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**FATE OF PHOSPHORUS AND ITS POTENTIAL OF INTERNAL RECHARGE  
IN TROPICAL RESERVOIRS**

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DIANA SOUZA MOURA

FATE OF PHOSPHORUS AND ITS POTENTIAL OF INTERNAL RECHARGE IN  
TROPICAL RESERVOIRS

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DIANA SOUZA MOURA

FATE OF PHOSPHORUS AND ITS POTENTIAL OF INTERNAL RECHARGE IN  
TROPICAL RESERVOIRS

Master thesis presented to the Graduate Program in Civil Engineering at the Federal University of Ceará, as a partial requirement to obtain the title of Master in Civil Engineering. Concentration area: Environmental Sanitation.

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PANEL

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## RESUMO

O fósforo tem sido vastamente reconhecido como o nutriente limitante da produtividade primária. Além da recarga externa de nutrientes pela ação antrópica, a recarga interna do sedimento para a coluna d'água pode contribuir significativamente para o incremento do estado trófico da água. Afim de investigar o potencial de liberação do fósforo (P) para a coluna d'água, este estudo realizou o fracionamento químico sequencial do fósforo inorgânico ( $P_I$ ) do sedimento de superfície de sete reservatórios localizados em bacia hidrográfica situada em Quixeramobim – CE. Sabendo que as frações de P comportam-se completamente diferentes em contato com a água, o  $P_I$  foi fracionado em fósforo móvel ( $P_M$ ), fração solúvel considerada disponível para a coluna d'água, fósforo ligado a ferro e alumínio ( $P_{FeAl}$ ), disponível em condições anóxicas, fósforo ligado a cálcio ( $P_{Ca}$ ) e fósforo residual ( $P_{Re}$ ), estes últimos considerados indisponíveis. Após o fracionamento químico, microcosmos contendo sedimento de três reservatórios e água natural foram construídos, e experimento foi realizado com a ausência e a presença de oxigênio, respectivamente. Foi possível observar que o sedimento do reservatório mais a montante da bacia hidrográfica, R#1, apresentou as maiores concentrações de fósforo total, e em sua forma mais disponível ( $P_{FeAl}$ ), confirmando o alto potencial de interferência na qualidade de água ao apresentar liberação de aproximadamente de  $2500 \mu\text{g.L}^{-1}$  TP na coluna d'água do microcosmo, não retornando as condições iniciais após a fase de aeração (fase reconhecida pela imobilização do P). Fatores como idade, elevação e armazenamento de água contribuíram diretamente com a quantidade e a forma de fósforo armazenada no sedimento dos reservatórios. Como por exemplo, o R#4, um dos mais recentes reservatórios construídos na bacia estudada, apresentou as menores concentração de  $P_T$  no sedimento e fração menos disponível ( $P_{Re}$ ) predominante. Além disso, este reservatório não apresentou liberação significativa de P para coluna d'água. A liberação e imobilização do fósforo não apresentou significativa diferença na velocidade, contudo a primeira estabilizou-se posteriormente a segunda. Em ambas etapas, a solubilização e a precipitação do P ocorreram majoritariamente nos primeiros dias em que a condição anóxica ou aeróbica foi estabelecida.

**Palavras-chave:** Fracionamento químico. Condição anóxica. Sedimento.

## ABSTRACT

Phosphorus has been widely recognized as the limiting nutrient of primary productivity. In addition to the external recharge of nutrients by the anthropic action, the internal recharge of the sediment to the water column may contribute significantly to the increase of the trophic level of the water. In order to investigate the phosphorus (P) release potential to the water column, this study carried out the sequential chemical fractionation of the inorganic phosphorus ( $P_I$ ) of the surface sediments of seven reservoirs located in a watershed located in Quixeramobim – CE. Knowing that the fractions of P behave completely different in contact with water, the  $P_I$  was fractionated into mobile phosphorus ( $P_M$ ), a soluble fraction considered available for the water column, aluminium-bound phosphorus ( $P_{FeAl}$ ), available under anoxic conditions, calcium-bound phosphorus ( $P_{Ca}$ ) and residual phosphorus ( $P_{Re}$ ), the last ones considered unavailable. After chemical fractionation, microcosms containing sediment from three reservoirs and natural water were constructed, and an experiment was performed with the absence and presence of oxygen, respectively. It was observed that the sediment of the reservoir most upstream of the watershed, R#1, presented the highest concentrations of total phosphorus, and the most available form of P ( $P_{FeAl}$ ), confirming the high potential of water quality interference when it presented a release of approximately  $2500 \mu\text{g.L}^{-1}$  TP in the water column of the microcosm. Not returning to the initial conditions after the aeration phase (phase responsible for the immobilization of P). Factors such as age, elevation and storage of water contributed directly with the quantity and the form of phosphorus stored in the reservoir sediment. Following this conclusion, the R#4, one of the most recent reservoirs built in the studied watershed, had the lowest concentration of  $P_T$  in the sediment and the least available fraction ( $P_{Re}$ ). In addition, this reservoir did not show significant release of P to the water column. The release and immobilization of phosphorus did not present a significant difference in reaction kinetics, but the first reservoir (R#1) stabilized after the second one (R#4). In both stages, solution and P precipitation occurred mostly in the first days of the anoxic or aerobic conditions being established.

**Keywords:** Chemical fractionation. Anoxic condition. Sediment.

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## LIST OF ABBREVIATIONS

|                         |  |
|-------------------------|--|
| <b>ANOVA</b>            | Analysis of variance   |
| <b>CAGECE</b>           | Companhia de Água e Esgoto do Ceará – Water and Waste Water Company of Ceará             |
| <b>CE</b>               | Ceará  |
| <b>COGERH</b>           | Companhia de Gestão de Recursos Hídricos – Company for the Management of Water Resources |
| <b>DO</b>               | Dissolved oxygen   |
| <b>OP</b>               | Dissolved phosphorus/ Orthophosphate   |
| <b>P</b>                | Phosphorus   |
| <b>P<sub>Ca</sub></b>   | Calcium-bound phosphorus from sediment   |
| <b>P<sub>FeAl</sub></b> | Iron-aluminium-bound phosphorus from sediment  |
| <b>P<sub>I</sub></b>    | Inorganic phosphorus from sediment   |
| <b>P<sub>M</sub></b>    | Mobile phosphorus  |
| <b>P<sub>O</sub></b>    | Organic phosphorus from sediment   |
| <b>P<sub>Re</sub></b>   | Resistant phosphorus/residual phosphorus from sediment                                   |
| <b>P<sub>T</sub></b>    | Total phosphorus from sediment   |
| <b>R#1</b>              | Reservoir #1 – Lagoa Cercada Reservoir/ Açude Lagoa Cercada                              |
| <b>R#2</b>              | Reservoir #2 – Riacho do Algodão Reservoir/ Açude Riacho do Algodão                      |
| <b>R#3</b>              | Reservoir #3 – Riacho Verde Reservoir/ Açude Riacho Verde                                |
| <b>R#4</b>              | Reservoir #4 – Cachoeira Reservoir/ Açude Cachoeira                                      |
| <b>R#5</b>              | Reservoir #5 – Chagas Manu dam/ Barreiro Chagas Manu                                     |
| <b>R#6</b>              | Reservoir #6 – Quandú Reservoir/ Açude Quandú  |
| <b>R#7</b>              | Reservoir #7 – Balanças Reservoir/ Açude Balanças  |
| <b>SMT</b>              | Standards, measurements and testing  |
| <b>SRP</b>              | Soluble reactive phosphorus  |
| <b>TP</b>               | Total phosphorus   |
| <b>UFC</b>              | Universidade Federal do Ceará – Federal University of Ceará                              |

## SUMMARY

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## 1 GENERAL INTRODUCTION

According Søndergaard, Jensen and Jeppesen (2003), the sediment plays an important role in the nutrient dynamics in the internal recharge in shallow lakes. These researchers observed that in ponds where external recharge was low, the internal recharge of phosphorus (P) prevented the improvement of water quality. According to the authors, in many situations the concentration of a fraction of the P contained in the sediment was 100 times greater than the total concentration of P present in the water, the latter being highly dependent on the sediment / water interaction. In some lakes the internal recharge may continue for decades as phosphorus can be released from sediments as deep as 20 cm. Pettersson (1998), also found that the concentration of P present in surface sediments are several orders of magnitude greater than that in the water column. This means that even if only a small amount of P in the sediment is released, there will be a significant effect on the phosphorus concentration in the spring water.

Domestic and industrial effluent discharges have been identified as the main nutrient contribution to water bodies (ARAUJO; LIMA NETO; BECKER, 2019). However, the sediment plays a major role in the internal recharge of nutrients, mainly P, which in its dissolved form is directly related to the growth of phytoplankton, mainly of cyanobacteria (BAKER *et al.*, 2014; JARVIE *et al.*, 2017; KANE *et al.*, 2014; MICHALAK *et al.*, 2013), to fish mortality and to the increase of the cost of water treatment. As a consequence of the extreme importance of preserving the quality of the scarce water in reservoirs in Ceará, the necessity to evaluate the contribution and interference of the sediment at the trophic level of lentic environments is evident.

