



Phosphorus fractionation in sediments of tropical semiarid reservoirs

Cavalcante H.^{a,*}, Araújo F.^b, Noyma N.P.^c, Becker V.^b

^a Federal University of Rio Grande do Norte, Natal, RN, Brazil

^b Laboratory of Water Resources and Environmental Sanitation, Department of Civil Engineering, Technology Center, Federal University of Rio Grande do Norte, Natal, RN, Brazil

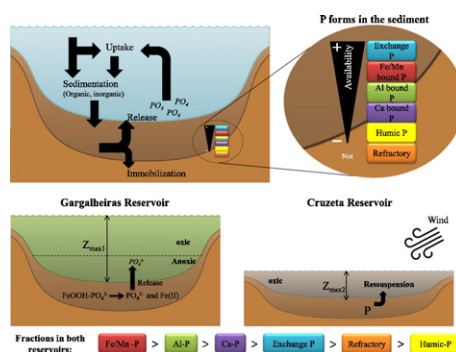
^c Laboratory of Ecology and Physiology of Phytoplankton, Department of Plant Biology, University of the State of Rio de Janeiro, Rio de Janeiro, RJ, Brazil



HIGHLIGHTS

- P loads from the sediments of 2 reservoirs in the semiarid region was evaluated.
- The mobile forms constituted the main P forms in both reservoirs.
- The P form was present mainly as P bound to Fe (P-BD) in both reservoirs sediment.
- Our results show the high amounts of labile P in the sediment of semiarid.

GRAPHICAL ABSTRACT



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ABSTRACT

The reduction of external loads of phosphorus (P) is the main action to control eutrophication in lakes. However, the elimination of these sources is not always sufficient for lakes' recovery, because the P accumulated in the sediment can be released for decades after it has accumulated. Thus, to restore a lake, it is also necessary to reduce its internal P loading. For this, it is essential to know the composition of P in the sediment to evaluate the potential P availability. In this study, the forms of P in the sediment of two reservoirs in a semiarid tropical region were investigated. The forms of P were determined by fractionation, sorting out the forms in loosely sorbed P (P-Water), reductant-soluble P (P-BD), metal oxide-bound P (P-NaOH), P bound to organic matter (P-Humic), calcium-bound P (P-HCl) and residual P (P-residual). The sediment was collected in September 2016 and sliced *in situ*. The total amount of P forms in the sediment varied from 5 mg kg⁻¹ to 349 mg kg⁻¹ in the Gargalheiras Reservoir and from 12 mg kg⁻¹ to 371 mg kg⁻¹ in the Cruzeta Reservoir. Despite some variation in amounts at different depths, the general range of fractions in Gargalheiras and Cruzeta was: P-BD > P-NaOH > P-HCl > P-water > P-Residual > P-Humic. In both reservoirs, the predominant form was BD, followed by NaOH and HCl. The first two forms are available and released easily, making them bioavailable for eutrophication processes and thus phytoplankton growth.

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1. Introduction

Eutrophication is a global problem that is a significant cause of the deterioration of aquatic ecosystems, which results in economic and

biodiversity losses (Dodds et al., 2009). Massive cyanobacterial blooms are a serious symptom of the eutrophication process and can directly affect human health; they may cause high turbidity, anoxia and fish kills, can produce food web alterations causing unpleasant odors and may contain potent toxins (Carpenter et al., 1998; Codd et al., 2005; Dittmann and Wiegand, 2006; Paerl and Otten, 2013). The first measure that should be taken to reverse eutrophication in aquatic systems is

* Corresponding author.

E-mail addresses: herikacavalcante@yahoo.com, silvahcd@gmail.com (H. Cavalcante).

to reduce the external load of phosphorus (P) (Søndergaard et al., 2003). This nutrient can limit primary productivity and has been recognized as a key factor in the eutrophication of lakes (Schindler et al., 1973).

External sources are the main contributors of P in these systems; they can be point (e.g. effluents) or non-point (e.g. soil leaching) (Carpenter et al., 1998). However, there are also sources such as aquatic plants, algae and sediments that are internal to the aquatic system itself (Kaiserli et al., 2002). Phosphorous can accumulate in the sediment of water bodies during periods of high P load and be continuously released into the water column for decades, reducing water quality and preventing recovery, even after the reduction of the P external loads (Granéli, 1999; Yu et al., 2017). Thus, the sediment can act as a mechanism of internal fertilization that is a new pollutant source for the water (Lijklema et al., 1994; Wu et al., 2001).

Knowing in detail the fractions that compose the P load, instead of simply the total P (TP), in sediments is essential, because TP cannot correctly predict the potential of the sediment as a P source of internal loading (Rydin, 2000). The specific fractions of different P forms in sediment are needed to evaluate the availability of P, and the fraction of available P is an important parameter for predicting future internal P loading (Kaiserli et al., 2002). The P content in sediments depends on the sediment composition, the sedimentation rate, the physicochemical conditions and the extent of any diagenetic processes (Gonsiorczyk et al., 1998).

