Internal phoshorus loading potential of a semiarid reservoir: an experimental study

Potencial de fertilização interna de fósforo de um reservatório semiárido: um estudo experimental

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Abstract: Aim: To determine the internal P loading potential of semiarid tropical reservoir sediment while verifying the driving factors that affect P release rates. Methods: An experiment was performed with water and sediment from the reservoir Boqueirão de Parelhas in Brazil. The effects of three variables on P release were studied: air temperature (region average of 28 °C and 32 °C, simulating an increase of 4 °C), pH (region average of pH 8, more acidic pH 6 and more alkaline pH 10) and oxygen (presence and absence). In addition, P fractionation analysis was performed on the P forms in the sediment. Results: It was found that the minimum P release was in an oxic treatment at pH 6 and temperature 28 °C (0.22 mg m⁻² d⁻¹ ± 0.13) and the maximum P release in an anoxic treatment at pH 10 and temperature 32 °C (2.1 mg m⁻² d⁻¹ ± 0.15). The total P in the sediment was 597 mg kg⁻¹, and the major P form in the sediment was NaOH-rP, the P bound to aluminum, corresponding to 42% of the total P. Conclusion: These results allow us to confirm that the sediment of the Boqueirão reservoir is susceptible to the release of P bound to aluminum due to the prevalence of this form in its sediments concomitant with the high temperatures and alkaline pH of the water. This scenario can be aggravated by climate change.

Keywords: eutrophication; phosphorus fractionation; internal loading; temperature increase.

Resumo: Objetivo: Determinar o potencial de fertilização interna de P do sedimento de reservatório tropical semiárido, ao mesmo tempo em que verificar os fatores que afetam as taxas de liberação de P. Métodos: Foi realizado um experimento com água e sedimento do reservatório Boqueirão de Parelhas, Brasil. Foram estudados os efeitos de três variáveis na liberação de P: temperatura do ar (região média de 28 °C e 32 °C, simulando aumento de 4 °C), pH (região média de pH 8, pH mais ácido 6 e pH mais alcalino 10) e oxigênio (presença e ausência). Além disso, a análise de fracionamento de P foi realizada nas formas de P no sedimento. Resultados: Verificou-se que a liberação mínima de P foi em tratamento óxico em pH 6 e temperatura 28 °C (0,22 mg m⁻² d⁻¹ ± 0,13) e a liberação máxima de P em tratamento anóxico em pH 10 e temperatura 32 °C (2,1 mg m⁻² d⁻¹ ± 0,15). O P total no sedimento foi 597 mg kg⁻¹, e a principal forma de P no sedimento foi o NaOH-rP, o P ligado ao...
1. Introduction

Eutrophication is a global problem that causes damage to aquatic ecosystems. This process involves the enrichment of nutrients in water, generally phosphorus (P) and nitrogen (N), resulting in phytoplankton growth, especially of potentially toxic cyanobacteria, and the alteration of the structure and function of these ecosystems (Dodds, 2006). Concentrations of P can be controlled more easily than nitrogen, so eutrophication generally control has focused on P (Smith & Schindler, 2009).

Whole-lake experiments have shown that a reduction in P inputs can cause a successful reversal of lake eutrophication (Schindler, 2012). However, in some cases, a delay in recovery has been observed because lake sediments can act as a P source: the P accumulated in the sediment can return to the water column through a process called internal loading (Søndergaard et al., 2001). The release of P from sediments can contribute significantly to the amount of bioavailable P in lake water, feeding the eutrophication process. In external loading, P enters the system largely in particulate form, which is not directly used by phytoplankton; however, with internal loading, the P is predominantly in inorganic dissolved form, which is directly available for algal growth (Nurnberg, 2009; Bormans et al., 2016).

Usually, internal loading can be attributed to the dissolution of P adsorbed to iron oxides and hydroxides on sediment, which return P to the water column under anoxic conditions (Mortimer, 1941), or the release of P from organic compounds (Gächter & Meyer, 1993) and polyphosphates in hypereutrophic sediments (Hupfer & Lewandowski, 2008). However, the phenomenon of P release from sediment is complex and involves others factors beyond redox potential such as pH and temperature (Søndergaard et al., 2001, 2003).