It is possible to evaluate the release potential of P to the water column by investigating the sequential chemical fractionation of the inorganic phosphorus ( $P_I$ ) of the reservoir upper sediment. It is known that the fractions of P behave completely different in contact with the water. The  $P_I$  can be divided into mobile phosphorus ( $P_M$ ), soluble fraction considered available for the water column, phosphorus bound to iron and aluminium ( $P_{FeAl}$ ), available in anoxic conditions, calcium-bound phosphorus ( $P_{Ca}$ ) and residual phosphorus ( $P_{Re}$ ), the last ones considered unavailable (CONG *et al.*, 2014; HIELTJES; LIJKLEMA, 1980; KAISERLI; VOUTSA; SAMARA, 2002; OLILA; REDDY; HARRIS, 1995; PETTERSSON, 1986, 1998; SANTOS *et al.*, 2010; SCHAEFER, 2015; SØNDERGAARD; JENSEN; JEPPESEN, 2003). Knowing the distribution of the P fractions in the sediment, it is possible to estimate the P release potential for the water column, and an accurate behaviour investigation

was performed by simulating the conditions found in the bottom of three of the seven reservoir of this study. A microcosm was built containing sediment and fresh water in condition of absence and presence of oxygen, respectively. The first condition (anoxic), the P is easily available, also is commonly found in the bottom of reservoirs in Ceará (BEUTEL, 2003). The second condition (aerobic) is a favourable environment for the immobilization and sedimentation of P.

To the author's knowledge no research has been published on the Forquilha watershed in relation to the behaviour of the recirculation of the phosphorus from the sediment to the water column and its interference in the water quality of this area. Considering that these reservoirs are extremely important for the human supply of the region, the need to assess the potential release of the phosphorus contained in the sediment into the water, and hence its interference in water quality of the area becomes evident.

Therefore, this study will be divided into two chapters.

The first one will study the forms of phosphorus contained in the bottom sediments of reservoirs present in an experimental watershed by sequential chemical fractionation of phosphorus, as well as its vertical distribution across seven reservoirs. In the second chapter, an investigation was made of the release and precipitation of P in interaction with the water column of upper sediment layers of selected reservoirs under anoxic conditions followed by aerobic conditions. These conditions are frequently found in the hypolimnium of reservoirs located in the North Eastern semiarid region.

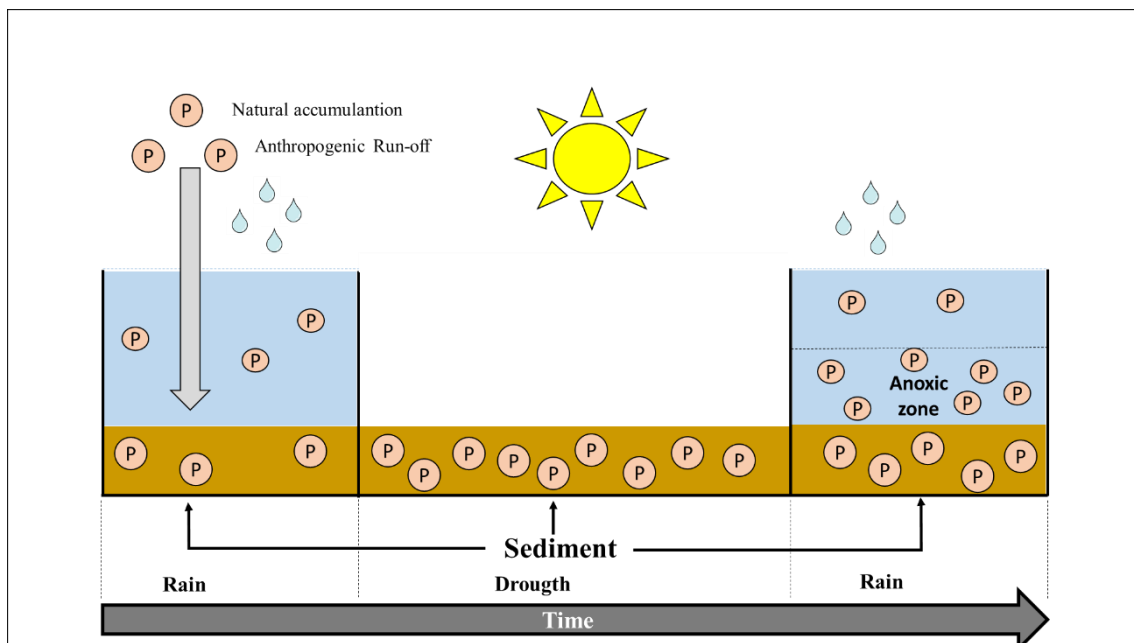
## Internal loading potential of phosphorus in reservoirs along a semiarid watershed

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### Highlights

- Phosphorus (P) can re-dissolve to water column; Internal P loading impacts water quality
- P fractions and distributions were analyzed; Hydro-, Litho- and Anthroposphere
- Sequential chemical extraction of the inorganic P was applied
- Different reservoirs presented different internal recharge potential
- Many effects influence internal P loading: water level; elevation; reservoir age

## Abstract

Sediments are important to nutrient dynamics, especially due to phosphorus internal loading. Several studies have observed that internal loading could prevent water quality from improving in lakes, even when external phosphorus loading is significantly decreased. Therefore, there is an urgent need to assess the potential release of phosphorus contained in the sediment, and thus its potential to impact water quality. In this study, the vertical and horizontal distributions of distinct phosphorus forms in the bottom sediments of artificial reservoirs, located at Forquilha watershed (Ceará, Brazil), were investigated through sequential chemical fractionation. The reservoirs Lagoa Cercada (R#1), Riacho do Algodão (R#2), Riacho Verde (R#3), Cachoeira (R#4), Chagas Manu (R#5), Quandu (R#6) and Balanças (R#7) were investigated. Reservoirs R#1 (most downstream reservoir of the watershed) and R#7 (most upstream reservoir of the watershed) had higher concentrations of total phosphorus ( $P_T$ ) and lower pH values, potentially exerting a greater influence in phosphorus concentration in the water column. Reservoirs R#3 and R#4 presented a predominance of the least available fractions of phosphorus and thus, lower potential for internal loading. Reservoirs R#5, R#1 and R#2 showed a tendency of decreasing total phosphorus ( $P_T$ ) as the sediment depth increased, probably indicating an increase in allochthonous phosphorus along time. This pattern was not observed in reservoir R#6. Mobile ( $P_M$ ) and iron and aluminum-bound phosphorus ( $P_{FeAl}$ ) were the least and the most abundant fractions in most of the samples analyzed, respectively.

**Key Words:** Water quality; Bottom sediment; Phosphorus availability; Eutrophication potential



## 2 INTRODUCTION

In superficial water bodies, phosphorus (P) has been recognized as the limiting nutrient of primary productivity (KAISERLI *et al.*, 2002). Besides the external loading of nutrients caused mainly by human activities, the internal loading from the bottom sediment to the water column can markedly contribute to the increase of the water's trophic state. According to a study developed by Søndergaard *et al.* (2003), sediment plays an important role in nutrient dynamics in shallow lakes. This group observed that in reservoirs where external contribution was low, the internal loading of phosphorus prevented the improvement of water quality. In many situations, the concentration of only one fraction of P in the sediment was 100 times greater than the total concentration of P in the water. In some water bodies, the internal loading may continue for decades as phosphorus can be released from sediments with depths as deep as 20 cm (PETTERSSON, 1998). Pettersson (1998) also found that the amounts of P present in sediments are several orders of magnitude higher than that in the water column. This means that even if only a small amount of P in the sediment is released, there will be a significant effect on the P concentration in the water.

Considering that surface reservoirs are the most important source of water for humans worldwide, it is necessary to evaluate the potential of phosphorus release contained in the bottom sediment into the water, and thus its impact on water quality. This investigation was carried out in the Forquilha river experimental watershed located in Ceará state – Brazil. The aim of this study was:

- to evaluate the potential of recirculation of phosphorous from the bottom sediment to the water column in different locations within the reservoir and along the watershed through sequential chemical fractionation of phosphorus,
- determine the contribution of each P fraction to the total P present in the sediments
- rank the seven reservoirs in the experimental watershed according to the potential and attempt to identify trends explaining the findings.