The forms in which P occurs in the sediment have received considerable attention over recent decades, and many sequential chemical extractions have been developed (Williams et al., 1971; Paludan and Jensen, 1995; Wang et al., 2013). Extraction methods provide information on the potential mobility of the P forms and allow for evaluation of the origin of the sedimented P (Horowitz, 1991; Wang et al., 2013). Moreover, in terms of potential bioavailability, the extracted fractions are in general characterized as loosely sorbed P (Water-P), reductant-soluble P (BD-P), metal oxide-bound P (NaOH-P) and calcium-bound P (HCl-P) (Kaiserli et al., 2002; Zhou et al., 2005).

Water-P is more bioavailable or immediately available because it is more labile and corresponds to the P in interstitial waters (Fytianos and Kotzakioti, 2005; Kaiserli et al., 2002). BD-P is associated with P-bound iron and manganese. This form is more mobile because its adsorption and sorption are controlled by redox conditions, so it can be released under anoxic conditions; this occurs with the reduction and dissolution of the iron hydroxide (FeOH_3) when the sediment surface is anoxic (Amirbahman et al., 2013). FeOH_3 has a strong capacity to adsorb inorganic phosphate in the water column and in aerobic sediments. However, when iron III is reduced to iron II in an anoxic environment, the iron and the P adsorbed are released and become bioavailable (Lake et al., 2007). NaOH-P is associated with aluminum oxides; like BD-P, it can also be released in anoxic conditions and is exchangeable with OH^- and inorganic P compounds soluble in bases (Kozerski and Kleeberg, 1998). This form can have an organic part and a part that is bound to humic acids, in which case it is called humic-P and is separated from the NaOH-P by acidification (Paludan and Jensen, 1995). HCl-P is associated with calcium, apatite and carbonates and can be released only when the pH of the environment is acidic ($\text{pH} < 6$) (Gonsiorczyk et al., 1998; Jin et al., 2006; Kim et al., 2003). In sequential schemes, P can also have others more refractory forms, called residual-P, that are more difficult to release.

Controlling external and internal P loads is essential and must be part of any management program designed to decrease eutrophication (Carpenter, 2008). The manipulation of biogeochemical processes using materials to achieve a desired chemical and/or ecological response has been termed geo-engineering in lakes; it is becoming a commonly considered eutrophication management tool (Spears et al., 2014). Geo-engineering techniques aim to control lakes' internal P loads in sediment and water sources, so the quantification mobility of the P forms in the sediment are both important factors in controlling

internal loading in lake restoration projects (Jensen et al., 2015; Reitzel et al., 2003; Waajen et al., 2015a, 2015b).

In semiarid regions, diffuse pollution, mainly from agriculture and livestock, is the main source of nutrients for the reservoirs. Regional characteristics like shallow soils with little cover and sparse vegetation (Oyama and Nobre, 2004) and long periods of precipitation shortages, intermittence of rivers, high rates of evaporation and intense rains concentrated over a few months of the year also contribute to the nutrient input (Barbosa et al., 2012; Costa et al., 2009). These characteristics promote greater erosion, increase the potential of carrying nutrients to water bodies (Haregeweyn et al., 2008) and intensify the accumulation and concentration of nutrients, making these aquatic systems considerably more vulnerable to eutrophication than others reservoirs in tropical humid areas (Barbosa et al., 2012; Costa et al., 2009).

The high water temperatures in semiarid regions are responsible for accelerating decomposition reactions promoting stratification in the water column (Dantas et al., 2008), leading to a condition of anoxia near the sediment. Furthermore, semiarid reservoirs are generally shallow and feature high water level variation as a consequence of prolonged periods of drought (Barbosa et al., 2012). The modest depth facilitates the resuspension of the sediment by wind action. These factors may influence the release of P from the sediment into the water column. However, the potential release of P from the sediment in semiarid reservoirs is not known in appropriate detail. In addition, during the extended drought periods of recent years, reduced external loading has been experienced by semiarid regions, increasing the relative importance of internal loading in these systems.

In view of the above, the aim of this study was to evaluate the potential contribution of P loads from sediments of two eutrophic shallow reservoirs, Gargalheiras and Cruzeta, in the maintenance of eutrophication in systems in semiarid regions. We examine the different forms of P present in the sediment in order to quantify the P that is potentially mobile.

2. Material and methods

2.1. Study area

The Gargalheiras and Cruzeta Reservoirs are located in the Piranhas-Açu watershed in the Rio Grande do Norte state of northeastern Brazil (Fig. 1). By Köppen's classification, the region's climate is tropical semiarid BS'h' (Alvares et al., 2014). The rainy season runs from February to June; on average, the region receives 550 mm year^{-1} of rain. The region suffered extreme droughts from 2012 to 2016, leading to a decrease the volumes and surface areas (Fig. 1) of its reservoirs.

The Cruzeta Reservoir has a maximum storage capacity of 35 million m^3 and a maximum depth of 14.5 m near the dam. In September 2016, its volume was 89,593 m^3 (0.38% of capacity) and the depth near the dam was 0.8 m, according to the Secretariat of Environment and Water Resources of Rio Grande do Norte (SEMARH, 2016). The Gargalheiras Reservoir has a maximum capacity of 44.4 million m^3 and a maximum 26.5 m depth. In September 2016, its volume was 516,251 m^3 (1.1% of capacity) and the depth was 6 m (SEMARH, 2016). Both reservoirs have multiple uses, such as water supply (their priority use), irrigation, fishing, recreation and animal watering.