The pH of the water-sediment interface is a factor that can affect sorption-adsorption, precipitation-dissolution and oxidation-reduction reactions, exerting control over available iron, aluminum and calcium concentrations and influencing P release from sediment (Christophoridis & Fytianos, 2006; Jiang et al., 2008). Increasing pH may release P bound to metal complexes due to competition between hydroxyl ions and the phosphate ions bound to these metals (Dong et al., 2011), while decreasing pH may influence the dissolution of calcium and apatite, causing the release of the P previously bound to these compounds (Golterman, 2001).

From classic investigations (Jensen & Andersen, 1992) to the more recent studies (Wang et al., 2015), the importance of temperature in P release has been demonstrated. An increase in temperature accelerates chemical processes, increases the chemical diffusion rate (Søndergaard, 2007) and can stimulate the mineralization of organic matter in sediment, causing inorganic phosphate release (Boström & Pettersson, 1982). Temperature also has a direct impact on the amount of available oxygen because the solubility of oxygen in water depends on temperature (Wetzel, 2001). The temperature can also lengthen and intensify the stratification periods of lakes, increasing anoxia conditions, thus stimulating the diffusion of P from sediments with redox sensitive P dynamics (Mosley, 2015). Because of this, regions with high temperatures, such as in semiarid regions, are more susceptible to internal P loading.

P can be present in sediment in several forms or fractions as it has an affinity for various organic and inorganic compounds. The analysis of P forms in sediment occurs through a sequential procedure known as fractionation that uses various extraction solutions. In decreasing order of potential bioavailability or mobility, P fractions can be characterized as follows: P still present in sediment is complex and involves others factors beyond redox potential such as pH and temperature (Søndergaard et al., 2003). Knowing the P fractions in sediment in detail rather than simply the total P (TP) is essential as TP cannot correctly predict the potential of sediment as a source of internal loading (Rydin, 2000).

Brazilian semiarid regions have been characterized by high temperatures and annual low precipitation levels that occur in a concentrated manner (Silva et al., 2010; Barbosa et al., 2012). Those
characteristics can result in an intensification of the eutrophication process and lead to a consequent increase in the occurrence of cyanobacterial blooms, rendering waters unfit for consumption and irrigation (Huszar et al., 2000; Medeiros et al., 2015; Brasil et al., 2016). In recent years, extreme events such as prolonged droughts have occurred with greater severity, and the period between them appears to have become shorter in some regions (Mishra & Singh, 2010; Moss, 2014). Semi-arid regions are highly vulnerable to droughts, and climate change scenarios indicate that these regions will be affected by rainfall deficits and increased aridity in the second half of 21st century (IPCC, 2014; Marengo et al., 2018), causing fluctuations in water levels and nutrient concentrations that can further intensify eutrophication symptoms (Moss, 2014).

The scenario in Brazilian semi-arid regions makes it important to take measures to control eutrophication, which require good knowledge about the dynamics of phosphorus in the lake. However, the region still has scarcity of data, mainly on P content in the sediment and how the release of P behaves in the face of the variation of the main factors that influence it. In light of prior reports and in order to better understand how this system functions, the aim of this study was to determine the internal P loading potential of a semi-arid tropical eutrophic reservoir while verifying the driving factors that affect P release rates.

2. Methods

2.1 Study site

This study was performed with water and sediment from the Boqueirão de Parelhas reservoir located in the Piranhas-Açu watershed of the Northeast Region of Brazil (Figure 1). According to the reservoir’s datasheet, available on the website of the Secretariat of environment and water resources of Rio Grande do Norte State (SEMARH), Boqueirão reservoir was built in 1988, has a maximum capacity of 84.8 million m$^3$, 29 m maximum depth and has multiple uses, with priority given to human water supply.

The climate of the region is described by Köppen’s climate classification as BSh: dry, semi-arid and low latitude and altitude (Alvares et al., 2014); with average temperature between 23 and 28 °C and annual precipitation between 400 and 800 mm (Silva et al., 2010; Barbosa et al., 2012). The predominant soil in the watershed is classified as Litholic Neosoil, which is characterized by being...
a young soil, poorly devolved genetically, small thickness and elevated sandy activity (Embrapa, 2018).