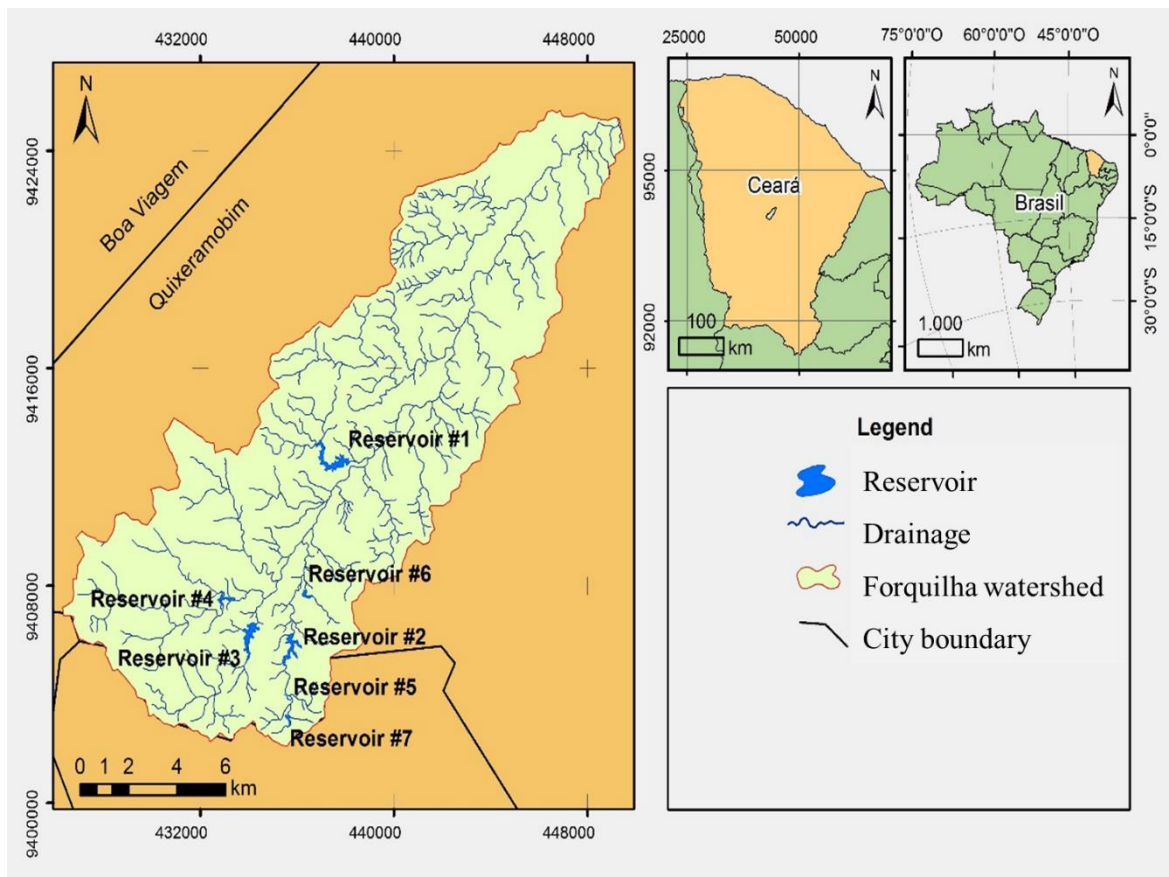
### 3 MATERIAL AND METHODS

#### 3.1 Study area

The study area is located in the experimental watershed of Forquilha River, municipality of Quixeramobim, central region of the state of Ceará, Brazil, and part of the watershed of the Banabuiú River (Figure 1). The experimental watershed has an area of 221 km<sup>2</sup>, an average elevation of 315 m and more than 70 surface reservoirs with capacities ranging from 10<sup>3</sup> to 6.7 x 10<sup>6</sup> m<sup>3</sup>. Most of these reservoirs dry out during the dry season (February to May). The climate in the watershed is semiarid; the vegetation is shrub-like, heavily degraded due to the widespread practice of fires for the preparation of areas for agricultural purposes. This region encompasses a geomorphological diversity representative of the crystalline area of the Brazilian semi-arid Northeast.

The population in Forquilha watershed is structured in 17 communities concentrated in small villages of 20 to 130 families. The main activity is extensive agriculture, especially beans and maize, and extensive livestock farming. Recently, irrigated horticulture and fruit production have been introduced in parts of the watershed thanks to the construction of tubular wells in the valley floodplain, allowing irrigation of areas between 0.5 and 5 hectares. The new farming system is attractive to farmers as they reach a higher level of income. However, the new agricultural system promotes the high consumption of fertilizers and agrochemicals, which has raised concerns in the community about the sustainability of this new agricultural practice and the impact on the environment and the health of the population.

Figure 1 – Study area: Experimental watershed of Forquilha in the semi-arid Northeast of Brazil (adapted from Sirgas, 2000)



Source: Autor (2017).

Due to five years of precipitation below the historical average, 129 of the 153 reservoirs monitored by the state's water resources company, were below 30 % of their total capacity in 2016 (COGERH, 2016). The watershed of Banabuiú, at the time of the experiment presented only 2% of its maximum capacity. This situation was confirmed in a visit to the experimental watershed where most of the reservoirs were completely dry. In this study, seven reservoirs were chosen due to variables such as location, age and, specially, relevance to the population. The names and acronyms of the reservoirs are presented in Table 1.

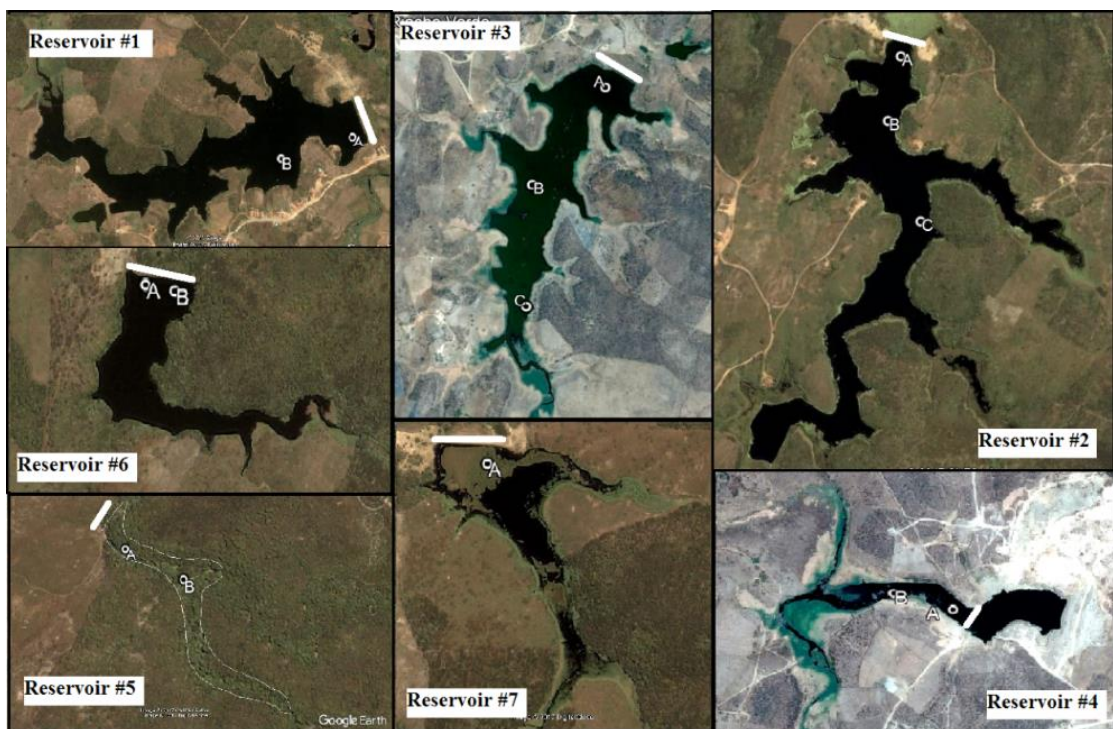
### 3.2 Sampling

Sampling was carried out in two ways, depending on the volume of water found in the reservoir. When the reservoir contained water, sampling was done with a sediment trap. If the reservoir was completely dry, a block of sediment was removed manually. Sample collection at each point was performed in duplicate within a distance between sampling points of approximately 30 cm. Samples were collected from the surface to the matrix rock and subsequently subdivided into layers of approximately 5 cm. Each subsample was then analyzed

twice and the results from the four subsamples belonging to the same depth and sampling point were averaged. The subsamples were stored in polyethylene bags labeled with the time of sampling, depth, and geographical coordinates.

In the first sampling campaign (July 2016), samples were collected in 2 points at the Reservoir R#1, three points at Reservoir R#2, and three points at Reservoir R#3 (Figure 2). Duplicates and stratification of each sample yielded 51 samples in total. During the second campaign (September 2016), the same sampling procedure was used, yielding a total of 31 samples (Figure 2): two points at Reservoir R#4, two points at Reservoir R#5, two points at Reservoir R#6, and one point at Reservoir R#7 (Table 1 and Figure 2). The number of samples were defined by the size of the reservoir and accessibility to the sites. Reservoirs #1, #6 and #7 were completely dry, Reservoir #5 contained no water, but the sediment was wet at the time of sample collection.

Figure 2 – Sampling points of stages one and two in seven reservoirs in Ceará state, 2016 (Images: Google Earth, 2010)



Source: Autor (2017).

