichtiger Fraktionen. *Arch Hydrobiol Suppl, 70*(1), 111–155.

Ribeiro, A. R., Biagioni, R. C., & Smith, W. S. (2014). Estudo da dieta natural da ictiofauna de um reservatório centenário, São Paulo. *Brasil. Iheringia. Série Zoologia, 104*, 404–412.

Santschi, P., Höhener, P., Benoit, G., & Buchholtz-ten Brink, M. (1990). Chemical processes at the sediment-water interface. *Marine Chemistry, 30*, 269–315.

da Silva, A. L. L., Hennemann, M. C., & Petrucio, M. M. (2020). Phosphorus dynamics in a subtropical coastal lake in Southern Brazil. *Journal of Limnology, 79*(1).

Simonetti, V. C., Frascareli, D., Gontijo, E. S. J., Melo, D. S., Friese, K., Silva, D. C. C., & Rosa, A. H. (2019). Water quality indices as a tool for evaluating water quality and effects of land use in a tropical catchment. *International Journal of River Basin Management*, 1-12. https://doi.org/10.1080/15715124.2019.1672706

Smith, W. S., & Petrere, M., Jr. (2008). Spatial and temporal patterns and their influence on fish community at Itupararanga Reservoir. *Brazil. Rev Biol Trop, 56*(4), 2005–2020.

Smolders, A. J. P., Moonen, M., Zwaga, K., Lucassen, E., Lamers, L. P. M., & Roelofs, J. G. M. (2006). Changes in pore water chemistry of desiccating freshwater sediments with different sulphur contents. *Geoderma, 132*(3–4), 372–383.

Soares, A., & Mozeto, A. A. (2006). Water Quality in the Tiete River Reservoirs(Billings, Barra Bonita, Bariri and Promissao, SP-Brazil) and Nutrient Fluxes across the Sediment-Water Interface(Barra Bonita). *Acta Limnologica Brasiliensia, 18*(3), 247–266.

Spears, B. M., Carvalho, L., Perkins, R., Kirika, A., & Paterson, D. M. (2006). Spatial and historical variation in sediment phosphorus fractions and mobility in a large shallow lake. *Water Research, 40*(2), 383–391.

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.*

Ullman, W. J., & Aller, R. C. (1982). Diffusion coefficients in nearshore marine sediments1. *Limnology and Oceanography, 27*(3), 552–556. https://doi.org/10.4319/lo.1982.27.3.0552

Wetzel, R. G. (2001). *Limnology: lake and river ecosystems*: gulf professional publishing.

Xia, F., Zhang, C., Qu, L., Song, Q., Ji, X., Mei, K., & Zhang, M. (2020). A comprehensive analysis and source apportionment of metals in riverine sediments of a rural-urban watershed. *Journal of Hazardous Materials, 381*, 121230.

Yuan-Hui, L., & Gregory, S. (1974). Diffusion of ions in sea water and in deep-sea sediments. *Geochimica Et Cosmochimica Acta, 38*(5), 703–714.

Zhang, L., Ni, Z., Wu, Y., Zhao, C., Liu, S., & Huang, X. (2020). Concentrations of porewater heavy metals, their benthic fluxes and the potential ecological risks in Daya Bay. *South China. Marine pollution bulletin, 150*, 110808.

Zhang, L., Wang, L., Yin, K., Lü, Y., Yang, Y., & Huang, X. (2014). Spatial and seasonal variations of nutrients in sediment profiles and their sediment-water fluxes in the Pearl River Estuary, Southern China. *Journal of Earth Science, 25*(1), 197–206.

Zhao, P., Wang, C., Wang, X., Yang, Z., & Liu, D. (2021). Effects of cascade reservoirs on the transformation of nitrogen in pore water of sediments in the Lancang River. *River Research and Applications*.