2.2 Samplings

Water and sediment samples were collected at a point near the reservoir dam and the water catchment tower for the human supply (Figure 1). Sediment cores of 10 cm were sampled in March 2018 using a manual Kajak core sampler (50 cm long, 7 cm in diameter). This core depth (10 cm) was chosen because it is used in several other studies (Reitzel et al., 2003, 2005; Jensen et al., 2015). Water samples were collected, through a Van Dorn bottle, monthly, between November 2017 and March 2018 at the surface and at the bottom, for the physical and chemical water characterization. For the Sediment phosphorus release experiment only bottom water was utilized, collected in March 2018. All samples (sediment and water) were closed, left in the dark and transported to the laboratory at room temperature.

2.3 Water sample analysis

The following variables were measured in situ: water depth, with a depth gauge; water temperature and dissolved oxygen (every meter of the water column), with oximeter (Instrutherm MO-900). The volume data stored in the reservoir were obtained from the SEMARH-RN website. Upon arriving at the laboratory, the following variables were measured: pH, with pHmeter (BEL W3B); soluble reactive P (SRP), by ascorbic acid method after filtration with cellulose membrane (Ø=0.45 µm), followed by spectrophotometry (Murphy & Riley, 1962); total P (TP), by oxidation with potassium persulfate (Valderrama, 1981) followed by ascorbic acid method and spectrophotometry (Murphy & Riley, 1962); chlorophyll-a (Chl-a), extracted after glass fiber membrane filtration (Ø=1.2 µm) with 95% ethanol (Jespersen & Christoffersen, 1988).

2.4 Sediment sample analysis

The P forms in the sediment were analyzed according the methodology described by Cavalcante et al. (2018). This method uses a sequential chemical extraction process called fractionation and determines seven P forms: (1) Water-P or porewater-P, extracted with anoxic water (by introduced N₂) and representing a more labile fraction present in the interstitial water in sediment; (2) BD-P, extracted with a solution of bicarbonate and sodium dithionite and representing P forms sensitive to low redox potential, such as P adsorbed on the surface of iron (Fe) and manganese (Mn); (3) NaOH-rP, extracted with a sodium hydroxide solution, representing the P exchangeable with OH⁻, mainly aluminum, but also inside iron oxides. Also extracted in this step and detected after digestion, is (4) NaOH-nrP, organic-P including bacteria-incorporated-P; still in this step is formed after acidification with sulfuric acid, a precipitate interpreted as (5) Humic-P, P bound to humic substances; (6) HCl-P, extracted with a hydrochloric acid solution, P forms sensitive to low pH, assumed to consist mainly of calcium and apatite; and (7) Residual-P, consisting mainly of refractory organic P and the inert inorganic P, considered to be non-mobile.

2.5 Sediment phosphorus release experiment

To evaluate the P release rate from the sediment to the water column, 150 g of the 10 cm of the sediment and 900 ml of bottom water were introduced into sealed glass vessels for 21 days. The water had been previously filtered (Ø=0.6 µm) to remove planktonic organisms, and to avoid oxygen generation by photosynthetic organisms, the recipients were kept in the dark.

The effects of three variables on P release were studied: i) air temperature (controlled by incubators), ii) pH (controlled by HCl or NaOH titration) and iii) DO (controlled by N gas injection or aeration through bombs). The temperatures used in the incubators were 28°C, chosen as an annual average reservoir temperature based on data from the Empresa Brasileira de Pesquisa Agropecuária (Silva et al., 2010), and 32°C, simulating a 4°C increase over the average value based on a pessimistic scenario from the IPCC (IPCC, 2014). The pH values were pH 8 used as an average for the water and based on the characterization of a semiarid region (Barbosa et al., 2012), pH 6 as more acidic than average and pH 10 as more alkaline than average. The DO conditions were anoxic conditions (ANOX), with DO less than 1 mg L⁻¹ and the samples kept in a closed beaker covered with plastic film, and oxic conditions (OXI), with DO higher than 5 mg L⁻¹. In summary, the experiment had a factorial design of 2 x 3 x 2 (temperature x pH x oxygen condition), in which 12 treatments were done in triplicate for a total of 36 experimental units.