Table 1 – Summary of sediment samples collected in stages one and two in seven reservoirs in Ceará state in 2016

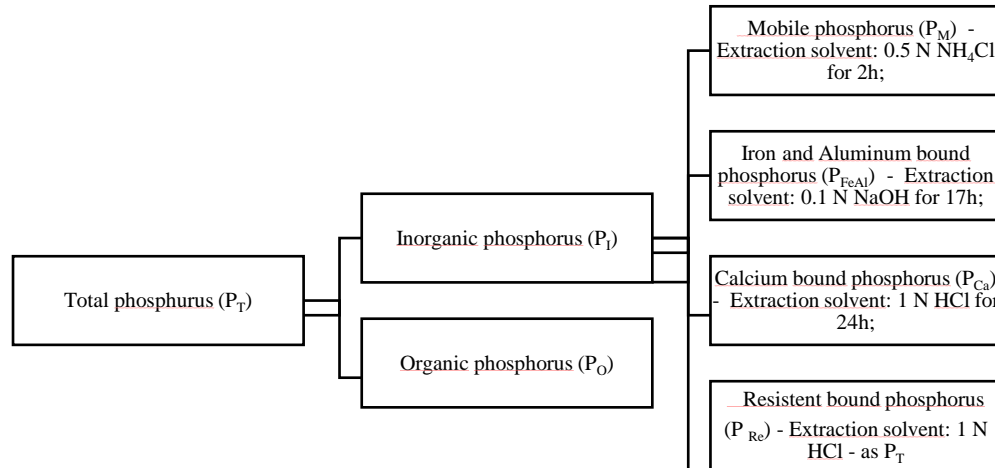
| <b>1st Sampling campaign</b> |               |                           |              |                   |
|------------------------------|---------------|---------------------------|--------------|-------------------|
| <b>Reservoir</b>             | <b>Points</b> | <b>Maximum Depth (cm)</b> | <b>Zone</b>  | <b>Subsamples</b> |
| R#1 – Lagoa Cercada          | A             | 59                        | Lacustrine   | 13                |
|                              | B             | 23                        | Transitional | 13                |
| R#2 – Riacho do Algodão      | A             | 12                        | Lacustrine   | 6                 |
|                              | B             | 4                         | Transitional | 2                 |
|                              | C             | 7                         | Riverine     | 2                 |
| R#3 – Riacho Verde           | A             | 11                        | Lacustrine   | 5                 |
|                              | B             | 19                        | Transitional | 5                 |
|                              | C             | 17                        | Riverine     | 5                 |
| <b>2nd Sampling campaign</b> |               |                           |              |                   |
| R#4 – Cachoeira              | A             | 11                        | Lacustrine   | 4                 |
|                              | B             | 5                         | Transitional | 2                 |
| R#5 – Chagas Manu            | A             | 5                         | Lacustrine   | 2                 |
|                              | B             | 5                         | Transitional | 2                 |
| R#6 – Quandu                 | A             | 39                        | Lacustrine   | 11                |
|                              | B             | 46                        | Lacustrine   | 7                 |
| R#7 – Balanças               | A             | 15                        | Lacustrine   | 3                 |

Source: Autor (2017).

### 3.3 Sample analysis

Samples were dried for 24 h at 110 ° C and stored at 4 ° C until analysis. The different P fractions were extracted according to Figure 3. To determine Total phosphorus ( $P_T$ ), samples were heated to 500 ° C for 1 h followed by extraction with HCl (1N). For the Inorganic phosphorus ( $P_I$ ), chemical extraction was carried out to obtain mobile phosphorus ( $P_M$ ), iron and aluminum-bound phosphorus ( $P_{FeAl}$ ), calcium bound phosphorus ( $P_{Ca}$ ) and residual phosphorus ( $P_{Re}$ ). Organic phosphorus ( $P_O$ ) was estimated by subtracting  $P_I$  from  $P_T$ . The method used for chemical phosphorus fractioning was based on Silva (2001). The organic matter was analyzed by measurement of organic carbon. Chemicals were sourced from Dinâmica and Quimis (Brazil) and were of analytical grade. A correlation test was performed using an Excel Data Analyze to verify the relation between fraction of P concentrations and other variables.

Figure 3 – Sequence of extraction methods for the different phosphorus fractions bound to the sediment. Extraction and analyses based on Silva (2001)



Source: Autor (2017).

## 4 RESULTS AND DISCUSSIONS

To determine the potential of phosphorus (P) internal loading, sediment samples were collected in two campaigns and the P fractions were evaluated. Different phosphorus fractions display different behaviors regarding resolubilization potential (SILVA, 1996).  $P_M$  is weakly bound or easily dissolved, and the most immediately available form of phosphorus. This feature suggests that this should be the fraction most responsible for the internal loading (OLILA *et al.*, 1995).  $P_{FeAl}$ , referred to by Gaspar (2009), as non-apatitic inorganic phosphorus, is considered reactive and bioavailable only when anoxic conditions are prevalent in the aquatic environment, condition normally found at the hypolimnion of eutrophic lakes. The  $P_{Ca}$  fraction (carbonates or apatite bound) was classified by Silva (1996) as apathetic phosphorus and thus it is not considered easily available for internal loading except at very low pH conditions. Williams *et al.* (1976) considered it mostly allogenic, originating from the erosion of sedimentary rocks.

### 4.1 Influence of pH conditions

Only in reservoirs R#1 and R#6 sediments were deep enough to attempt a pH versus depth correlation test. Correlation coefficients ( $R^2$ ) showed no consistent trend in the four points

evaluated (R#1 Point A = 0.18, Point B = -0.98; R#2 Point A = -0.79, Point B = 0.70). Furthermore, considering all points in all reservoirs, no consistent correlation trend was found between pH and any fraction of phosphorus.

Table 2 shows the pH average, standard deviation (SD) and coefficient of variation (CV) across the whole depth at each point. CV across each point's depth was  $\leq 15\%$ , which is considered low variability for soil samples and could be attributed to random errors such as sampling, analysis or handling. Therefore, there was no considerable variation of pH in different strata in the same point.

Point A at R#3 displayed a pH of  $7.1 \pm 0.1$  and point A at R#1 showed a pH of  $4.8 \pm 0.5$ , respectively the highest and lowest pH value amongst the seven reservoirs. R#1 presented sediment with acidic characteristics while the others presented values from slightly acidic to neutral (Table 2). According to Ranno *et al.* (2007), neutral and slightly acidic soils usually contain four fractions of phosphorus ( $P_M$ ,  $P_{FeAl}$ ,  $P_{Ca}$  and  $P_{Re}$ ) in similar amounts while in alkaline and limestone soils the  $P_{Ca}$  fraction is often dominant. In this study, however, no correlation was found between pH and P fractions probably due to the low variability of sediment pH.

Reservoir R#1, the most acidic, presented the larger concentration of organic matter ( $152.68 \pm 9.14 \text{ g.Kg}^{-1}$ ). According to Ferreira Nunes (2013), water bodies receiving large amounts of organic matter are normally the most acidic and present conditions that are not favorable to phosphorus adsorption by clay minerals. In this study, the most acidic sediment (R#1) the predominant fraction was  $P_{FeAl}$ . Machado *et al.* (1993) and Frink (1969) observed that sediments close to neutral pH, inorganic phosphorus was abundant, trend that was also observed in this study as well.  $P_{FeAl}$  mobilization is strongly regulated by the redox potential and an increase in pH may release phosphorus due to  $\text{OH}^-$  substitution, which replaces iron bound phosphate (PROVINI; PREMAZZI, 1985).

Table 2 – Summary of the pH for all sampling points in both sampling campaigns

| Reservoir | Point | pH      |     |        |
|-----------|-------|---------|-----|--------|
|           |       | Average | SD  | CV (%) |
| R#1       | A     | 4.8     | 0.5 | 11     |
|           | B     | 5.6     | 0.6 | 11     |
| R#2       | A     | 6.2     | 0.9 | 15     |
|           | B     | 5.5     | 0.6 | 11     |
|           | C     | 6.1     | 0.2 | 10     |
| R#3       | A     | 7.0     | 0.5 | 7      |
|           | B     | 6.9     | 0.4 | 6      |
|           | C     | 6.1     | 0.8 | 13     |
| R#4       | A     | 6.5     | 0.1 | 1      |
|           | B     | 6.5     | 0.3 | 4      |
| R#5       | A     | 7.1     | 0.1 | 1      |
|           | B     | 7.0     | 0.3 | 4      |
| R#6       | A     | 6.1     | 0.2 | 3      |
|           | B     | 6.1     | 0.1 | 2      |
| R#7       | A     | 6.1     | 0.1 | 2      |

Source: Autor (2017).

#### 4.2 Effects of vertical characteristic of the sediment on phosphorus

In the first campaign, the concentration of phosphorus decreased as a function of the depth ( $R^2 \geq -0.79$ ), except for R#3 (Figure 4). This phenomenon was also observed by Silva (1996). A study by Paula Filho (2004) showed a tendency of higher concentrations of  $P_T$ ,  $P_O$  and  $P_I$  in the upper layers indicating that in recent years the water body has retained significantly more phosphorus.

In reservoir R#1,  $P_I$  was the most present in all 13 samples, varying from 49 to 100% (point A) and from 58 to 63% (point B) of the  $P_T$ . R#1 was also the reservoir that presented the highest concentrations of  $P_T$ . At point A of R#3,  $P_I$  also prevailed while point B displayed a balanced concentration between  $P_O$  and  $P_I$  and at point C, a higher concentration of  $P_O$  was observed. This  $P_I$  concentration decrease and subsequent  $P_O$  increase trend from point A to point C was also observed at R#2 (Figure 4). According to Schaefer (2015), in environments with a low influence of anthropic action, organic and inorganic forms are found in similar concentrations.

