Acta Limnologica Brasiliensia



# Sediment phosphorus fractionation and flux in a tropical shallow lake

Fracionamento e fluxo de fósforo em um lago raso tropical

Jéssica Papera<sup>1\*</sup> 💿, Fabiana Araújo<sup>1</sup> 💿 and Vanessa Becker<sup>1</sup> 💿

<sup>1</sup>Programa de Pós-graduação em Engenharia Sanitária, Laboratório de Recursos Hídricos e Saneamento Ambiental, Departamento de Engenharia Civil, Universidade Federal do Rio Grande do Norte – UFRN, Av. Senador Salgado Filho, 3000, CEP 59078-970, Natal, RN, Brasil \*e-mail: jesspapera@gmail.com

**Cite as:** Papera, J., Araújo, F. and Becker, V. Sediment phosphorus fractionation and flux in a tropical shallow lake. *Acta Limnologica Brasiliensia*, 2021, 33, e5

**Abstract:** Aim: The aim of the present study is to evaluate the potential phosphorus (P) release from the sediment to the water column of a tropical shallow lake in the northeast of Brazil, based on the sediment P fractions and on the flux of P between water and sediment. Methods: We used a sequential extraction method to analyse the different P fractions of the sediment of Lake Extremoz. We also carried out a 40-day microcosm experiment to analyse the flux of P between water and sediment. We did so by flooding 200g of sediment from the lake with 800 mL of  $1.2 \,\mu\text{m}$  filtered lake water in 1 L beakers. Every 5 days we analysed: soluble reactive phosphorus (SRP), total phosphorus (TP), organic phosphorus (Org-P), dissolved oxygen (DO), temperature, and pH of the water. Results: The largest fraction of P in the sediment of Lake Extremoz is Refractory-P, which is non-mobile. The main mobile fraction of this lake's sediment is composed of P bound to Fe and Mn oxides (BD-P) which is redox sensitive. During the P flux experiment, the water was always oxic and with nearly neutral pH, however the temperature increased by almost 4 °C due to the increase of the temperature of the air. SRP, TP and Org-P concentrations in the water had a general decrease in the first 20 days. But, on the second half of the experiment, those concentrations increased and the fluxes of P from sediment to water, mainly Org-P, were positive. Even with this increase in concentrations, indicating a period of P release, overall fluxes were negative. Conclusions: The main mobile fraction of the sediment is redox sensitive, therefore it has the potential to be released in case of oxygen depletion. Under current conditions, most of the P released by the sediment is in organic forms, indicating that, in the presence of oxygen, the balance of P between water and sediment is controlled by the effects of organisms on P as well as temperature.

Keywords: internal loading; oxic conditions; mobile phosphorus; Lake Extremoz.

**Resumo: Objetivo:** O objetivo deste estudo é avaliar o potencial de liberação de fósforo (P) do sedimento para a coluna d'água de um lago raso tropical no nordeste do Brasil, com base nas frações de P do sedimento e no fluxo de P entre água e sedimento. **Métodos:** Nós empregamos um método de extração sequencial a fim de analisar as diferentes frações de P do sedimento da Lagoa de Extremoz. Também realizamos um experimento de 40 dias para analisar os fluxos de P entre água e sedimento. Nós alagamos 200 g de sedimento da lagoa com 800 mL água da lagoa filtrada em 1.2 µm. A cada 5 dias, nós medimos fósforo reativo solúvel (SRP), fósforo total (TP), fósforo orgânico (Org-P), oxigênio dissolvido (DO), temperatura, e pH da água. **Resultados:** A principal fração de fósforo no sedimento da lagoa de Extremoz é P-Refratário, que é considerada não-móvel. A principal fração móvel é composta por P ligado a óxidos de Fe e Mn (BD-P), a qual é sensível a condições redox. Durante



todo o experimento de fluxos, as condições nos microcosmos foram óxicas e o pH se manteve próximo a valores neutros. No entanto, a temperatura da água aumentou cerca de 4 °C devido ao aumento da temperatura atmosférica. As concentrações de SRP, TP e Org-P diminuíram nos primeiros 20 dias. Porém, as concentrações de P aumentaram na segunda metade do experimento e houve fluxos positivos, principalmente de Org-P. Apesar desse aumento nas concentrações, os fluxos globais foram negativos. **Conclusões:** A principal fração móvel do sedimento é sensível a condições redox, portanto ela tem potencial para ser liberada em caso de anoxia. Nas condições atuais, a maior parte do P liberado pelo sedimento foi orgânica, indicando que, na presença de oxigênio, essa liberação é controlada pelos efeitos da ação de organismos bem como da temperatura.

Palavras-chave: fertilização interna; condições óxicas; mobilidade de fósforo; Lagoa de Extremoz.

#### 1. Introduction

Phosphorus (P) is considered a key nutrient in the eutrophication of inland water (Carpenter, 2008) as it is usually a limiting factor for primary production. Increased P availability can lead to enhanced primary productivity and nuisance algae blooms (Heisler et al., 2008). Known consequences of P enrichment and dense algae blooms include increased turbidity, bottom water hypoxia, and fish kills. Nitrogen (N) enrichment is also a cause of eutrophication, and some argue that it should be controlled as well (Paerl et al., 2011). However, the P cycle is simpler and, thus, easier to control. Therefore, controlling P is often a better approach when dealing with freshwater eutrophication (Schindler, 2012). Especially in tropical environments, as higher temperatures favour the cyanobacteria population growth, and total P is more likely to be directly correlated with persistent algae blooms (Figueredo et al., 2016).

External nutrient sources are considered the main cause of eutrophication, thus the first measure to mitigate it is to control external P loading (Jeppesen et al., 2007). Sources of allochthonous P can be point, e.g. disposal of human sewage, and non-point such as rearing livestock and synthetic fertilisers. This means that whole catchment measures are necessary to control the nutrient input, and non-point sources can be quite difficult to control. However, in many cases, even if external input is greatly reduced, this is not enough to achieve the desired restoration of the environment as legacy P keeps being released from the sediment into the water column (Jeppesen et al., 2005; Søndergaard et al., 2001; Søndergaard et al., 2013; Spears et al., 2012). In tropical regions which have dry seasons, P release from the sediment is also particularly relevant as the water bodies spend several months of the year with very low external nutrient input due to the reduced run-off and increased water residence times (Braga et al. 2015). A consequence of this internal nutrient loading

Acta Limnologica Brasiliensia, 2021, vol. 33, e5

is the perpetuation of the eutrophic state of the system.