Aliquots (20 ml) for the SRP analysis were taken on days: 0 (initial conditions, before water insertion), 1 (24 hours after water insertion), 7, 14 and 21. On the days of aliquot collection, the
variables of water temperature, pH and DO were measured only for verification and to ensure the experimental conditions. The removed water was replaced with filtered (Ø=0.6 µm) reservoir water (kept in incubators together with the microcosms). Based on the TP concentrations in the water per the day of analysis, it was possible to calculate the P flux from the sediment to the water, that is, the release rate of the P (Equation 1) (He et al., 2017).

\[ P_{\text{flux}} = \frac{(C_i - C_t)V}{A t} \times 1000 \]

\[ P_{\text{flux}} = \text{P flux from the sediment to the water (mg m}^{-2}\text{d}^{-1}) \]

\[ C_i = \text{P concentration in the water at time “t” (µg L}^{-1}) \]

\[ C_t = \text{Initial P concentration in the water (µg L}^{-1}) \]

\[ V = \text{Water volume = 0.9 L} \]

\[ A = \text{Sediment surface area in the beaker or beaker base area} = 0.008 \text{ m}^{-2} \]

\[ t = \text{Experiment duration time} = 21 \text{ days} \]

2.6 Statistical analyses

To verify the significant effects of temperature, pH and oxygen level and their interaction with the P release rate, a three-way ANOVA was performed. This was followed by Tukey’s multiple comparison tests. Normality and homoscedasticity were assessed using Kolmogorov-Smirnov and Levene’s tests, respectively. Statistical analyses were performed using R Software for Windows, considering a significance level of 5%.

3. Results

During the sampling period for this study, water volume was around 19 million m³, which corresponds to 23% of the maximum capacity (Table 1). This reduced the reservoir’s surface area (Figure 1) and the depth of the sampling point, which was approximately 10 m (Table 1). In addition, the water from the reservoir showed high temperature, low oxygen (without anoxic conditions), alkaline pH, high total phosphorus, high reactive phosphorus and high chlorophyll-a (Table 1).

The results of the experiment showed an increase in P concentration in the water of each sample treatment throughout the experiment period (Figure 2). The largest increase was observed between days 7 and 14. After that, there was a decrease or stabilization in the amount of P in the water for some of the treatments, and so day 21 was chosen as the last day of aliquot collection for analysis. The driving factors affecting P release rates were high pH and temperature, as the highest P release rates were in the treatments with pH 10 mainly at 32 °C (Figure 2c and d).

All treatments showed positive P release rates during the 21 days of the experiment (Figure 3). P release increased proportionally to an increase in pH (F(1,24) = 77; p < 0.0001) and temperature (F(1,24) = 38.6; p < 0.0001) and under anoxic conditions (F(1,24) = 21; p = 0.001), with significant interaction between pH x temperature (F(1,24) = 5; p = 0.0019), pH x oxygen (F(1,24) = 4; p = 0.033) and temperature x oxygen (F(1,24) = 4.6; p = 0.042). The lowest release rate was in the pH 6 OXI 28°C treatment (0.22 mg m⁻² d⁻¹ ± 0.13) and the highest in the pH 10 ANOX 32°C treatment (2.1 mg m⁻² d⁻¹ ± 0.15).

The results for the P fractionation before the experiment (PBE) showed that there was a pool of 594 mg of P per kilogram of sediment in the Boqueirão reservoir (Figure 4). The decreasing order of P forms was: NaOH-P (250 mg kg⁻¹, 42%) > BD-P (120 mg kg⁻¹, 20%) > NaOH-nrP (83.3 mg kg⁻¹, 14%) > HCl-P (61.8 mg kg⁻¹, 10%) > residual-P (40 mg kg⁻¹, 7%) > humic-P (22.9 mg kg⁻¹, 4%) > water-P (15.8 mg kg⁻¹, 3%). NaOH-P was the major fraction in the sediment, with an average value greater than double the second most prevalent form. P values after the experiment were slightly reduced in some treatments but were not significantly different from the results prior to the experiment either in mass or percentage (Figure 4).