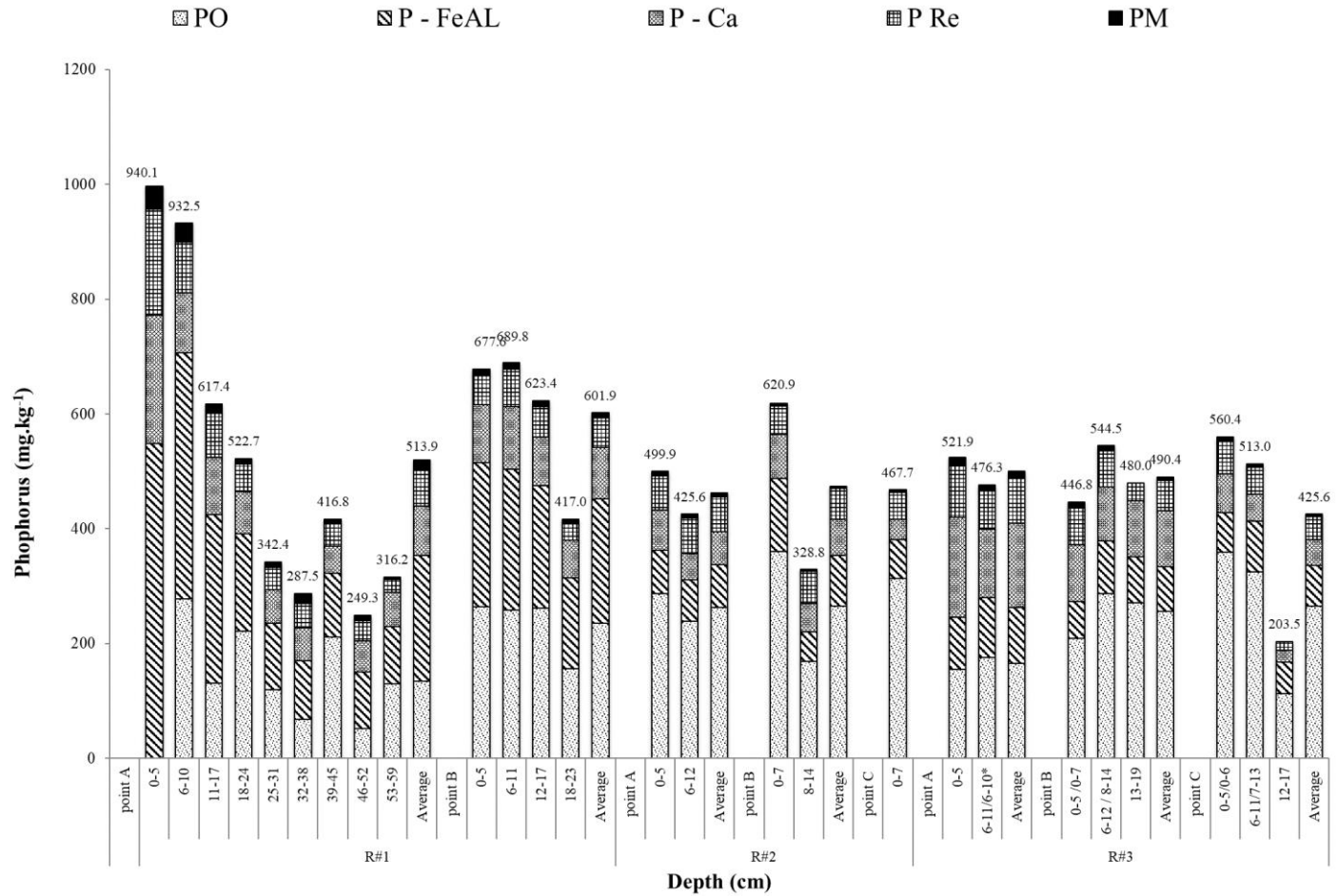
In R#1 and R#2,  $P_{FeAl}$  was the most abundant form of  $P_I$ , similar to what was found by other investigators (SALOMONS; GERRITSE, 1981; SILVA, 1996; PAULA FILHO, 2004; RANNO *et al.*, 2007). This fact shows that most of the  $P_I$  present in these reservoirs are dependent on anoxic conditions in the sediment/water interface to be released into the water



column. Additionally, Salomons and Gerritse (1981) demonstrated that whenever  $P_{FeAl}$  was the main  $P_I$  fraction found, most probably it was from allochthonous source.

In R#3,  $P_{Ca}$  fraction is the predominant form of  $P_I$  at points A and B with an average of 29 and 20 % of  $P_T$ , respectively.  $P_{Ca}$  concentration decreases to 11 % of  $P_I$  and  $P_O$  was the dominant form at point C. According to Ranno *et al.* (2007),  $P_{Ca}$  is generally considered the most likely form of phosphorus occurring in soils before chemical weathering.  $P_{Ca}$  was also considered by Williams *et al.* (1976) as being of allogenic or dendritic origin. Therefore, it appears that most of the sediment found in R#3 could be the product of recent erosion. The  $P_M$ , which is readily available and is easily released from the sediment to the water column, was only detected at low concentrations (0 to 6% of  $P_T$ ) in comparison to the other fractions. This was also found to be the case in a study by Ranno *et al.* (2007), where  $P_M$  concentrations were below the limit of detection of the analysis method used.

Figure 4 – Duplicate average of total phosphorus and fractions determined in three reservoirs during the first sampling campaign. The different shading denotes different phosphorus fractions and values represent total phosphorus

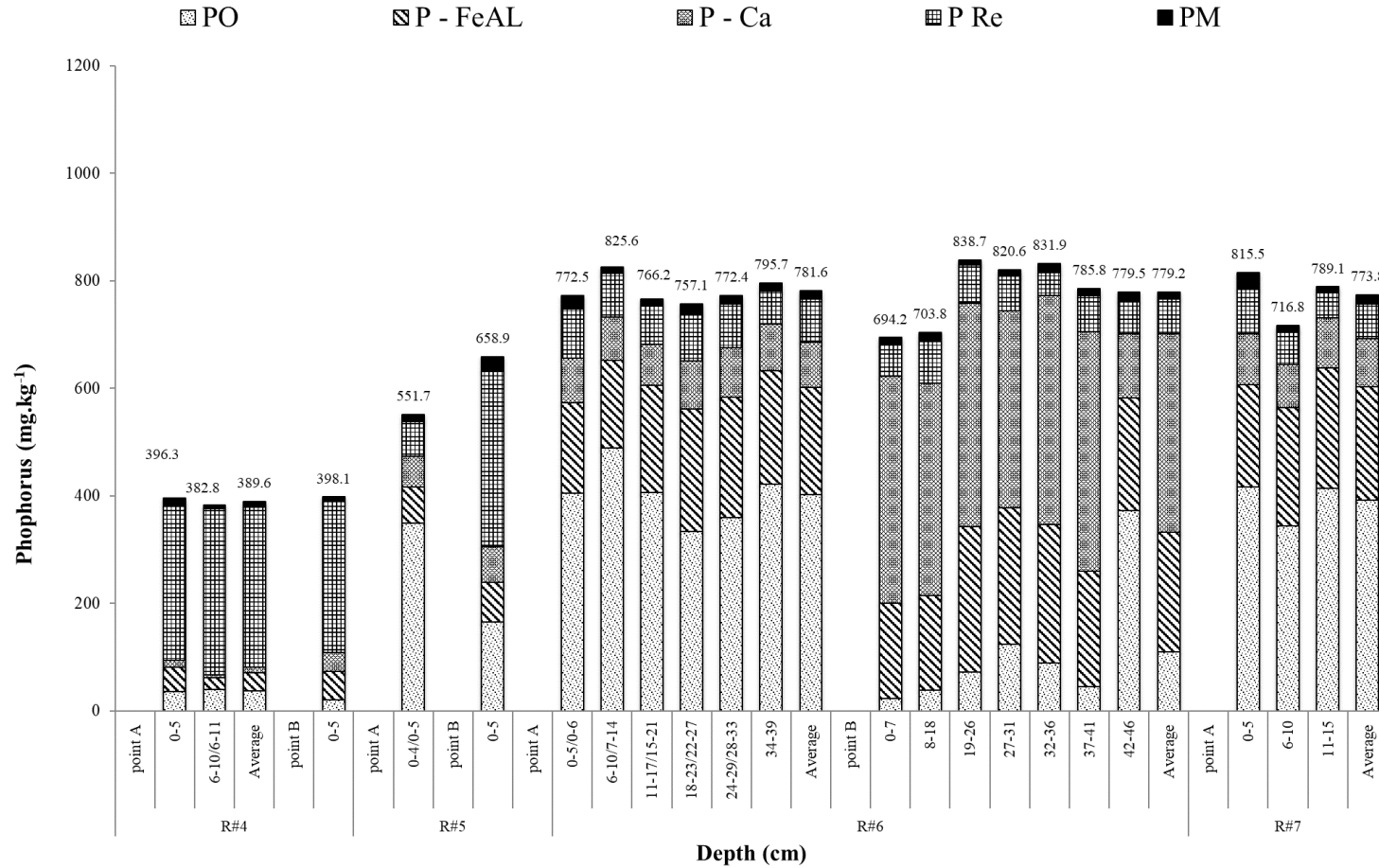


Source: Autor (2017).