In Brazil's semiarid regions, the majority of soils are in the P-deficient range, justifying the assertion that P limits the growth of plants in much of the northeastern semiarid region (Araújo et al., 2004). The watershed that contributes to the Gargalheiras Reservoir has a shallow, poorly developed *neossolo lítolico* soil (EMBRAPA, 2006), while the watershed that contributes to the Cruzeta Reservoir has a *luvissole crômico* soil (EMBRAPA, 2006). Among the main soil classes found in the Brazilian semiarid region, *luvissole* soils present the highest mean values of total P, while *neossolo lítolico* soils have intermediate to low values (Silveira et al., 2006).

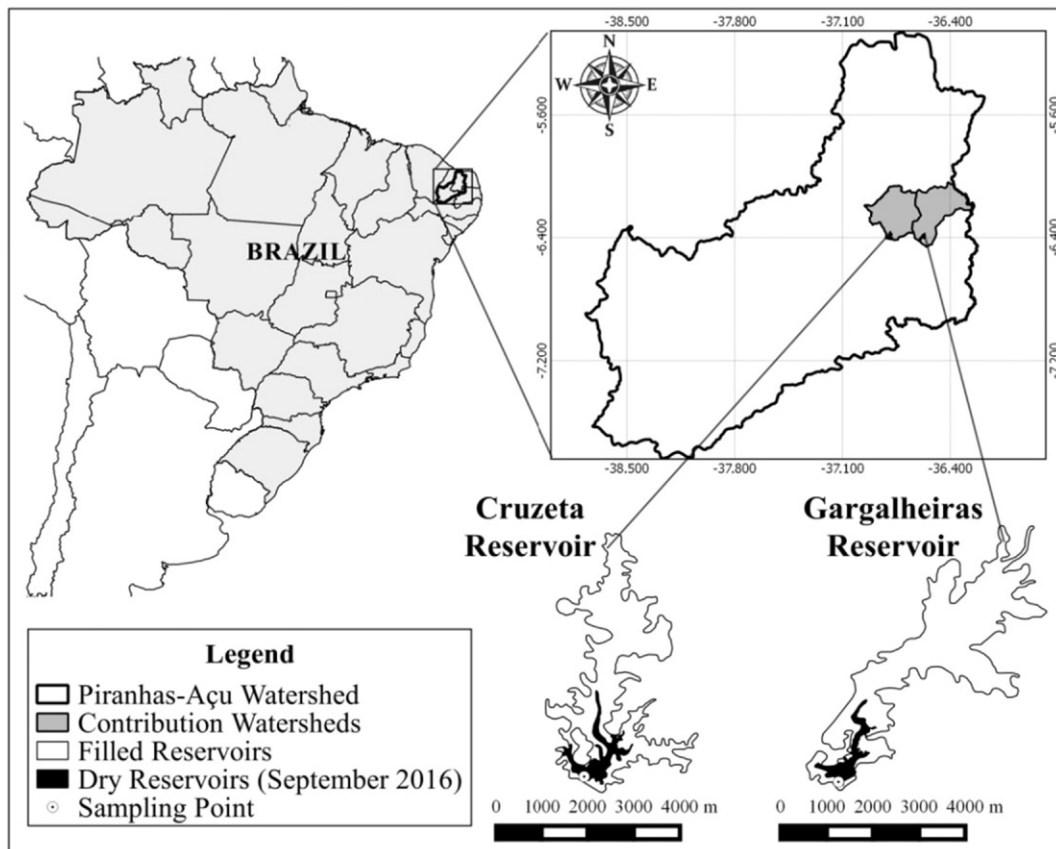


Fig. 1. Location of the Cruzeta and Gargalheiras reservoirs in northeastern Brazil.

Both reservoirs are classified as eutrophic according to Thornton and Rast (1993) (Table 1) (Cavalcante et al., unpublished results). The TP and chlorophyll-*a* (chl-*a*) concentrations are higher in the Gargalheiras than in the Cruzeta Reservoir, and soluble reactive phosphorus (SRP) and inorganic suspended solids (ISS) are greater in Cruzeta. The dissolved oxygen (DO) in Gargalheiras varied from 0 to 8 mg L⁻¹, presenting anoxia in a few months, while Cruzeta had values ranging from 0.7 to 14, presenting a homogeneous and well-aerated water column, but presenting hypoxia within a few months.

Table 1

Water conditions (minimum, maximum, average and standard deviation) in the Gargalheiras and Cruzeta Reservoirs at the sampling point near the dams during the period from May 2015 to June 2016 (Cavalcante et al., unpublished results).

Parâmetro	Gargalheiras	Cruzeta
DO (mg L ⁻¹)	0–8 (3.09 ± 0.28)	0.37–14 (5.07 ± 0.44)
ISS (mg L ⁻¹)	2–260.83 (76.45 ± 19.43)	3–317.5 (81.73 ± 28.48)
OSS (mg L ⁻¹)	12.75–254.20 (80.18 ± 20.33)	3.89–570 (86.72 ± 41.89)
SRP (µg L ⁻¹)	6.7–504.55 (106.29 ± 38.00)	65.17–467.5 (174.17 ± 32.75)
TP (µg L ⁻¹)	203.65–1853.33 (744.29 ± 132.51)	169.6–3030 (559.88 ± 198.57)
Chl- <i>α</i> (µg L ⁻¹)	77.93–2960.13 (789.89 ± 210.65)	43.47–3369.31 (416.72 ± 238.71)

Variables: DO = Dissolved Oxygen; ISS = Inorganic Suspended Solids; OSS = Organic Suspended Solids; SRP = Soluble-Reactive Phosphorus; TP = Total Phosphorus; Chl-*α* = chlorophyll-*α* concentrations.