Not every form of P in the sediment is likely to be released into the water column (Wang et al., 2013). P in the sediment is divided into fractions according to what compounds it is bound to. Following the sequential P fractionation proposed by Paludan & Jensen (1995), P forms include interstitial water and loosely adsorbed P (Water-P), redox sensitive P bound to iron (Fe) compounds (BD-P), P bound to aluminium (Al) hydroxides (NaOH-P), calcium (Ca) bound P (HCl-P), humic bound P (Humic-P), and Refractory-P. Of these fractions, the mobile pool is considered to comprise the sum of the inorganic parts of Water-P and BD-P, and the organic parts of Water-P, BD-P and NaOH-P. The inorganic parts of NaOH-P, HCl-P, Humic-P and Refractory-P are considered to be the non-mobile pool (Jensen et al., 2015).

One way of analysing P in the water is to divide the total P into soluble reactive P (SRP) and organic P (Org-P). SRP corresponds to dissolved compounds of inorganic P, specifically orthophosphate ions, which are readily available to contribute to primary production (Reynolds & Davies, 2001). Org-P corresponds to P in organic compounds, including particulate such as biomass. Part of this form of P can be introduced in the food chain when incorporated into bacterial biomass via microbial loop.

The P flux between water and sediment is influenced by several factors, such as temperature, dissolved oxygen concentration, organisms, pH, and sediment resuspension (Søndergaard et al., 2003). These factors affect each P form differently. For instance, anoxic conditions near the sediment cause Fe reduction, which results in the release of the BD-P fraction (Zhu et al., 2012), thus oxygen depletion is often seen as a main enabler of P release from the sediment. The presence of oxygen, on the other hand, is associated with P retention (Olszewska et al., 2017), to such a degree that hypolimnion oxygenation is regarded

as a lake restoration method (Beutel & Horne, 1999; Singleton & Little, 2006). However, in oxic environments P can still be released through processes other than the classic Fe reduction release mechanism, such as mineralisation of organic matter, bioturbation and pH or temperature induced solubilisation (Søndergaard et al., 2001). Temperature is an important factor for internal loading, as higher temperatures can increase P compounds solubility (Jensen & Andersen, 1992), as well as affect the biota in both water and sediment, which is involved in the P cycling through immobilisation of inorganic P and mineralisation of organic matter. The pH can influence P release as well. Low pH values are related to the release of calcium bound P, whereas high pH values induce the release of NaOH-P (Jin et al., 2006).

In tropical regions such as the northeast of Brazil, there is a seasonality in the precipitation regime, which means they are subject to a dry season. During this time, there is a decrease in water runoff, hence a decrease in external loading of nutrients. In this context, the potential P release from the sediment can be an important cause of eutrophication. This is of particular concern for the quality of the water of natural and man-made lakes that are used for domestic supply.

Finally, internal loading of P is a complex process, and its understanding is not restricted to the release mechanisms related to redox reactions. The aim of the present study is to evaluate the potential P release from the sediment of a tropical eutrophic shallow lake, based on the P fractions of its sediment and on an experiment measuring the flux of P between water and sediment.

### 2. Materials and Methods

#### 2.1. Study area

Lake Extremoz (05°42'76"S; 35°17'69"O) is a natural tropical lake in the Doce River catchment, in the Northeast region of Brazil (Figure 1). According to Köppen's classification, the climate of the region is As, tropical with dry summer (Alvares et al., 2014). The average temperature of the region is of 26 °C. It has a wet season that extends from February to July, with average precipitation of 184 mm per month, and a dry season from August to January, with average precipitation of 43 mm per month (INMET, 2020). Its maximum storage capacity is 11 million m<sup>3</sup>, it has a surface area of 3.59 km<sup>2</sup> (Rio Grande do Norte, 2015), and average depth of 4 m (Pinto & Becker, 2014). The lake's main use is water supply, as it provides water for 60%-80% of the population of the north region of Natal, Brazil (Araújo et al., 2000), therefore the quality of its water is of great importance. It is located in an urban area close to industrial plants. There are also agricultural, livestock rearing and leisure activities in its vicinity. These activities have degraded the soil around the lake and compromised the native vegetation. In addition, the lake is surrounded



Figure 1. Location of the Lake Extremoz in the northeast of Brazil.

by quartzarenic neossols with a low water storage capacity, which favours the transportation of nutrients and heavy metals through soil leaching (De Faria, 2013). The water column is described as well-mixed throughout the year (Pinto & Becker, 2014).

# 2.2. Water and sediment sampling

We collected samples of the water overlying the sediment in August 2018, with the aid of a Van Dorn sampler at the sampling point indicated on the map in Figure 1. The sampling point is in the pelagic zone and at the deepest point of the lake. At the time of the sampling, the water column at that point was 4 m deep. It is a particularly relevant part of the lake as it is close to the point of water intake for the supply system. The experiment was expected to last roughly 6 weeks and require approximately 13 L of water. 20 L of water were sampled to give a large margin of error. We placed the water in large polyethylene bottles for transportation to the laboratory.