Table 1. Mean, minimum (Min), maximum (Max) and standard deviation (SD) of physicochemical variables and chlorophyll-a in Boqueirão reservoir water analyzed monthly from November 2017 to March 2018.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mean (%)</th>
<th>Min (%)</th>
<th>Max (%)</th>
<th>Sd (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stored volume (%)</td>
<td>23%</td>
<td>11%</td>
<td>42%</td>
<td>15%</td>
</tr>
<tr>
<td>Water depth (m)</td>
<td>10</td>
<td>8</td>
<td>12</td>
<td>2</td>
</tr>
<tr>
<td>Water Temperature (°C)</td>
<td>29</td>
<td>28</td>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td>Dissolved Oxygen (mg L⁻¹)</td>
<td>4.8</td>
<td>1.6</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>pH</td>
<td>8.2</td>
<td>7.3</td>
<td>9.2</td>
<td>0.9</td>
</tr>
<tr>
<td>Total Phosphorus (µg L⁻¹)</td>
<td>74.6</td>
<td>52</td>
<td>153</td>
<td>65</td>
</tr>
<tr>
<td>Soluble Reactive Phosphorus (µg L⁻¹)</td>
<td>56</td>
<td>14</td>
<td>97</td>
<td>32</td>
</tr>
<tr>
<td>Chlorophyll-a (µg L⁻¹)</td>
<td>77</td>
<td>22</td>
<td>197</td>
<td>81</td>
</tr>
</tbody>
</table>
During the period studied, Boqueirão presented a low stored volume, around 20% of the water maximum capacity, following the trend of several other reservoirs in semiarid regions. This reduction occurred due a prolonged drought event that region experienced during 2012 to 2016 (Marengo et al., 2018). The water quality of these environments also
decreased considerably in this period (Figueiredo & Becker, 2018; Rocha Junior et al., 2018; Leite & Becker, 2019). Some years earlier, Boqueirão reservoir was considered oligotrophic, and since 2014 the eutrophication process has begun to intensify (Mendonça-Júnior et al., 2018). Actually, according to the total phosphorus (TP) and Chlorophyll-a analyzed in this study, the reservoir is eutrophic by Thornton & Rast (1993) classification. In addition, the experimental results showed that the sediment from the Boqueirão has a potential for P release, further worsening the eutrophication of the environment.

The values of P release rates found in this study (0.22 – 2.1 mg m\(^{-2}\) d\(^{-1}\)) were lower than the P flux found in recent studies: in Jacarepaguá Lagoon, Brazil (2.5 – 9.2 mg m\(^{-2}\) d\(^{-1}\)) (Marinho et al., 2020); in two semiarid reservoirs, Brazil (4 and 10 mg m\(^{-2}\) d\(^{-1}\)) (Moura et al., 2020); and lake Diefenbaker, Canada (15 – 20 mg m\(^{-2}\) d\(^{-1}\)) (Doig et al., 2017). However, the rates of this study were similar to the values found in hypereutrophic lakes in China, as Yangcheng (1.1 to 1.5 mg m\(^{-2}\) d\(^{-1}\)) (Yang et al., 2020b) and Lake Chaohu (0.03 to 3.34 mg m\(^{-2}\) d\(^{-1}\)) (Yang et al., 2020a); and higher than other environments also in China: wetlands sediments (0.002 to 0.014 mg m\(^{-2}\) d\(^{-1}\)) (He et al., 2017) and Yangtze river (0.105 to 0.143 mg m\(^{-2}\) d\(^{-1}\)) (Zhu et al., 2012). This variation in values of sediment release rates demonstrates how complex the internal loading process is, which can be the result of many variables: pollution level of environment (external loading), soil composition, water physicochemical parameters, sedimentation rates and other factors.

The main aim of this study was to verify the driving factors of the P release rates. Of the three variables analyzed (OD, pH and temperature), pH had the greatest influence on P release. All pH values (6, 8 and 10) tested in this study showed a positive P release, but it was lower in pH 6 and higher in pH 10. Previous studies have demonstrated that P release occurs under both acidic and alkaline conditions, but the release is greater in alkaline (Jin et al., 2006; Li et al., 2013; Yang et al., 2020a), which we also found in this study.