In the second sampling campaign, 14 of the 21 samples (67%) showed a predominance of  $P_I$  (Figure 5). In R#4, sampling point B of R# 5, and sampling point B of R#6,  $P_I$  predominated, reaching up to 90 % of  $P_T$  (Table 3). The point A of R#6 and R#7 had similar values of  $P_I$  and  $P_O$ , approximately 50% of the  $P_T$  each fraction. Only point A of R#5 displayed a predominance of  $P_O$ . In relation to the  $P_I$  composition, reservoir R#7 and point A of R#6 showed a predominance of  $P_{FeAl}$  fraction. On the other hand, point B of R#6  $P_{Ca}$  was the predominant fraction, showing that the characteristics of the sediment may vary throughout the same reservoir. Point A of R#5 had similar percentages of  $P_{FeAl}$ ,  $P_{Ca}$ , and  $P_{Re}$  fractions while at point B,  $P_{Re}$  was the largest fraction (50%). Sediments in R#5 were amongst the shallower and less available to the water of both campaigns probably due to it being relatively new (less than 5 years old).

The least available phosphorus dominance in the water column ( $P_{Re}$ ) was observed in the R#4 and the point B of R#5, a phenomenon not observed in the results of the first sampling campaign. The  $P_M$  was the fraction with the lowest concentrations in all samples analyzed in this study in the two sampling campaigns (Figure 5).

Figure 5 – Phosphorus fractions and total phosphorus determined in three reservoirs during second stage sampling in September 2016. The different shading denotes different phosphorus fractions and values represent total phosphorus



Source: Autor (2017)

Table 3 – Concentration of forms of P of the first sampling campaigns per sediment depth

| Reservoir      | Depth              | P <sub>M</sub>      | P <sub>FeAL</sub>    | P <sub>Ca</sub>    | P <sub>Re</sub>      | P <sub>I</sub>       | P <sub>O</sub>      | P <sub>T</sub>     |
|----------------|--------------------|---------------------|----------------------|--------------------|----------------------|----------------------|---------------------|--------------------|
|                |                    | mg.kg <sup>-1</sup> |                      |                    |                      |                      |                     |                    |
| R#4            | <b>Point A</b>     |                     |                      |                    |                      |                      |                     |                    |
|                | 0-5                | 13.3 ± 1.9          | 44.2 ± 22.6          | 14 ± 0.3           | 288.3 ± 55.5         | 359.8 ± 80.4         | 36.5 ± 40.6         | 396.3 ± 39.8       |
|                | 6-10/6-11          | 7 ± 0               | 22.8 ± 0             | 4.8 ± 2.5          | 309 ± 78.7           | 343.5 ± 81.3         | 39.3 ± 41.4         | 382.8 ± 39.8       |
|                | <b>Average</b>     | <b>10.2 ± 4.5</b>   | <b>33.5 ± 15.2</b>   | <b>9.4 ± 6.5</b>   | <b>298.6 ± 14.6</b>  | <b>351.6 ± 11.5</b>  | <b>37.9 ± 2</b>     | <b>389.6 ± 9.6</b> |
|                | <b>Point B</b>     |                     |                      |                    |                      |                      |                     |                    |
|                | 0-5                | 8.8 ± 2.6           | 52.1 ± 17.2          | 35.6 ± 6           | 280.8 ± 4.5          | 377.2 ± 25.1         | 20.8 ± 21.6         | 398.1 ± 3.5        |
| R#5            | <b>Point A</b>     |                     |                      |                    |                      |                      |                     |                    |
|                | 0-4/0-5            | 14 ± 1              | 67.6 ± 4.8           | 56.1 ± 10.2        | 64.7 ± 7.6           | 202.5 ± 23.5         | 349.2 ± 20.3        | 551.7 ± 3.2        |
|                | <b>Point B</b>     |                     |                      |                    |                      |                      |                     |                    |
|                | 0-5                | 26.6 ± 23.3         | 74.1 ± 1.9           | 66.5 ± 8.3         | 326.7 ± 3            | 493.9 ± 19.9         | 165 ± 8.2           | 658.9 ± 11.7       |
| R#6            | <b>Point A</b>     |                     |                      |                    |                      |                      |                     |                    |
|                | 0-5/0-6            | 24.6 ± 22.3         | 168.4 ± 13.3         | 83 ± 9.9           | 91.6 ± 39.9          | 367.6 ± 14.3         | 404.9 ± 133.6       | 772.5 ± 119.4      |
|                | 6-10/7-14          | 11.5 ± 3.8          | 162.7 ± 23.4         | 80.5 ± 5           | 81.6 ± 40.4          | 336.3 ± 18.2         | 489.3 ± 49.8        | 825.6 ± 68         |
|                | 11-17/15-21        | 12.4 ± 3.8          | 199.6 ± 24.7         | 76.4 ± 5.2         | 72.1 ± 22            | 360.5 ± 48.1         | 405.8 ± 107.3       | 766.2 ± 59.1       |
|                | 18-23/22-27        | 17.9 ± 8.2          | 228.6 ± 53.9         | 89.2 ± 2.8         | 88 ± 34.2            | 423.7 ± 82.7         | 333.5 ± 9           | 757.1 ± 73.7       |
|                | 24-29/28-33        | 15.3 ± 8.6          | 222.8 ± 82.6         | 92.6 ± 2           | 81.6 ± 16.2          | 412.3 ± 88.2         | 360.1 ± 161.5       | 772.4 ± 73.3       |
|                | 34-39              | 15.8 ± W/D          | 210.7 ± W/D          | 86.9 ± W/D         | 60.8 ± W/D           | 374.3 ± W/D          | 421.5 ± W/D         | 795.7 ± W/D        |
|                | <b>Average</b>     | <b>16.3 ± 4.7</b>   | <b>198.8 ± 27.7</b>  | <b>84.8 ± 6</b>    | <b>79.3 ± 11.2</b>   | <b>379.1 ± 32.9</b>  | <b>402.5 ± 53.8</b> | <b>781.6 ± 25</b>  |
|                | <b>Point B</b>     |                     |                      |                    |                      |                      |                     |                    |
|                | 0-7                | 12 ± W/D            | 177.7 ± W/D          | 421.9 ± W/D        | 59.7 ± W/D           | 671.3 ± W/D          | 22.9 ± W/D          | 694.2 ± W/D        |
|                | 8-18               | 16.9 ± W/D          | 176.1 ± W/D          | 394.7 ± W/D        | 77.3 ± W/D           | 665.1 ± W/D          | 38.7 ± W/D          | 703.8 ± W/D        |
| 19-26          | 9.7 ± W/D          | 270.5 ± W/D         | 415.9 ± W/D          | 70.3 ± W/D         | 766.4 ± W/D          | 72.3 ± W/D           | 838.7 ± W/D         |                    |
| 27-31          | 12 ± W/D           | 253 ± W/D           | 366 ± W/D            | 65.1 ± W/D         | 696.1 ± W/D          | 124.5 ± W/D          | 820.6 ± W/D         |                    |
| 32-36          | 16.9 ± W/D         | 257.5 ± W/D         | 425.4 ± W/D          | 43.1 ± W/D         | 742.9 ± W/D          | 89 ± W/D             | 831.9 ± W/D         |                    |
| 37-41          | 12.9 ± W/D         | 214.8 ± W/D         | 445.5 ± W/D          | 67.8 ± W/D         | 741 ± W/D            | 44.8 ± W/D           | 785.8 ± W/D         |                    |
| 42-46          | 16.5 ± W/D         | 208.9 ± W/D         | 119.7 ± W/D          | 61.5 ± W/D         | 406.6 ± W/D          | 372.9 ± W/D          | 779.5 ± W/D         |                    |
| <b>Average</b> | <b>13.8 ± 2.9</b>  | <b>222.6 ± 38.4</b> | <b>369.9 ± 113.2</b> | <b>63.6 ± 10.7</b> | <b>669.9 ± 122.3</b> | <b>109.3 ± 121.2</b> | <b>779.2 ± 59.1</b> |                    |
| R#7            | <b>Point A</b>     |                     |                      |                    |                      |                      |                     |                    |
|                | 0-5                | 31.8 ± W/D          | 190.1 ± W/D          | 94.5 ± W/D         | 82.3 ± W/D           | 398.7 ± W/D          | 416.8 ± W/D         | 815.5 ± W/D        |
|                | 6-10               | 10.2 ± W/D          | 219.6 ± W/D          | 79.5 ± W/D         | 62.9 ± W/D           | 372.2 ± W/D          | 344.6 ± W/D         | 716.8 ± W/D        |
|                | 11-15              | 10.6 ± W/D          | 224.5 ± W/D          | 93.5 ± W/D         | 47.1 ± W/D           | 375.7 ± W/D          | 413.4 ± W/D         | 789.1 ± W/D        |
| <b>Average</b> | <b>17.5 ± 12.4</b> | <b>211.4 ± 18.6</b> | <b>89.2 ± 8.4</b>    | <b>64.1 ± 17.6</b> | <b>382.2 ± 14.4</b>  | <b>391.6 ± 40.7</b>  | <b>773.8 ± 51.1</b> |                    |

Source: Autor (2017).