The sediment was sampled from the lake using a manual Kajac corer (50 cm long and 7 cm diameter). First, we collected a core and sliced it in situ into 2 cm slices: 0-2, 2-4, 4-6, 6-8, 8-10. We did this to measure the different P fractions at each depth and build the P fractions profile of Lake Exremoz's sediment, as it had never been done before. We stored the slices separately in transparent polyethylene containers. Near that same sampling area, avoiding the previously disturbed points, we collected between 5 and 10 samples of the most superficial 10 cm of the sediment. We used the 10 most superficial centimetres as this is the depth range believed to contribute to P release from sediment into the water column, and it is the depth used when calculating the amount of product needed for restoration efforts which focus on controlling P internal loading (Wang et al., 2006; Meis et al., 2012; Zhang et al., 2016). These samples were stored together in a polyethylene container for use in the phosphorus flux experiment. All the containers with sediment were transported to the laboratory in a thermally insulated box. Temperature and dissolved oxygen (DO) near the bottom of the lake were measured in situ (Table 1), utilising a portable digital dissolved oxygen meter (INSTRUTHERM/MO-900).

#### 2.3. Phosphorus fractions in the sediment

For the sequential extraction of phosphorus fractions in the sediment, we followed the method

Acta Limnologica Brasiliensia, 2021, vol. 33, e5

described by Cavalcante et al. (2018). We used 1 g of moist sediment, which is called a pellet, in triplicates. We placed the pellets into 50 mL polyethylene centrifuge tubes and extracted the most available P fraction (Water-P) with anoxic deionised water. We removed the oxygen from the water with the addition of nitrogen gas. In the next step, we extracted the P associated with Fe compounds (BD-P) using bicarbonate-buffered dithionite (0.11 M). In the third step, we used sodium hydroxide (1 M) to extract both NaOH-P and Humic-P, whereupon we separated Humic-P from NaOH-P by acidifying the supernatant with sulfuric acid. Next, we extracted HCl-P using hydrochloric acid (0.5 M). Finally, in the fifth step, we extracted the last, least available P fraction, Refractory-P, using hydrochloric acid (1 M). Referring back to the second step, where we extracted BD-P, we aerated the supernatant to remove the excess of dithionite. If the excess of dithionite is not completely removed, upon acidification a white sulphur precipitate is formed in the supernatant. When this happened, we aerated the original sample again and allowed the precipitate to settle overnight (Lukkari et al., 2007), so the cloudiness created by the precipitate would not interfere with the colorimetric analysis. We acidified all the supernatants with sulfuric acid  $(H_2SO_4, 2M)$  and then filtered them through a 0.45 µm membrane. Later, we determined the SRP concentrations in each filtered sample following Murphy & Riley (1962), and the total dissolved phosphorus (TDP) after digestion according to Valderrama (1981) and Murphy & Riley (1962). Subtracting SRP from TDP, we have the organic part of each fraction, namely non-reactive phosphorus (NRP), which is calculated for Water-P, BD-P and NaOH-P. We performed the fractionation of the sediment profile by depth using 3 subsamples for each slice.

To measure the TDP of all the supernatants of the fractionation we registered the absorbance (UV/VIS spectrophotometer, Kasuaki) 2 minutes

**Table 1.** Water quality parameters of the water overlayingthe sediment from Lake Extremoz.

Parameter	Value
DO (mg.L <sup>-1</sup> )*	6.7
T (°C)*	26.6
рН	7.37
TP (μg.L <sup>-1</sup> )	76.0
SRP (µg.L <sup>-1</sup> )	1.0

DO: Dissolved Oxygen; T: Temperature; TP: Total phosphorus; SRP: Soluble reactive phosphorus. \*measured *in situ*.

after the addition of the reagent. We did so as we noticed that, for these specific samples, the peak of absorbance occurred at this time.

We calculated the mobile P pool in the sediment, which is composed by the fractions with higher potential to contribute to the internal loading. The mobile P pool is comprised of the SRPs of Water-P and BD-P fractions, and the NRPs of Water-P, BD-P and NaOH-P (de Vicente et al., 2008; Jensen et al., 2015; Reitzel et al., 2005). The SRP of NaOH-P, Humic-P, HCl-P and Refractory-P are considered non-mobile.

#### 2.4. Phosphorus flux experiment

Before setting up the experiment, we measured the DO and pH of the lake water with a portable pH meter (AKSO/AK103). We measured the total phosphorus (TP) in the water by digesting the samples (Valderrama, 1981) and then employing a colorimetric analysis (Murphy & Riley, 1962) (Table 1). To measure the SRP, the water sample was filtered through glass fibre membranes (0.45  $\mu$ m), and a colorimetric analysis was employed (Murphy & Riley, 1962) (Table 1). We filtered the whole of the water through a 1.2  $\mu$ m glass microfiber filter (VWR 696) to remove particulate matter and larger organisms before the experiment.

We set up the experiment using three beakers with 1 L capacity each. All of them received 200 g of homogenised wet lake sediment from the top 10 cm. The sediment covered the bottoms of the beakers completely. We filled the beakers with 800 mL of filtered water from the lake. We covered them to ensure a dark environment and placed them in a room with no control of temperature. Their distribution was random to avoid environment bias.

To allow the sediment and the water to settle, we defined that day 1 of the experiment was 24h after its setup. We sampled 60 mL of water from each beaker on the days 1, 5, 10, 15, 21, 26, 33 and 40 of the experiment. On each sampling day we measured the TP in water using the method described by Murphy & Riley (1962), after digestion (Valderrama, 1981), and SRP concentrations in the water following Murphy & Riley (1962). For SRP, the water samples were filtered through glass fibre membranes (0.45  $\mu$ m). We calculated the concentrations of organic P (Org-P) in water by subtracting SRP from TP. On each sampling day, the volume of water that was removed from the beakers was replaced with filtered lake water. The replacement water was kept under the same conditions as the experiment units, except for the contact with the sediment.

$$f_{t_{0-i}} = \frac{(C_i - C_0).V}{(t_i - t_0).A}$$
(1)

Equation 1 takes into account P concentration in the water ( $\mu$ g.<sup>L-1</sup>) at the beginning (C<sub>0</sub>) and at the end (C<sub>i</sub>) of each time interval (t<sub>i</sub>-t<sub>0</sub>), the volume of water overlying the sediment (L), and the approximate area of sediment in contact with the water (m<sup>2</sup>). We calculated the fluxes of SRP, TP and Org-P.

Based on the variation of the P concentrations throughout the experiment, we calculated the fluxes at two intervals, from day 0 to day 21 (first half) and from day 21 to day 40 (second half).