The surface charge properties of soil particles are altered by pH, changing their aggregation and cohesion behavior (Illés & Tombácz, 2006). Under acidic conditions, there is no aggregation or sedimentation as the particles are negatively charged. This scenario is conducive to the release of the P linked to calcium and apatite as acidic pH increases the dissolution of these compounds (Golterman, 2001). However, this P form is a relatively stable fraction and has been attributed to the permanent burial of P in sediments (Gonsiorczyk et al., 1998). Under neutral conditions, an electric equilibrium occurs, decreasing release. However, pH interferes more greatly in the release of metal-bound P, such as on iron and aluminum, under mainly alkaline conditions (Kim et al., 2003). Under alkaline conditions, the capacity for P to bind to iron and aluminum compounds is decreased due to ion exchange reactions in which hydroxide (OH\(^{-}\)) ions replace orthophosphate ions because OH\(^{-}\) has a stronger coordination competition capacity than phosphate, which is then released to the water column (Wang et al., 2015). That is most likely what happened in this study due to the predominance (42%) of the NaOH-rP form in the sediment. NaOH-rP represents the P bound to aluminum oxide surfaces and inside iron oxides, and under high pH conditions, this P can be exchanged with OH\(^{-}\) and released to the water column (Kozerski & Kleeberg, 1998).

Increasing the temperature also significantly increased the P-release rate. Temperature can interfere with internal loading in several ways: accelerate chemical processes, increase diffusion rates, stimulate mineralization of organic matter and solubilize oxygen in water (Jensen & Andersen, 1992; Gächter & Meyer, 1993; Coffman & Kildsig, 1996; Cornelissen et al., 1997). In this study, the greatest P release was at 32 °C, which may be due to the increased intensity in the coordination competition between the OH\(^{-}\) and phosphate of the NaOH-rP form, which was also found by Wang et al. (2015). In addition, the temperature presented a significant interaction with pH, proving that there was a synergistic relationship between these factors: increasing temperature and pH promoted the release of P in this experiment, most likely from the NaOH-rP fraction because this fraction is the most affected by alkaline pH and high temperatures.

The DO factor did not interfere as much as the other factors: P release was only slightly increased when conditions were anoxic. Oxygen level is an important factor in the P release process, affecting mainly the P forms considered more mobile: water-P, BD-P and NaOH-nrP (Rydin, 2000). The water-P is the loosely bound form on the surface of sediment or in interstitial water and considered immediately available (Hupfer & Lewandowski, 2008). BD-P is the P bound to reducible forms of iron and manganese. NaOH-nrP corresponds to...
organic forms of P such as polyphosphates, which can be released from bacterial cells (Gächter et al., 1988), or phytate (inositol hexaphosphate), which is strongly adsorbed to iron oxides and can be mobilized when exposed to anoxic conditions (De Groot & Golterman, 1993). However, oxygen level has not shown a fundamental role in the P release from the Boqueirão reservoir sediment, possibly due to the low values of the P forms considered mobile (water – 3%, BD – 20% and NaOH-nrP – 14%) in comparison to the NaOH-rP. This fact can demonstrate that the concept of “potentially mobile P” depends on the studied environment.

In restoration projects or studies aimed at reducing the internal loading, some products, such as clays or other material with an affinity for P, can be applied over the sediment, in order to form a layer that prevents the P release (Mackay et al., 2014). Most of the time, these products are dosed based on the amount of “potentially mobile P”, which is the sum of water-P, BD-P, and NaOH-nrP, since these fractions are considered the P that can be released during anoxic periods and by degradation of organic matter (Reitzel et al., 2005; Vicente et al., 2008). The concept of “potentially mobile P” was developed based on studies of the environments with characteristics different to tropical semiarid reservoirs. In a study about dosing aluminum relative to mobile P, realized in a Denmark Lake, Reitzel et al. (2005) suggest that the development of the concept of “potentially mobile P” to other sediment types provide important information regarding the source for internal P loading, and thereby this concept is an important tool in lake management. The results of this study suggest that Boqueirão reservoir sediments are susceptible to release of NaOH-rP content due to natural alkaline pH (mean 8) and elevated water temperature (mean 29 °C). In practical terms, this means that the amount of NaOH-rP should be considered when calculating the dosage of products for application in environments with similar characteristics, especially in the tropical semiarid, a region with limited data about internal loading and where the “potentially mobile P” concept may still needs to be developed.