2.2. Sediment sampling

In September 2016, the sediment was sampled at a sampling point near the dams, because the reservoirs contained only approximately 1% of their maximum volume, which drastically reduced the surface area (Fig. 1). These sampling points are also near the catchment outputs at which all surface runoff converges and are thus crucial points for the accumulation of sediments. For sediment sampling, a manual Kajak corer (50 cm long, 7 cm diameter) was used. The sediment core was sliced *in situ* into subsamples from 0 to 2 cm, 2–4 cm, 4–6 cm, 6–8 cm and 8–10 cm depth in the core. The samples were stored in polyethylene transparent containers and transported in a thermally insulated box with ice. At the laboratory, the samples were kept refrigerated in the same containers until analysis. The sediment dry weight (24 h at 105 °C) and loss of ignition (3 h at 550 °C), for determination of the organic matter content were carried out on 5 ml subsamples.

2.3. Phosphorus fractionation scheme

Phosphorus fractions were determined using an adaptation of the sequential extraction method developed by Paludan and Jensen (1995) and modified by Miquel Lüring (personal communication), using a five-step process (Fig. 2). There are several methods in the literature for quantifying P in sediments, but some make no distinction between inorganic P associated with Al oxides and reducible Fe, because sodium hydroxide is used as a common extractant for both P pools. The likelihood of anoxic conditions in lake and wetland sediments makes it desirable to discriminate between P associated with Al oxides and P associated with reducible Fe because only iron-bound P is subject to release under anoxic conditions (Paludan and Jensen, 1995). The

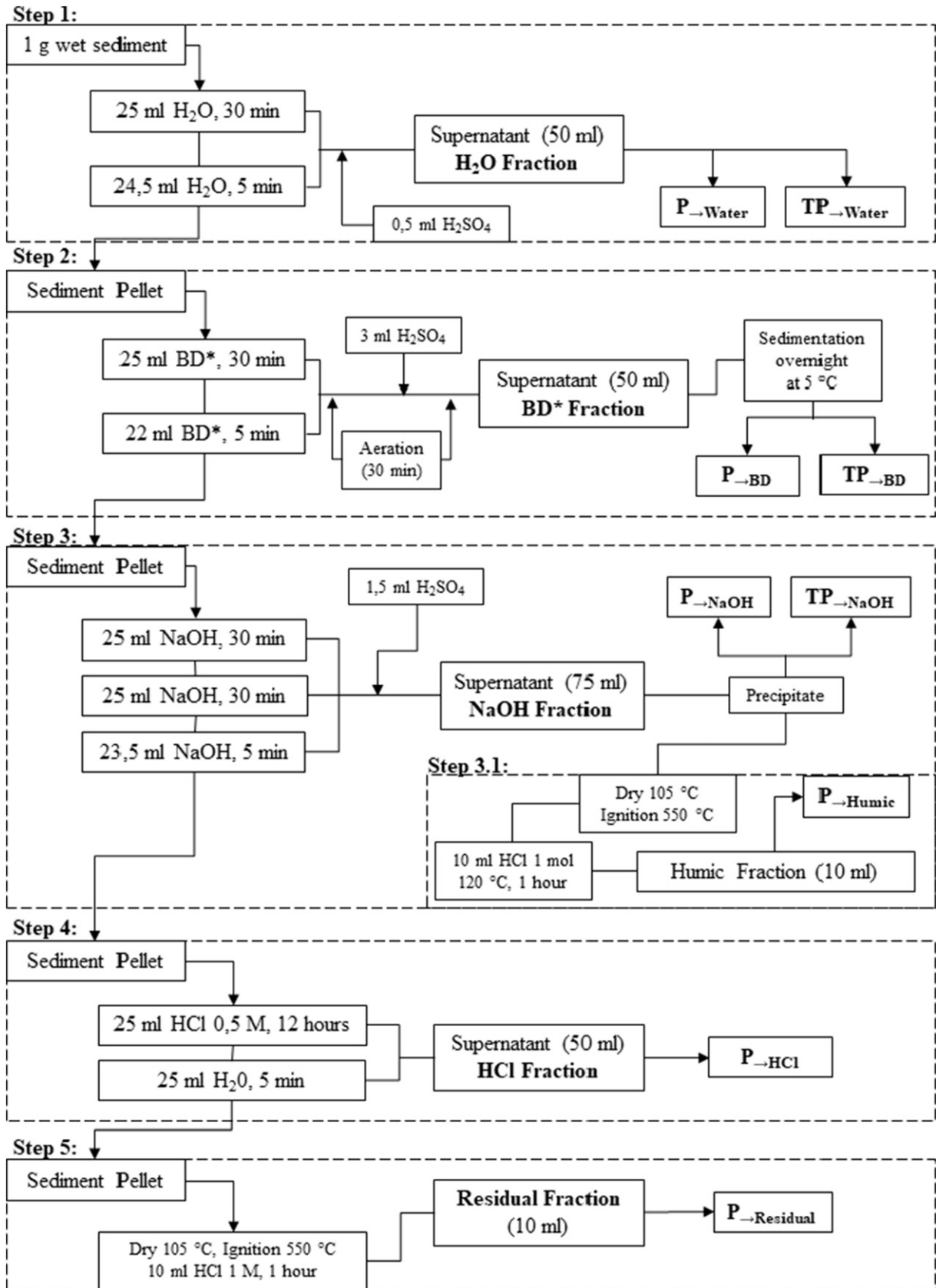


Fig. 2. Phosphorus fractionation scheme, modified from Paludan and Jensen (1995) by Lürling (personal communication). *BD = bicarbonate-buffered dithionite.