# 3. Results

# 3.1. Phosphorus fractions in the sediment profile of the Lake

The sediment of Lake Extremoz is mostly composed of Refractory-P, as it is the largest fraction of P in 4 out of the 5 layers (Figure 2). The total amount of P decreases with depth from the most superficial layer to the 4-6 cm depth range (Figure 2a). In the 6-8 cm range the total amount of P was almost twice the value of the most superficial layer, mostly due to the larger amount of refractory P (Figure 2).

The largest mobile P fraction of Lake Extremoz's sediment is iron bound P (BD-P), and its values varied from 26.53 to 94.48 mg.kg<sup>-1</sup>. The total mobile P values vary from 39.21 to 135.32 mg.kg<sup>-1</sup> (Figure 2a). The depth with the largest percentage of mobile P is 0-2 cm, in which 48.44% is considered mobile (Figure 2b). Also, the relative contribution of the mobile P pool decreased with increasing depth, going from 48.44% in the most superficial layer to 10.21% in the deepest layer.

#### 3.2. Phosphorus flux experiment

The water temperature varied by up to 4 °C throughout the experiment. It started with an average of 24.3 °C, then increased sharply between the days 15 and 26, finally reaching values of up to 28.3 °C (Figure 3a). The increase in the temperature of the water is due to the increase in the temperature of the air during the experiment. On day 0, the average air temperature was 24.3 °C, and, on day 40, it was 27.2 °C (INMET, 2019). The average temperature for the whole experiment was 26.6 ± 1.2 °C. The water remained oxygenated during the whole of the experiment, with DO concentrations above 4.0 mg.L<sup>-1</sup> (Figure 3b), the global average was of 5.7 ± 0.7 mg.L<sup>-1</sup>. At the start, the pH of



Figure 2. Content of P forms in the sediment profile (a), and the relative content of mobile and non-mobile pools (b).



**Figure 3.** Changes in water temperature (a), dissolved oxygen (b) and pH (c).

the water was neutral to basic  $(7.37 \pm 0.14)$  and it became slightly more acidic over time, reaching a final average of 6.65 ± 0.30 (Figure 3c). The global average of the pH was 7.1 ± 0.2.

After the settling period, SRP concentrations increased, reaching average concentrations of 27.2  $\mu$ g.L<sup>-1</sup> in the beginning of the experiment (Figure 4a). The initial concentration of TP was



**Figure 4.** Concentrations of P compounds in the water overlying the sediment. SRP (a), TP (b) and organic P (c). SRP = Soluble reactive phosphorus TP= Total phosphorus Org-P = Organic phosphorus.



**Figure 5.** P fluxes between sediment and water throughout the experiment calculated for the intervals between day 0 to day 21, and day 21 to day 40 for SRP, TP, and Org-P (a). Overall P fluxes between the sediment and water (b). Error bars represent the standard deviation. SRP = Soluble reactive phosphorus TP= Total phosphorus Org-P = Organic phosphorus.

76.0  $\mu$ g.L<sup>-1</sup> (Figure 4b) and, after the settling period, it increased slightly to 88.8  $\mu$ g.L<sup>-1</sup>, while Org-P decreased from 75.0  $\mu$ g.L<sup>-1</sup> to 61.6  $\mu$ g.L<sup>-1</sup>.

During the first half of the experiment (day 0 - day 21), all P concentrations showed a general decrease (Figure 4). The average concentrations of SRP, TP and Org-P reached values of 3.4 µg.L<sup>-1</sup>, 23.6 µg.L<sup>-1</sup> and 17.6 µg.L<sup>-1</sup> respectively. Only SRP had a positive flux in the cited period (Figure 5a).

At the start of the second half of the experiment (day 21 - day 40) (Figure 4), all of the P concentrations increased. However, around day 26, SRP concentrations decreased (Figure 4a), while the increase in TP and Org-P lasted until the end of the experiment, reaching average concentrations of 68.1 µg.L<sup>-1</sup> and 67.8 µg.L<sup>-1</sup>, respectively. The second half had positive fluxes of TP and Org-P, however, the SRP fluxes were negative (Figure 5a).

Although there was an increase in P concentrations in the water from the middle to the end of the experiment, the overall fluxes were still negative (Figure 5b), with average values of -2.49 µg.L<sup>-1</sup>.m<sup>-2</sup>.d<sup>-1</sup> for SRP, -17.68 µg.L<sup>-1</sup>.m<sup>-2</sup>.d<sup>-1</sup> for Org-P and -19.31 µg.L<sup>-1</sup>.m<sup>-2</sup>.d<sup>-1</sup> for TP.

#### 4. Discussion

The largest fraction of P in the sediment of Lake Extremoz is Refractory-P, which is composed by highly recalcitrant compounds and the most unavailable P form of freshwater sediments (Wang et al., 2006). This fraction will not contribute to P concentrations in the water, even if there is a change in environmental conditions near the water-sediment interface (Meis et al., 2013). The deepest layers of the sediment of Lake Extremoz have a total amount of P much higher than the most superficial layers, which may indicate that a rather large P contribution to the sediment has occurred in the past.

The largest mobile fraction in the sediment is BD-P, which is redox sensitive and expected to be released under anoxic conditions (Smolders et al., 2006). At the time of sampling, the bottom of the lake was not anoxic, and this lake is characterised by a well-mixed water column (Pinto & Becker, 2014), thus the BD-P fraction in this sediment is not likely to be released. However, this could change, as Lake Extremoz is enriched with nutrients, and one of the main consequences of eutrophication is oxygen depletion (Smith & Schindler, 2009). It had an average TP concentration of 30.4 µg.L<sup>-1</sup> for 2017-2018, and the chlorophyll-a average concentration was 30.9 µg.L<sup>-1</sup> for the same period (Moreira, unpublished data), which correspond to values of a mesotrophic and eutrophic system, respectively, according to the classification proposed by Salas and Martino (1991).