ND – Not detected

W/D – Without duplicate

Table 4 – Concentration of forms of P of the second sampling campaigns per sediment depth

| Reservoir      | Depth              | P <sub>M</sub>       | P <sub>FeAL</sub>  | P <sub>Ca</sub>     | P <sub>Re</sub>      | P <sub>I</sub>       | P <sub>O</sub>       | P <sub>T</sub>       |  |
|----------------|--------------------|----------------------|--------------------|---------------------|----------------------|----------------------|----------------------|----------------------|--|
|                |                    | mg.kg <sup>-1</sup>  |                    |                     |                      |                      |                      |                      |  |
| R#1            | <b>Point A</b>     |                      |                    |                     |                      |                      |                      |                      |  |
|                | 0-5                | 40.2 ± 25.4          | 549.1 ± 26         | 223.3 ± 150.1       | 184.7 ± 9.7          | 997.3 ± 105.6        | ND                   | 940.1 ± 82.8         |  |
|                | 6-10               | 33 ± 28.1            | 429.3 ± 277.4      | 104.3 ± 26.7        | 88.1 ± 37.1          | 654.7 ± 315.8        | 277.8 ± 91.5         | 932.5 ± 224.3        |  |
|                | 11-17              | 15.8 ± 1.3           | 293.6 ± 68.6       | 99.7 ± 80.3         | 77.6 ± 28.6          | 486.7 ± 176.2        | 130.8 ± 104          | 617.5 ± 72.2         |  |
|                | 18-24              | 9.5 ± 2.5            | 170 ± 168.2        | 74 ± 52.8           | 47.8 ± 22.3          | 301.3 ± 245.8        | 221.4 ± 223.4        | 522.7 ± 22.4         |  |
|                | 25-31              | 9.5 ± 2.5            | 115 ± 95.7         | 59.1 ± 47.2         | 38.8 ± 31.3          | 222.4 ± 171.6        | 120 ± 98.4           | 342.4 ± 73.2         |  |
|                | 32-38              | 17.2 ± 4.4           | 101.6 ± 15.1       | 57.3 ± 26.7         | 43.4 ± 6.9           | 219.5 ± 53.2         | 68.1 ± 83.3          | 287.5 ± 30.1         |  |
|                | 39-45              | 5.9 ± 5.1            | 111.4 ± 21.7       | 46.9 ± 30           | 41.1 ± 11.5          | 205.2 ± 58           | 211.6 ± 183.1        | 416.8 ± 125.1        |  |
|                | 46-52              | 9.5 ± 0              | 98.6 ± 21.8        | 53.6 ± 38.3         | 35.6 ± 11.5          | 197.2 ± 71.6         | 52.1 ± 104.7         | 249.3 ± 33           |  |
|                | 53-59              | 5.3 ± 5.9            | 99.5 ± 51.1        | 59.8 ± 35.8         | 21.5 ± 13.5          | 186.2 ± 106.4        | 130 ± 45.8           | 316.2 ± 60.7         |  |
| <b>Average</b> | <b>16.2 ± 12.3</b> | <b>218.7 ± 168.1</b> | <b>86.5 ± 55.2</b> | <b>64.3 ± 49.7</b>  | <b>385.6 ± 279.7</b> | <b>128.3 ± 89.1</b>  | <b>513.9 ± 266.2</b> |                      |  |
| R#2            | <b>Point B</b>     |                      |                    |                     |                      |                      |                      |                      |  |
|                | 0-5                | 8.6 ± 1.6            | 250.6 ± 17.8       | 100.9 ± 6           | 53.4 ± 8.9           | 413.4 ± 31.2         | 264.2 ± 86.5         | 677.6 ± 55.3         |  |
|                | 6-11               | 11.5 ± 0.6           | 246.1 ± 24.9       | 108.1 ± 14.7        | 65.9 ± 22.6          | 431.6 ± 17.5         | 258.2 ± 109.3        | 689.8 ± 91.7         |  |
|                | 7-17               | 11.1 ± 5.1           | 213.4 ± 96.2       | 85.2 ± 27.1         | 52.1 ± 5.1           | 361.7 ± 133.5        | 261.6 ± 113.1        | 623.4 ± 20.4         |  |
|                | 18-23              | 5.7 ± 4              | 158 ± 111.7        | 65.2 ± 46.1         | 31.8 ± 22.5          | 260.6 ± W/D          | 156.4 ± W/D          | 417 ± W/D            |  |
|                | <b>Average</b>     | <b>9.2 ± 2.7</b>     | <b>217 ± 42.7</b>  | <b>89.8 ± 19</b>    | <b>50.8 ± 14.1</b>   | <b>366.8 ± 76.7</b>  | <b>235.1 ± 52.5</b>  | <b>601.9 ± 126.6</b> |  |
| R#2            | <b>Point A</b>     |                      |                    |                     |                      |                      |                      |                      |  |
|                | 0-5                | 7.2 ± 3.5            | 75.8 ± 12.6        | 69.8 ± 0.2          | 59.7 ± 0.1           | 212.5 ± 9.2          | 287.4 ± 3.1          | 499.9 ± 6.1          |  |
|                | 6-12               | 6.6 ± 2.6            | 72.2 ± 37.9        | 46.1 ± 21.5         | 61.8 ± 55.2          | 186.6 ± 112          | 239 ± 104.4          | 425.6 ± 216.4        |  |
|                | <b>Average</b>     | <b>6.9 ± 0.5</b>     | <b>74 ± 2.6</b>    | <b>57.9 ± 16.7</b>  | <b>60.7 ± 1.5</b>    | <b>199.5 ± 18.3</b>  | <b>263.2 ± 34.3</b>  | <b>462.7 ± 52.6</b>  |  |
|                | <b>Point B</b>     |                      |                    |                     |                      |                      |                      |                      |  |
|                | 0-7                | 4.8 ± 1.3            | 126.5 ± 32.2       | 76.7 ± 17.1         | 49.8 ± 0.1           | 259.9 ± 53.8         | 360.9 ± 130.2        | 620.9 ± 184          |  |
| 8-14           | 3.9 ± 2.6          | 52 ± 4.5             | 49.3 ± 0.6         | 56.1 ± 14.7         | 160.1 ± 17.6         | 168.7 ± 1.1          | 328.9 ± 18.6         |                      |  |
| <b>Average</b> | <b>4.3 ± 0.6</b>   | <b>89.2 ± 52.6</b>   | <b>63 ± 19.3</b>   | <b>52.9 ± 4.4</b>   | <b>210 ± 70.6</b>    | <b>264.8 ± 135.9</b> | <b>474.9 ± 206.5</b> |                      |  |
| R#3            | <b>Point C</b>     |                      |                    |                     |                      |                      |                      |                      |  |
|                | 0-7                | 4.5 ± 1.6            | 67.6 ± 46.8        | 35.4 ± 39.5         | 46.5 ± 30.3          | 154 ± 118.2          | 313.7 ± 5.8          | 467.7 ± 124.1        |  |
|                | <b>Point A</b>     |                      |                    |                     |                      |                      |                      |                      |  |
|                | 0-5                | 14.2 ± 2             | 90.9 ± 31.3        | 174.6 ± 50          | 89.5 ± 7.9           | 367.1 ± 36.7         | 154.8 ± 44.7         | 521.9 ± 24.6         |  |
|                | 6-11/6-10          | 9 ± 1.6              | 104.4 ± 2.6        | 118.6 ± 16.2        | 68.1 ± 12.4          | 300.3 ± 24.8         | 176 ± 7.4            | 476.3 ± 32.2         |  |
|                | <b>Média</b>       | <b>11.6 ± 3.7</b>    | <b>97.6 ± 9.5</b>  | <b>146.6 ± 39.6</b> | <b>78.8 ± 15.2</b>   | <b>333.7 ± 47.2</b>  | <b>165.4 ± 15</b>    | <b>499.1 ± 32.3</b>  |  |
| R#3            | <b>Point B</b>     |                      |                    |                     |                      |                      |                      |                      |  |
|                | 0-5 / 0-7          | 10.8 ± 6.7           | 63.8 ± 22.3        | 99.2 ± 21.4         | 63.6 ± 49.4          | 237.4 ± 99.8         | 209.4 ± 33.5         | 446.8 ± 133.4        |  |
|                | 6-12 / 8-14        | 8.8 ± 1.3            | 92 ± 25.1          | 94.2 ± 13           | 62.4 ± 17.2          | 257.4 ± 54.1         | 287.2 ± 85.3         | 544.5 ± 31.2         |  |
|                | 13-19              | ND                   | 80.5 ± W/D         | 97.2 ± W/D          | 31.8 ± W/D           | 209.3 ± W/D          | 270.7 ± W/D          | 480 ± W/D            |  |
|                | <b>Average</b>     | <b>6.5 ± 5.8</b>     | <b>78.8 ± 14.2</b> | <b>96.9 ± 2.5</b>   | <b>52.6 ± 18</b>     | <b>234.7 ± 24.2</b>  | <b>255.8 ± 41</b>    | <b>490.4 ± 49.7</b>  |  |
| <b>Point C</b> |                    |                      |                    |                     |                      |                      |                      |                      |  |
| 0-5/0-6        | 8.8 ± 0.6          | 68.7 ± 24.1          | 68.5 ± 9.8         | 55.4 ± 2.9          | 201.5 ± 30.4         | 359 ± 115.7          | 560.4 ± 85.3         |                      |  |