method developed by Paludan and Jensen (1995) does make this distinction, a key reason for choosing this method. This extraction scheme also allows for discrimination between P-Humic and inorganic P

species. This is especially important with respect to iron-bound P because the latter P pool can be mobilized under anoxic conditions (Paludan and Jensen, 1995).

For sequential extraction, 1 g of fresh (still moist) sediment, called pellet, was used in triplicate. In this method, anoxic distilled water extracts readily available P (P-Water). The oxygen is withdrawn from the water by nitrogen stripping. In step two, bicarbonate-buffered dithionite (0.11 M) solution extracts inorganic P associated with reducible iron and P-BD. The sodium hydroxide (1 M) in step three extracts inorganic P (P-NaOH), together with P-Humic, which is separated from P-NaOH by means of acidification with sulfuric acid. In the extraction of P-BD, the supernatant was aerated to remove the excess of dithionite. When the removal was not complete, a white precipitate of sulfur formed in the sample after the addition of sulfuric acid (Lukkari et al., 2007; Paludan and Jensen, 1995). In these cases, the original sample was aerated again, and the precipitate was allowed to settle overnight at 5 °C; the supernatant was taken for P analysis (Lukkari et al., 2007). Subsequently, hydrochloric acid (0.5 M) extracts P-HCl in step four. In step five, hydrochloric acid (1 M) extracts the more refractory and less mobile forms (P-Residual). The extractions were performed in triplicate for each sediment slice.

After extraction, all supernatants were acidified by adding sulfuric acid (H₂SO₄, 2 M), then filtered through a nitrocellulose membrane (0.45 µm; Unifil®). From the filtered samples, the SRP was determined following Murphy and Riley (1962), and the total dissolved phosphorus (TDP) was determined following the methods described by Valderrama (1981) and Murphy and Riley (1962). The difference between the TDP and SRP gives the amount of non-reactive phosphorus (NRP), which was estimated for the P-Water, P-BD and P-NaOH forms the NRP represents the organic part of each form. All P forms were expressed as amount of P in milligrams per kilogram of sediment (mg kg⁻¹). The mobile P was determined by the sum of the SRPs of the P-Water and P-BD forms and the NRP from the P-NaOH form, which is the P that can be released in anoxic conditions and by organic matter degradation (Vicente et al., 2008). The sum of the other P forms represents the non-mobile sediment P pool.

3. Results

In the Gargalheiras Reservoir sediment sample, the portion of organic matter was 5.5–5.8%, while the Cruzeta sample had 3.6–5.0%. The total P pool in the upper 10 cm of the Gargalheiras sediment was 3603.96 mg kg⁻¹, while the Cruzeta sediment had a P pool of 4106.22 mg kg⁻¹. The total P pool varied with depth in the core from 487 to 1081 mg kg⁻¹ and from 711 to 982 mg kg⁻¹ in the Gargalheiras and Cruzeta sediments, respectively; the P distribution in the depth range was non-linear in either sediments (Fig. 3). The potential releasable sediment P from Gargalheiras ranged from 130 to 610 mg kg⁻¹ (Fig. 1a) and from 254 to 479 mg kg⁻¹ for Cruzeta sediment (Fig. 3b), depending on depth in both cases. In most of the sediment from both reservoirs, the mobile forms constituted the main P forms, ranging from 29% to 59% of the Gargalheiras sediment and from 26% to 62% of the Cruzeta sediment.

The different P forms varied with depth in the sediment, and the relation between the P form and the depth within the sediment was not clear (Fig. 4). The P form was present mainly as P-BD in both reservoirs' sediments; P-BD ranged from 55 to 349 mg kg⁻¹ for Gargalheiras (Fig. 4a) and from 153 to 371 mg kg⁻¹ for Cruzeta (Fig. 4b), thus representing 27% and 37% on average of their respective total P pools (Fig. 4c–d). P-NaOH was the second most important P form relative to the total P pool in both reservoirs' sediment, followed by the P-HCl form. P-NaOH ranged from 119 to 271 mg kg⁻¹ in Gargalheiras (Fig. 2a) and from 124 to 279 mg kg⁻¹ in Cruzeta (Fig. 4b), thus representing 26% and 22% on average of the total P pool (Fig. 4c–d), respectively. P-HCl contributed 18% of the total P pool, (ranging from 46 to 211 mg kg⁻¹) in the Gargalheiras sediment and 21% (ranged from 96 to 366 mg kg⁻¹) in the Cruzeta sediment (Fig. 4).