The most superficial layers of the lake's sediment have a larger percentage of potentially mobile P, which is due to the fact that they are still going through processes of release/retention and diagenetic transformations, and have a tendency to become more recalcitrant with time as they are buried (Rydin et al., 2011; Xu et al., 2013).

The general increase in SRP and TP concentrations immediately after the settling period of the experiment can be attributed to the physical disturbance of the sediment, similarly to a resuspension (Huang et al., 2015; Søndergaard et al., 1992). This is an expected consequence of setting up the experiment, even when the water is added carefully. Org-P, however,

did not have the same increase at the start. SRP and Org-P are parts that constitute TP, so, if the total amount of P increased along with its inorganic portion, but its organic portion did not, perhaps we can assume that mineralisation occurred. This could be an indication of possible bacterial activity.

Additionally, specifically for the SRP concentrations, the initial release and positive P fluxes can be partially attributed to the initial lack of SRP in the water. That is, the concentration of inorganic P in the pore water of the sediment, the most mobile fraction, was, initially, higher than the inorganic P concentration in water overlying the sediment. This created a concentration gradient, so P was released through diffusion (Golterman, 2004; Roy et al., 2012).

During the rest of the first half of the experiment, the concentrations decreased, and this caused the TP flux for the whole of the first half to be negative, showing a tendency of the sediment to act as a P sink. This is most likely due to the conditions of neutral pH and presence of oxygen, favouring P deposition from water to sediment. However, at the start of the second half of the experiment, all of the P concentrations increased and carried on increasing until the end of the experiment, except for SRP, which had a slight decrease towards the end. The P fluxes for the second half indicate that there was a release of P from the sediment to the water, but it was P in organic compounds rather than inorganic (Figure 5a).

Equation 1 does not account for the interference in the concentrations caused by mixing the experiment water in the beakers with the replacement water. As a consequence, the fluxes from the second half of the experiment are underestimated by an average of 21.6%. We advise readers take this into consideration when comparing our results to others. This, however, does not change the overall trend.

P can be released under oxic conditions, as oxygen deficit is not always the prime cause of P release, due to the involvement of multiple other factors (Hupfer & Lewandowski, 2008). In aerobic conditions, temperature seems to be the most important environmental factor influencing P release from sediment (Jensen & Andersen, 1992; Suplee & Cotner, 2002; Wu et al., 2014). In this case, it is most likely related to the influence of temperature on organisms, because higher temperatures increase their metabolism as well as favour their reproduction, thus increasing biomass and having a larger effect on Org-P (Jiang et al., 2008). High temperatures can also increase solubilisation of P compounds (Jensen & Andersen, 1992). So, the release that occurred in the second half of the experiment was probably influenced by the simultaneous increase in temperature.

In the second half of the experiment, Org-P increased until the end, while SRP did not. This pattern shows that the increase of P in organic compounds could have been supported by a release of SRP by the sediment, at which point there was a SRP uptake from bacteria, as they can consume large portions of inorganic nutrients (Kirchman, 1994). This uptake of SRP by organisms possibly resulted in an increased biomass.

We draw attention to the role of organisms in the sediment because, even though the water had been filtered through a 1.2  $\mu$ m membrane, it is fair to assume that there were still microorganisms, such as bacteria, in the water of the lake and also in the sediment, as it was not sterilised. In this case, the increase in SRP and TP in the water could be linked to an increase in bacterial metabolism and biomass, as this has previously been shown for dark environments (Jiang et al., 2008).

Each system has its own characteristics to be considered when it comes to understanding and controlling eutrophication. We found an indication that P release from the sediment can occur under oxic conditions in Lake Extremoz. This can contribute to the increase of P concentrations in its water and deteriorate the water quality of the lake. If we compare the fractionation of P in Lake Exremoz with other tropical lakes previously studied by Cavalcante et al. (2018), the amount of mobile P in the upper 10 cm of Extremoz's sediment is 4 times lower than the values that they found using the same sequential extraction method (Table 2). However, the TP concentrations in the water of

Table 2. Literature data of P in the sediment of freshwater bodies in the northeast of E	3razil.
--	---------

	Rio Grande do Norte, Brazil			Ceará, Brazil					
Location	Lake Extremoz	Gargalheiras Reservoir¹	Cruzeta Reservoir <sup>1</sup>	R#1 <sup>2</sup>	R#2 <sup>2</sup>	R#3 <sup>2</sup>			
P in the sediment (mg.kg <sup>-1</sup> )									
MOBILE P	423.8	1920	2075	625.6	189.7	40.14			
NOM-MOBILE P	1151.91	1780	2065	521.04	481.61	262.77			

<sup>1</sup>(Cavalcante et al., 2018) Top 10 cm divided into 5 slices. <sup>2</sup>(Moura et al., 2020) Top 5 cm.

Lake Extremoz was almost 40 times lower than that of those reservoirs (Cavalcante et al., 2018). Perhaps this is an indication that the sediment of Lake Extremoz has enough mobile P to contribute to the eutrophication of its water if the conditions of the environment favour the release. Lake Extremoz's sediment also has more mobile P than two out of the three reservoirs studied by Moura et al. (2020), also located in the northeast of Brazil (Table 2).

# 5. Conclusion

Lake Extremoz's sediment main fraction is P-Refractory, which is non-mobile. Its main mobile form is BD-P, showing a potential for release in case of oxygen depletion. The lake has a store of mobile P, which can be enough to have significant impact on its trophic state in the case of a change in the environmental conditions to ones which favour P release. Under oxic conditions, P balance between water and sediment is likely to be largely influenced by the balance between mineralisation and immobilisation as well as temperature, giving particular relevance to organic P forms.

# Acknowledgements

The authors thank James Hobson and members of the Project Limnological Studies in the Semiarid (ELISA) for the laboratory assistance, especially Hérika Cavalcante, Sara Raquel, Keyla Aquino and Daniel Lima. We also thank Victoria Hayes for proofreading the English. This research was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brazil (CAPES).