Even with an increase in the concentration of P in the water column of treatments, there were no significant differences between the P-form values in the sediment before and after the experiment as estimated by fractionation. This is most likely because the amount of P released in 21 days was much less than the amount in the sediment. However, the release of P from sediment can sustain the concentrations of nutrients in overlying water thereby inducing the blooming of algae (Yang et al., 2020a). In this study, the results showed that for the water, there was already been a significant increase in the P during the experiment days. Under natural conditions, this P can be quickly incorporated by primary producers in just 21 days, mainly in shallow water bodies. This feeds the eutrophication process and worsens over years of internal loading. It is well established that sediment P is an important internal P source until the pool of accumulated and releasable P decreases or is deeply buried and permanently in sediment (Søndergaard et al., 2013). Moreover, internal P loading may be very persistent and even after meaningful reductions in external loading, it can still last for at least 10–15 years (Jeppesen et al., 2005).

The amount of P in the Boqueirão sediment can be considered high, despite being lower than the values found for other reservoirs in the same basin (Cavalcante et al., 2018), which can be justified by the age of reservoir. An experimental study with sediment from three Brazilian Semiarid reservoirs was able to develop a model to describe the effect of the age of the reservoir on the concentration of P bound to iron and aluminium (Moura et al., 2020). According to the linear relationship found by Moura et al. (2020), a reservoir 30 years old reservoir (i.e. Boqueirão age) should have an amount of P bound to iron and aluminium of approximately 510 mg kg⁻¹, which matches the amount found in this work, a mean of 453 mg kg⁻¹. The reservoirs studied by Cavalcante et al. (2018), located in the same basin that Boqueirão, which is between 60 and 90 years, therefore, they presented higher P values. It is worth mentioning that, although the Moura et al. (2020) model seems to adjust to the quantification of P-Fe/Al according to the age of the reservoirs in the semiarid region, the amount of P in the sediment may still depend on sedimentation rates and local soil composition (Gonsiorczyk et al., 1998; Kaiserli et al., 2002).

The region around the contribution basin of the Boqueirão reservoir, more specifically the municipalities of Parelhas (Rio Grande do Norte State) and Pedra Lavrada (Paraíba State), have a consolidated ceramic industry. The soils in the region, from which the raw materials used in the consolidated industries are extracted, are commonly rich in such as kaolinite, mineral with high alumina (Al₂O₃) content (Dutra et al., 2008; Formiga et al., 2013; Silva et al., 2013; Ramos et al., 2019). Studies show that P adsorption can happen intensely in soils
with an abundance of kaolinite (Novais et al., 2007; Vilar et al., 2010). Therefore, the high P bound to aluminium (NaOH-rP) value in the Boqueirão sediment may be associated with high amounts of kaolinite from the soils in the region.

In summary, this study provides information on the internal loading potential of a tropical semi-arid reservoir, a region that has a scarcity of studies on this topic. In addition, despite having P inputs from point sources, most P inputs in reservoirs in the studied region are diffuse, coming from sources such as cropland and pastureland cover and entering the water body by allochthonous runoff during sporadic rainy events (Nobre et al., 2020). However, in the periods of drought experienced by the region, diffuse inputs are practically nonexistent, so internal loading ends up having an even greater importance. This scenario can be further aggravated by climate change. The IPCC has indicated four scenarios for global temperature increase, including among them one of approximately 4° C, which was the scenario simulated in the experiment of this study. If these forecasts are confirmed, there may be a major impact on the internal P loading of aquatic environments, increasing autochthonous materials especially in warmer regions such as semi-arid (Roland et al., 2012). Thus, this work provides basic support for attempts to reduce or control P release from sediments in environments with characteristics similar to the studied environment. It is worth mentioning that however similar the characteristics may be, each lake is unique, and the mitigation should be a tailor made solution (Björk, 1972; Lürling & Van Oosterhout, 2013), and so it is necessary to understand each specific aquatic environment.

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