The Gargalheiras and Cruzeta sediments differed in composition of mobile P forms: P-BD concentrations were higher in the Cruzeta than in the Gargalheiras sediment (Fig. 5a–b). This fraction represented 60–78% and 40–58% of the mobile P pool for Cruzeta and Gargalheiras, respectively (Fig. 5c–d). Meanwhile, the concentration and relative contribution of P-water and NRP fractions were higher in the Gargalheiras than in the Cruzeta sediment (Fig. 5).

4. Discussion

The sediments investigated in this study are characterized by high P content, reflecting the degree of pollution and high potential for internal P release, since the main P fraction in both sediments reservoir is the P bound to Fe and thus represents a potential ecological danger because it supports eutrophication.

The P pool found in the sediment in this study is very high when compared with that found in other regions, like Singapore (Ting and Appan, 1996), Greece (Kaiserli et al., 2002) and even in heavily polluted lake sediments in China (Wang et al., 2006; Zhou et al., 2001) (Table 2). The P content in sediments depends on the edaphic (type of soil) characteristics of the drainage basin (Boström et al., 1988), on the sediment composition and on physicochemical conditions, but also on the sedimentation rate and the extent of diagenetic processes (Gonsiorczyk et al., 1998). The reservoirs in semiarid regions suffer long water retention times due to extended drought seasons (Barbosa et al., 2012), which can increase the sedimentation rate. In addition, a large quantity of material can be transported from a reservoir's catchment and drainage basin during rainy periods. The soil of the region in this study is shallow, and the vegetation cover is sparse, which contributes to soil erosion and the transportation of nutrients into the reservoirs (Barbosa et al., 2012). The combination of these conditions with human activities in the catchment area can explain the high P content in the sediments studied.

P-BD is related to oxides that may appear in sediments and represents redox-sensitive P forms that bind mainly to Fe-hydroxides and Mn compounds. This fraction is considered a potentially mobile P pool that may be released from anoxic sediments, thus turning into an

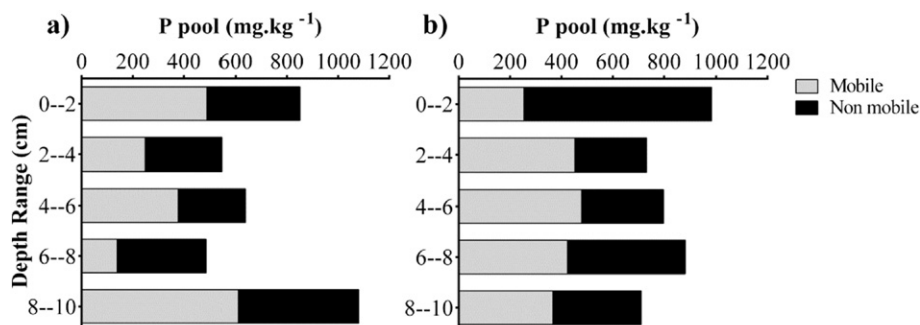


Fig. 3. Amount of phosphorus contents in a sediment profile from (a) Gargalheiras Reservoir and (b) Cruzeta Reservoir.

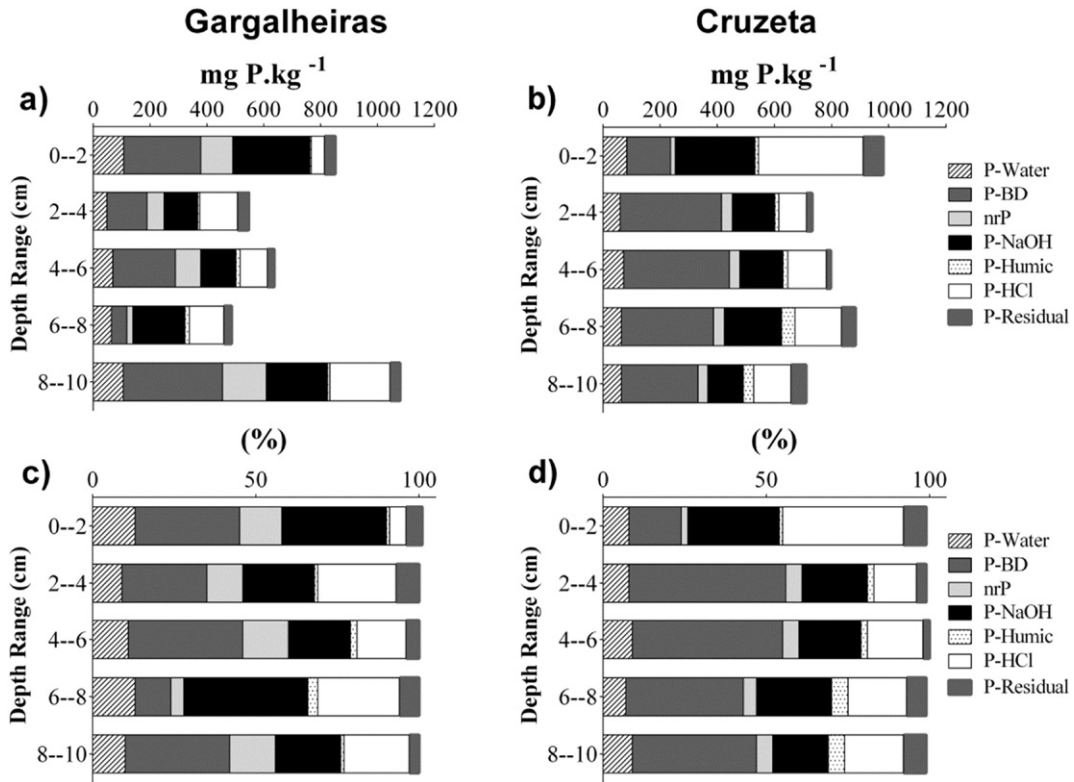


Fig. 4. Content of P forms in sediment profiles from (a) Gargalheiras Reservoir and (b) Cruzeta Reservoir and the relative contribution of each fraction to the total pools in (c) Gargalheiras and (d) Cruzeta sediment.