# References

- ALVARES, C.A., STAPE, J.L., SENTELHAS, P.C., DE MORAES GONÇALVES, J.L. and SPAROVEK, G. Köppen's climate classification map for Brazil. *Meteorologische Zeitschrift*, 2014, 22(6), 711-728. http://dx.doi.org/10.1127/0941-2948/2013/0507.
- ARAÚJO, M.F.F., COSTA, I.A.S. and CHELLAPA, N.T. Comunidade fitoplanctônica e variáveis ambientais na lagoa de Extremoz, Natal-RN, Brasil. *Acta Limnologica Brasiliensia*, 2000, 12, 127-140.
- BEUTEL, M.W. and HORNE, A.J. A review of the effects of hypolimnetic oxygenation on lake and reservoir water quality. *Lake and Reservoir Management*, 1999, 15(40), 285-297. http://dx.doi. org/10.1080/07438149909354124.
- BRAGA, G.G., BECKER, V., OLIVEIRA, J.N.P., MENDONÇA JUNIOR, J.R., BEZERRA, A.F.M., TORRES, L.M., GALVÁO, Â.M.F. and MATTOS, A. Influence of extended drought on water quality in tropical reservoirs in a semiarid region. Acta

- CARPENTER, S.R. Phosphorus control is critical to mitigating eutrophication. *Proceedings of the National Academy of Sciences of the United States of America*, 2008, 105(32), 11039-11040. http://dx.doi. org/10.1073/pnas.0806112105. PMid:18685114.
- CAVALCANTE, H., ARAÚJO, F., NOYMA, N.P. and BECKER, V. Phosphorus fractionation in sediments of tropical semiarid reservoirs. *The Science of the Total Environment*, 2018, 619-620, 1022-1029. http://dx.doi.org/10.1016/j.scitotenv.2017.11.204. PMid:29734580.
- DE FARIA, B.G. Alteração da qualidade do solo em zona ripária sob diferentes usos: potencial de poluição para um manancial tropical. [Dissertação de Mestrado em Ecologia]. Natal: Universidade Federal do Rio Grande do Norte, 2013.
- DE VICENTE, I., HUANG, P., ANDERSEN, F.Ø. and JENSEN, H.S. Phosphate adsorption by fresh and aged aluminum hydroxide. Consequences for lake restoration. *Environmental Science & Technology*, 2008, 42(17), 6650-6655. http://dx.doi. org/10.1021/es800503s. PMid:18800544.
- FIGUEREDO, C.C., PINTO-COELHO, R.M., LOPES, A.M.M.B., LIMA, P.H.O., GÜCKER, B. and GIANI, A. From intermittent to persistent cyanobacterial blooms: identifying the main drivers in an urban tropical reservoir. *Journal of Limnology*, 2016, 75(3), 445-454. http://dx.doi.org/10.4081/ jlimnol.2016.1330.
- GOLTERMAN, H.L. *The chemistry of phosphate and nitrogen compounds in sediments*. New York: Kluwer Academic Publishers, 2004.
- HEISLER, J., GLIBERT, P.M., BURKHOLDER, J.M., ANDERSON, D.M., COCHLAN, W., DENNISON, W.C., DORTCH, Q., GOBLER, C.J., HEIL, C.A., HUMPHRIES, E., LEWITUS, A., MAGNIEN, R., MARSHALL, H.G., SELLNER, K., STOCKWELL, D.A., STOECKER, D.K. and SUDDLESON, M. Eutrophication and harmful algal blooms: A scientific consensus. *Harmful Algae*, 2008, 8(1), 3-13. http://dx.doi.org/10.1016/j. hal.2008.08.006. PMid:28781587.
- HUANG, L., FANG, H., FAZELI, M., CHEN, Y., HE, G. and CHEN, D. Mobility of phosphorus induced by sediment resuspension in the Three Gorges Reservoir by flume experiment. *Chemosphere*, 2015, 134, 374-379. http://dx.doi.org/10.1016/j. chemosphere.2015.05.009. PMid:25978560.
- HUPFER, M. and LEWANDOWSKI, J. Oxygen controls the phosphorus release from lake sediments
   A long-lasting paradigm in limnology. *International Review of Hydrobiology*, 2008, 93(4–5), 415-432. http://dx.doi.org/10.1002/iroh.200711054.

- INSTITUTO NACIONAL DE METEOROLOGIA – INMET. Database of weather station: Natal (RN) [online]. Brasília: INMET; 2019 [viewed 29 May 2019]. Available from: http://www.inmet.gov.br
- INSTITUTO NACIONAL DE METEOROLOGIA – INMET. Database of weather station: Ceará Mirim (RN) [online]. Brasília: INMET; 2020 [viewed 1 November 2020]. Available from: http://www. inmet.gov.br
- JENSEN, H.S. and ANDERSEN, F.O. Importance of temperature, nitrate, and pH for phosphate release from aerobic sediments of four shallow, eutrophic lakes. *Limnology and Oceanography*, 1992, 37(3), 577-589. http://dx.doi.org/10.4319/lo.1992.37.3.0577.
- JENSEN, H.S., REITZEL, K. and EGEMOSE, S. Evaluation of aluminum treatment efficiency on water quality and internal phosphorus cycling in six Danish lakes. *Hydrobiologia*, 2015, 751(1), 189-199. http://dx.doi.org/10.1007/s10750-015-2186-4.
- JEPPESEN, E., MEERHOFF, M., JACOBSEN, B.A., HANSEN, R.S., SØNDERGAARD, M., JENSEN, J.P., LAURIDSEN, T.L., MAZZEO, N. and BRANCO, C.W.C. Restoration of shallow lakes by nutrient control and biomanipulation - The successful strategy varies with lake size and climate. *Hydrobiologia*, 2007, 581(1), 269-285. http://dx.doi. org/10.1007/s10750-006-0507-3.
- JEPPESEN, E., SØNDERGAARD, M., JENSEN, J.P., HAVENS, K.E., ANNEVILLE, O., CARVALHO, L., COVENEY, M.F., DENEKE, R., DOKULIL, M.T., FOY, B., GERDEAUX, D., HAMPTON, S., HILT, S., KANGUR, K., KOHLER, J., LAMMENS, E.H.H.R., LAURIDSEN, T.L., MANCA, M., MIRACLE, M.R., MOSS, B., NOGES, P., PERSSON, G., PHILLIPS, G., PORTIELJE, R., ROMO, S., SCHELSKE, C.L., STRAILE, D., TATRAI, I., WILLEN, E. and WINDER, M. Lake responses to reduced nutrient loading - An analysis of contemporary long-term data from 35 case studies. *Freshwater Biology*, 2005, 50(10), 1747-1771. http://dx.doi.org/10.1111/ j.1365-2427.2005.01415.x.
- JIANG, X., JIN, X., YAO, Y., LI, L. and WU, F. Effects of biological activity, light, temperature and oxygen on phosphorus release processes at the sediment and water interface of Taihu Lake, China. *Water Research*, 2008, 42(8–9), 2251-2259. http://dx.doi.org/10.1016/j.watres.2007.12.003. PMid:18191171.
- JIN, X., WANG, S., PANG, Y. and WU, F.C. Phosphorus fractions and the effect of pH on the phosphorus release of the sediments from different trophic areas in Taihu Lake, China. *Environmental Pollution*, 2006, 139(2), 288-295.
- KIRCHMAN, D.L. The uptake of inorganic nutrients by heterotrophic bacteria. *Microbial Ecology*,