internal P source in water bodies that suffer from occasional DO depletion (Kleeberg and Dudel, 1997). The P-BD fraction was the largest in both reservoirs' sediments. The Gargalheiras Reservoir experienced

anoxia for many months from May 2015 to June 2016 (Cavalcante et al., unpublished results) prior to the sediment sampling for this study. Based on its high P-BD, it seems likely that P-BD in the

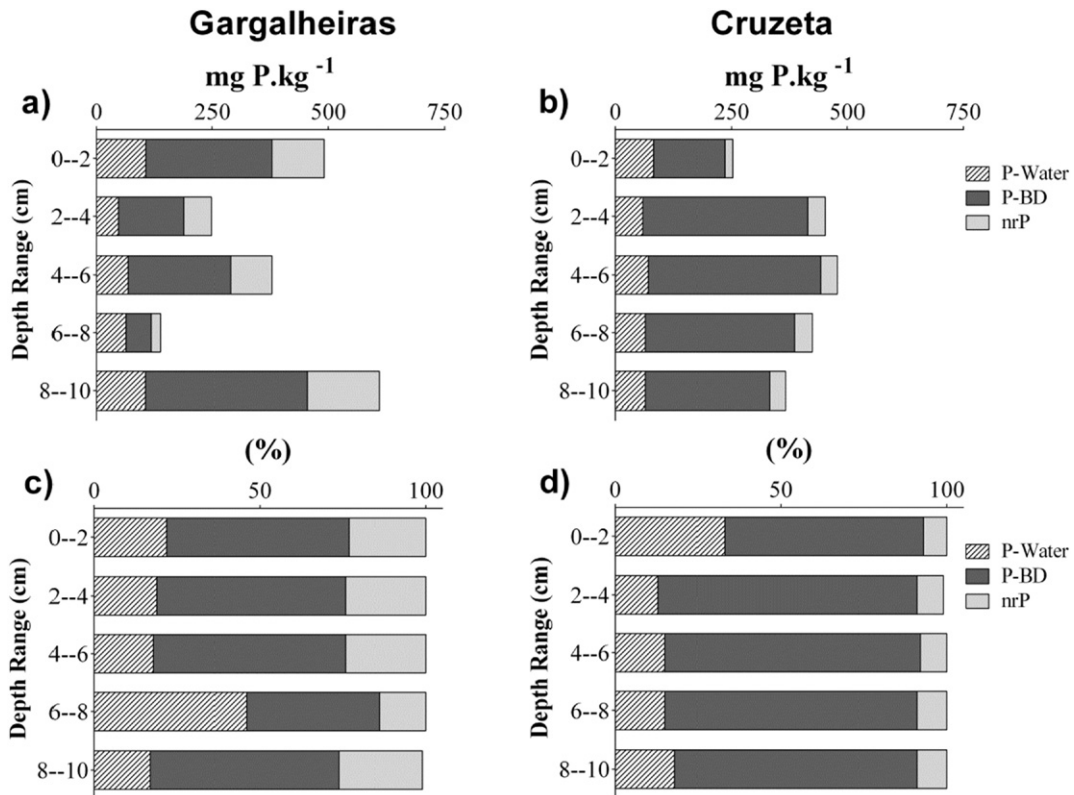


Fig. 5. Concentration of mobile P forms in sediment profiles from (a) Gargalheiras and (b) Cruzeta Reservoirs, and the relative contribution of each fraction to the total mobile pool in (c) Gargalheiras and (d) Cruzeta sediment.

Table 2
Literature data of concentration (mg kg^{-1}) of P fractions in lake sediments.

Location	Gargalheiras Reservoir	Cruzeta Reservoir	Kranji Reservoir ^a	MacRitchie Reservoir ^a	Lake Stechlin ^b	Lake Feldberger Hausee ^b	Lake Volvi ^c	Lake Koronia ^c	Lakes of the Yangtze River region ^d	Lake Erken ^e	Lake Pontchartrain ^f
	This study	This study	Singapore	Singapore	Germany	Germany	Greece	Greece	China	Sweden	USA
Loosely sorbed P (P-water)	394.50	345.72	6	0.6	50–100*	100–205*	7.3	8.2	1–23	27	1.4
Reductant soluble phosphorus (P-BD)	1036	1468.30	870	60	200–1300*	70–300*	771.7	974.4	48–112	345	119
Metal oxide bound phosphorus (P-NaOH)	913.18	902.30	121	0.4	50–250*	270–450*	10.6	94.6	180–426	85	142
Calcium bound inorganic P (P-HCl)	606.62	889.44	643	182	150–250*	450–1500*	250.3	219.3	1–129	287	525

^a (Ting and Appan, 1996) Sediment collected in the top 5 cm.

^b (Gonsiorczyk et al., 1998) Sediment collected superficially (*values roughly estimated from figure data).

^c (Kaiserli et al., 2002) Sediment collected superficially.

^d (Wang et al., 2006) Sediment collected in the top 30 cm.

^e (Rydin, 2000) Sediment collected in the top 15 cm.

^f (Roy et al., 2017) Sediment collected in the top 10 cm (data from near the Bonnet Carré spillway and pre-opening).

Gargalheiras reservoir can be released during periods with anoxic conditions.

Anoxic conditions did not occur in the Cruzeta Reservoir (Cavalcante et al., unpublished results). Despite a similar predominance of P-BD as in Gargalheiras, it is less likely that Fe and Mn are released into the Cruzeta Reservoir due to its low oxygen conditions. However, as the region was suffering drought during the study period, the Cruzeta Reservoir presented a very low depth (<2 m) from May 2015 to June 2016 (Cavalcante et al., unpublished results). As a result, the sediment in this reservoir is highly susceptible to wind resuspension (Braga et al., 2015; Medeiros et al., 2015). It was thus no surprise to find high values of SRPs and inorganic solids, which averaged $174.17 \mu\text{g L}^{-1}$ and 81.73 mg L^{-1} , respectively, from May 2015 to June 2016 (Cavalcante et al., unpublished results), causing the high inorganic turbidity characteristic of this reservoir (Braga et al., 2015; Medeiros et al., 2015). The potential release of P to the water column by sediment resuspension may be an important source of pollution and is thus a growing concern (Kim et al., 2004). Some studies have demonstrated that resuspension increases the release rates of P (Fan et al., 2001; Søndergaard et al., 1993; Søndergaard et al., 1992). More labile or mobile forms (P-Water, P-BD and the inorganic part of P-NaOH) are likely more susceptible to release by resuspension (Søndergaard et al., 1992).

The inorganic part of P-NaOH was the second highest fraction of P in both systems; its absolute amounts and relative contributions were similar in both sediment samples studied. This fraction is exchangeable and includes P bound to metal oxides, mainly Al and Fe (Kozerski and Kleeberg, 1998). This form may be released when anoxic conditions prevail in the sediment-water interface (Ting and Appan, 1996). It has been shown that this fraction is reduced by 60% under anoxic conditions (Rydin, 2000). Thus, P-NaOH may be released from the sediment in Gargalheiras reservoir, when anoxic conditions occurred most of the time at the sediment-water interface.

P-HCl represents the P fraction sensitive to low pH; it corresponds to P bound to calcium, including apatite-P, and P bound to carbonates (Wang et al., 2006; Jin et al., 2006). P-HCl was the third largest P fraction in the sediment of both reservoirs. This form is considered to be non-bioavailable and difficult to release because it is relatively stable, which can be attributed to the permanent burial of P in sediments (Gonsiorczyk et al., 1998; Kozerski and Kleeberg, 1998). However, under weakly acidic conditions, it can be partly released (Jin et al., 2006; Li et al., 2015); the release rate increases fourfold at pH 2 (Kim et al., 2003).

In reality, extreme pH affects the release of different forms of P. High pH can promote the release of NaOH-P (NRP), while low pH can promote the release of HCl-P (Jin et al., 2006). The increase of pH in

overlying water and in the sediment may decrease the P-binding capacity of iron and aluminum compounds, mainly due to ligand exchange reactions in which hydroxide ions may replace orthophosphate (Lijklema, 1977).

The bottom water pH values from reservoirs in semiarid regions present high alkalinity values and are usually above pH 8, with the highest values typically observed in the dry season (Huszar et al., 2000). The release of P-HCl is thus more difficult in semiarid regions, mainly in periods of extreme drought, since water generally has alkaline conditions. Therefore, P-HCl is not considered a fraction that is likely to be released, but P-NaOH NRP can be released from the sediment.

In semiarid regions, reservoirs present high concentrations of algal biomass, mainly in drought periods, that are indicative of accelerated eutrophication with possible cyanobacterial blooms (Barbosa et al., 2012; Braga et al., 2015). The release of P from the sediment certainly contributes substantially to this problem, because the P pool is very high. Therefore, semiarid reservoirs need effective treatments to control eutrophication to mitigate the nuisances caused by cyanobacterial blooms. As far as we could verify, our study is the first to show the different P fractions in sediments in semiarid region, so our results add to the knowledge needed to understand the dynamics of sediment P in semiarid reservoirs. Our results indicate that the reservoirs studied here may benefit from in-lake geoengineering techniques that immobilize the potential releasable P pool in water and sediment (Lüring and van Oosterhout, 2013). Many techniques can be employed in water bodies to reduce eutrophication. The first step is to tackle the direct input of nutrients (Cooke et al., 2005), but the internal P load can delay recovery (Søndergaard et al., 1992). A technique known as P capping can be used to control legacy P stored in sediments through the application of three types of products: (1) aluminosilicate minerals (e.g., modified zeolites), (2) existing catchment soils amended with natural materials (e.g., chitosan) and (3) mineral-based byproducts (Spears et al., 2013, 2014; Zamparas and Zacharias, 2014).

In summary, our results highlight the possible impact of potentially high amounts of labile P in the sediment of semiarid reservoirs. We encourage later research to apply the method we used to investigate the P fractions in a broader number of lakes and the future application of products for the restoration of semiarid lakes.

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