1994, 28(2), 255-271. http://dx.doi.org/10.1007/ BF00166816. PMid:24186453.

- LUKKARI, K., HARTIKAINEN, H. and LEIVUORI, M. Fractionation of sediment phosphorus revisited: I Fractionation steps and their biogeochemical basis. *Limnology and Oceanography, Methods*, 2007, 5, 433-444.
- MEIS, S., SPEARS, B.M., MABERLY, S.C. and PERKINS, R.G. Assessing the mode of action of Phoslock\* in the control of phosphorus release from the bed sediments in a shallow lake (Loch Flemington, UK). *Water Research*, 2013, 47(13), 4460-4473. http://dx.doi.org/10.1016/j.watres.2013.05.017. PMid:23764596.
- MEIS, S., SPEARS, B.M., MABERLY, S.C., O'MALLEY, M.B. and PERKINS, R.G. Sediment amendment with Phoslock<sup>®</sup> in Clatto Reservoir (Dundee, UK): Investigating changes in sediment elemental composition and phosphorus fractionation. *Journal of Environmental Management*, 2012, 93(1), 185-193. http://dx.doi.org/10.1016/j.jenvman.2011.09.015. PMid:22054585.
- MOURA, D.S., LIMA NETO, I.E., CLEMENTE, A., OLIVEIRA, S., PESTANA, C.J., APARECIDA DE MELO, M. and CAPELO-NETO, J. Modeling phosphorus exchange between bottom sediment and water in tropical semiarid reservoirs. *Chemosphere*, 2020, 246, 125686. http://dx.doi.org/10.1016/j. chemosphere.2019.125686. PMid:31918079.
- MURPHY, J. and RILEY, J. A modified single solution method for determination of phosphate in natural waters. *Analytical Chemistry ACTA*, 1962, 27, 31-36. http://dx.doi.org/10.1016/S0003-2670(00)88444-5.
- OLSZEWSKA, J.P., HEAL, K.V., WINFIELD, I.J., EADES, L.J. and SPEARS, B.M. Assessing the role of bed sediments in the persistence of red mud pollution in a shallow lake (Kinghorn Loch, UK). *Water Research*, 2017, 123(15), 569-577.
- PAERL, H.W., XU, H., MCCARTHY, M.J., ZHU, G., QIN, B., LI, Y. and GARDNER, W.S. Controlling harmful cyanobacterial blooms in a hyper-eutrophic lake (Lake Taihu, China): The need for a dual nutrient (N & P) management strategy. *Water Research*, 2011, 45(5), 1973-1983. http://dx.doi.org/10.1016/j. watres.2010.09.018. PMid:20934736.
- PALUDAN, C. and JENSEN, H.S. Sequential extraction of phosphorus in freshwater wetland and lake sediment: Significance of humic acids. *Wetlands*, 1995, 15(4), 365-373. http://dx.doi.org/10.1007/ BF03160891.
- PINTO, T.S. and BECKER, V. Diel dynamic of phytoplankton functional groups in a tropical water supply, Extremoz Lake, northeastern Brazil. *Acta Limnologica Brasiliensia*, 2014, 26(4), 356-366. http:// dx.doi.org/10.1590/S2179-975X2014000400004.

- REITZEL, K., HANSEN, J., ANDERSEN, F.O., HANSEN, K.S. and JENSEN, H.S. Lake restoration by dosing aluminum relative to mobile phosphorus in the sediment. *Environmental Science & Technology*, 2005, 39(11), 4134-4140. http://dx.doi. org/10.1021/es0485964. PMid:15984792.
- REYNOLDS, C.S. and DAVIES, P.S. Sources and bioavailability of phosphorus fractions in frashwaters: a British perspective. *Biological Reviews of the Cambridge Philosophical Society*, 2001, 76(1), 27-64. http://dx.doi.org/10.1017/S1464793100005625. PMid:11325053.
- RIO GRANDE DO NORTE. Governo do Estado.
  Secretaria do Meio Ambiente e Recursos Hídricos

  SEMARH. Ficha Técnica do Reservatório Lagoa de Extremoz [online]. Natal: SEMARH, 2015 [viewed 7 February 2019]. Available from: http://sistemas. searh.rn.gov.br/MonitoramentoVolumetrico/ Monitoramento/FichaTecnica?idReservatorio=1038
- ROY, E.D., NGUYEN, N.T., BARGU, S. and WHITE, J.R. Internal loading of phosphorus from sediments of Lake Pontchartrain (Louisiana, USA) with implications for eutrophication. *Hydrobiologia*, 2012, 684(1), 69-82. http://dx.doi.org/10.1007/s10750-011-0969-9.
- RYDIN, E., MALMAEUS, J.M., KARLSSON, O.M. and JONSSON, P. Phosphorus release from coastal Baltic Sea sediments as estimated from sediment profiles. *Estuarine, Coastal and Shelf Science*, 2011, 92(1), 111-117. http://dx.doi.org/10.1016/j. ecss.2010.12.020.
- SALAS, H. and MARTINO, P. A simplified phosphorus trophic state model for warm-water tropical lakes. *Water Research*, 1991, 25(3), 341-350. http://dx.doi. org/10.1016/0043-1354(91)90015-I.
- SCHAANNING, M., BREYHOLTZ, B. and SKEI, J. Experimental results on effects of capping on fluxes of persistent organic pollutants (POPs) from historically contaminated sediments. *Marine Chemistry*, 2006, 102(1-2), 46-59. http://dx.doi.org/10.1016/j. marchem.2005.10.027.
- SCHINDLER, D.W. The dilemma of controlling cultural eutrophication of lakes. *Proceedings of the Royal Society B: Biological Sciences*, 2012, 279(1746), 4322-4333. PMid:22915669.
- SINGLETON, V.L. and LITTLE, J.C. Designing hypolimnetic aeration and oxygenation systems - A review. *Environmental Science & Technology*, 2006, 40(24), 7512-7520. http://dx.doi.org/10.1021/ es060069s. PMid:17256488.
- SMITH, V.H. and SCHINDLER, D.W. Eutrophication science: where do we go from here? *Trends in Ecology* & *Evolution*, 2009, 24(4), 201-207. http://dx.doi. org/10.1016/j.tree.2008.11.009. PMid:19246117.
- SMOLDERS, A.J.P., LAMERS, L.P.M., LUCASSEN, E.C.H.E.T., VAN DER VELDE, G. and ROELOFS,

J.G.M. Internal eutrophication: How it works and what to do about it — a review. *Chemistry and Ecology*, 2006, 22(2), 93-111. http://dx.doi. org/10.1080/02757540600579730.

- SØNDERGAARD, M., BJERRING, R. and JEPPESEN, E. Persistent internal phosphorus loading during summer in shallow eutrophic lakes. *Hydrobiologia*, 2013, 710(1), 95-107. http://dx.doi. org/10.1007/s10750-012-1091-3.
- SØNDERGAARD, M., JENSEN, J.P. and JEPPESEN, E. Role of sediment and internal loading of phosphorus in shallow lakes. *Hydrobiologia*, 2003, 506–509(1-3), 135-145. http://dx.doi.org/10.1023/ B:HYDR.0000008611.12704.dd.
- SØNDERGAARD, M., JENSEN, P.J. and JEPPESEN, E. Retention and Internal Loading of Phosphorus in Shallow, Eutrophic Lakes. *TheScientificWorldJournal*, 2001, 1, 427-442. http://dx.doi.org/10.1100/ tsw.2001.72. PMid:12806078.
- SØNDERGAARD, M., KRISTENSEN, P. and JEPPESEN, E. Phosphorus release from resuspended sediment in the shallow and wind-exposed Lake Arresø, Denmark. *Hydrobiologia*, 1992, 228(1), 91-99. http://dx.doi.org/10.1007/BF00006480.
- SPEARS, B.M., CARVALHO, L., PERKINS, R., KIRIKA, A. and PATERSON, D.M. Long-term variation and regulation of internal phosphorus loading in Loch Leven. *Hydrobiologia*, 2012, 681(1), 23-33. http://dx.doi.org/10.1007/s10750-011-0921-z.
- SUPLEE, M.W. and COTNER, J.B. An evaluation of the importance of sulfate reduction and temperature to P fluxes from aerobic-surfaced, lacustrine sediments. *Biogeochemistry*, 2002, 61(2), 199-228. http://dx.doi.org/10.1023/A:1020291130333.
- VALDERRAMA, J.C. The simultaneous analysis of total nitrogen and total phosphorus in natural waters. *Marine Chemistry*, 1981, 10(2), 109-122. http:// dx.doi.org/10.1016/0304-4203(81)90027-X.
- WANG, C., ZHANG, Y., LI, H. and MORRISON, R.J. Sequential extraction procedures for the determination of phosphorus forms in sediment. *Limnology*, 2013, 14(2), 147-157. http://dx.doi. org/10.1007/s10201-012-0397-1.
- WANG, S., JIN, X., ZHAO, H. and WU, F. Phosphorus fractions and its release in the sediments from the shallow lakes in the middle and lower reaches of Yangtze River area in China. *Colloids and Surfaces. A, Physicochemical and Engineering Aspects*, 2006, 273(1-3), 109-116. http://dx.doi.org/10.1016/j. colsurfa.2005.08.015.
- WU, Y., WEN, Y., ZHOU, J. and WU, Y. Phosphorus release from lake sediments: Effects of pH, temperature and dissolved oxygen. *KSCE Journal* of *Civil Engineering*, 2014, 18(1), 323-329. http:// dx.doi.org/10.1007/s12205-014-0192-0.

- XU, D., DING, S., LI, B., BAI, X., FAN, C. and ZHANG, C. Speciation of organic phosphorus in a sediment profile of Lake Taihu I: Chemical forms and their transformation. *Journal of Environmental Sciences (China)*, 2013, 25(4), 637-644. http:// dx.doi.org/10.1016/S1001-0742(12)60136-3. PMid:23923771.
- ZHANG, Y. HE, F., KONG, L., LIU, B., ZHOU, Q., WU, Z. Release characteristics of sediment P in all fractions of Donghu Lake, Wuhan, China. *Desalination and Water Treatment*, 2016, 57(53), 25572-25580.
- ZHU, Y., ZHANG, R., WU, F., QU, X., XIE, F. and FU, Z. Phosphorus fractions and bioavailability in relation to particle size charactaristics in sediments from lake Hongfeng, Southwest China. *Environmental Earth Sciences*, 2012, 68(4), 1041-1052. http://dx.doi. org/10.1007/s12665-012-1806-9.

Received: 23 September 2020 Accepted: 01 March 2021

Associate Editor: André Megali Amado.