| Reservoir | Depth          | P <sub>M</sub>      | P <sub>FeAL</sub>  | P <sub>Ca</sub>  | P <sub>Re</sub>    | P <sub>I</sub>      | P <sub>O</sub>       | P <sub>T</sub>       |
|-----------|----------------|---------------------|--------------------|------------------|--------------------|---------------------|----------------------|----------------------|
|           |                | mg.kg <sup>-1</sup> |                    |                  |                    |                     |                      |                      |
|           | 6-11/7-13      | 5.4 ± 8.6           | 88.2 ± 28.7        | 46.9 ± 8.6       | 47.8 ± 13.7        | 188.3 ± 59.6        | 324.8 ± 92.7         | 513 ± 152.3          |
|           | 12-17          | ND                  | 55.3 ± W/D         | 20.5 ± W/D       | 15.6 ± W/D         | 91.1 ± W/D          | 112.4 ± W/D          | 203.5 ± W/D          |
|           | <b>Average</b> | <b>4.7 ± 4.4</b>    | <b>70.7 ± 16.5</b> | <b>45.3 ± 24</b> | <b>39.6 ± 21.2</b> | <b>160.3 ± 60.2</b> | <b>265.4 ± 133.6</b> | <b>425.6 ± 193.8</b> |

Source: Autor (2017).

ND – Not detected

W/D – Without duplicate

### 4.3 Effects of longitudinal characteristic of the sediment on phosphorus

According Morris and Fan (2010), most sediments enter reservoirs as a consequence of rainfall erosion and subsequent transport by streams. For the analysis of the longitudinal contribution of nutrients, only the concentrations of phosphorus in the upper layer of the sediment (top 5 cm) of each reservoir were considered. This layer of sediment was the most affected by the recent transport of sediments.

Reservoirs R#1 and R#7 are most downstream and upstream of the watershed, respectively. R#1 presented the highest concentrations of P<sub>T</sub> in the superficial sediment (940 ± 82.8 mg.kg<sup>-1</sup>), followed by the R#7 reservoir (815.8 mg.kg<sup>-1</sup> ± W/D). Reservoirs R#4, R#3, and R#7 are located upstream of the watershed and in different sub-watersheds, thus they do not receive contribution from any other reservoir in the Forquilha watershed. Additionally, they have different construction ages (Table 5), which makes it difficult to analyze their contributions of P to the other reservoirs.

On the other hand, reservoirs R#7, R#5 and R#2 are in a cascade, which allows them to receive nutrient contribution from the most upstream reservoir during the rainy seasons (DE LIMA; SEVERI, 2014). However, it was found that the highest concentrations of P<sub>T</sub> were found in the R#7, upstream (308 m), and the lowest at R#2 reservoir, downstream (284 m), opposite behavior to what was expected (Figure 6). This phenomenon could be attributed to the different ages of construction and to the difference between the volumes. In this study, reservoirs that were completely dry, such as the R#7, tended to present higher concentrations of P<sub>T</sub> in the sediment, most likely due to the precipitation of the dissolved phosphorus once present in the water column. R#5 is the most recently constructed reservoir and may not be old enough to have contributed to other reservoirs.

In R#1, R#2 and R#3, the oldest in this study (>10 years), as the collection point moved away from the reservoir dam, a decrease of the inorganic phosphorus fraction was observed. The P<sub>I</sub> fraction is larger in the lacustrine zone, decreasing towards

the riverine zone. The lacustrine zone located near the dam is where the largest volume of water is accumulated. Due to high ambient temperatures (annual average 27°C; CLIMATE-DATA.ORG, 2017) thermal stratification is common, resulting in chemical stratification in Ceará reservoirs (FREIRE *et al.*, 2009; SANTOS *et al.*, 2017; SOUSA *et al.*, 2006). Thus, the hypolimnium near the dam constantly becomes anoxic, releasing the phosphorus contained in the sediment, mainly the fraction of the iron and aluminum-bound phosphorus ( $P_{FeAl}$ ). This may explain the sediment characteristic in presenting the highest concentrations of  $P_T$  and the predominance of  $P_{FeAl}$  in the R#1 and R#2. In addition, in reservoirs older than 10 years,  $P_O$  concentrations represented  $44 \pm 22\%$  of the  $P_T$ . According to Santos (2017), the increased concentration of organic detritus at the bottom of the water column and the subsequent decomposition of this material consumes large amounts of oxygen and induces anoxia at the hypolimnium.

However, this trend was not observed in the other four reservoirs. Due to physical limitations in sampling at R#7, only one point was collected, making it unfeasible to analyze the sediment characteristics along the reservoir. In the more recent reservoirs (<5 years), R#4 and R#5, it is probable that the profile of sediment transport is not as well defined as in the older reservoirs. In addition, in these reservoirs, the presence of the smaller proportions of  $P_O$  to  $P_T$  were determined. The largest fraction of  $P_I$  found was that of  $P_{Re}$ , which indicates that the more recent reservoirs do not have, yet, a high potential of internal P recharge.

As mentioned before, the study area has been suffering from a severe drought for approximately 5 years. It has to be considered that reservoirs that are more recent were built during this period of drought. It is probable that there was no flow of water through the watershed, and thus, there was low or no nutrient contribution to the reservoirs and from one reservoir to the other, which may explain the low concentrations of  $P_O$  in the sediment and the low concentrations of  $P_T$  in R#4. Reservoir R#7 had the second largest concentration of  $P_T$  in the upper sediment, which may indicate that the nutrients that flowed to this reservoir remained in the reservoir and did not contribute to the others.

Where the sediment in the reservoirs was completely dry (R#1, R#6 and R#7), besides having the highest concentrations of  $P_T$  in the upper layer of sediment (up to 5 cm), the predominant fraction of P in the sediment was  $P_{FeAl}$  with a ( $33 \pm 7\%$  of  $P_T$ ). Only one point (B) in R#6 showed dominance of the  $P_{Ca}$  fraction, ( $48 \pm 15\%$  of  $P_T$ ), albeit with a high degree of variance. The dry reservoirs presented the highest concentrations of  $P_T$



the superficial layer, from 677 to 940 mg.kg<sup>-1</sup>, while in the wet reservoirs P<sub>T</sub> concentrations ranged from 154 to 494 mg.kg<sup>-1</sup> in the upper sediment layer.

The distribution of P in each reservoir was dependent on the elevation of the sampling point. In the older reservoirs, it was found that the higher elevation collection points presented a lower concentration of P<sub>T</sub> than in the lower points, which indicates the internal contribution of P in the reservoirs, as a nutrient drag from the highest to the lowest point may occur. As previously mentioned, it was not possible to perform longitudinal analysis of the other four reservoirs, due to their recent construction and to the short distance between the collection points.

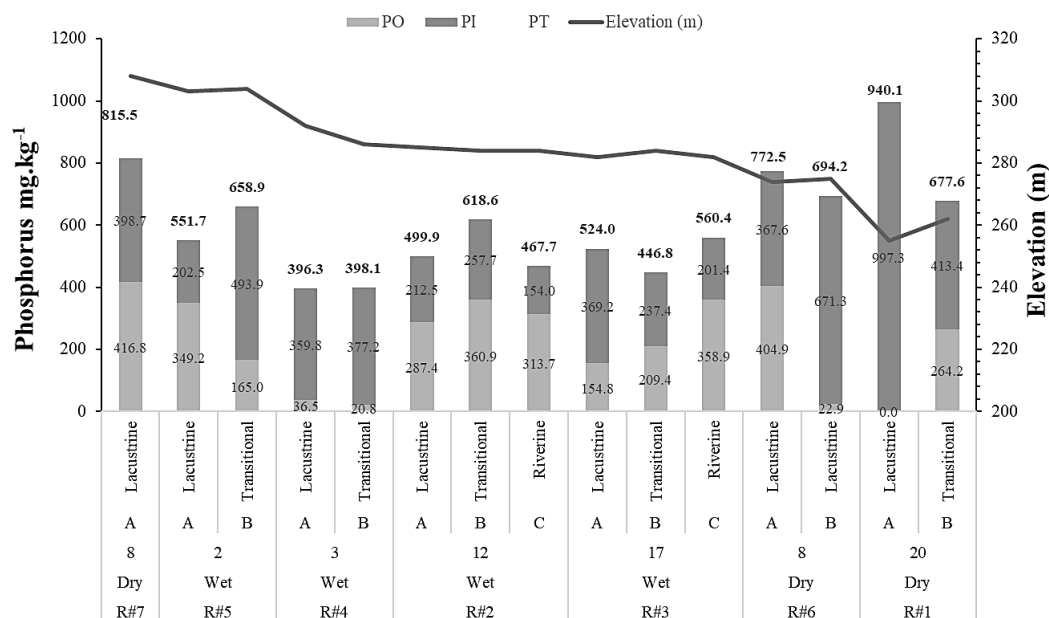
The potential of P internal recharge base on the fractions present at each reservoir is presented in Figure 7. As discussed earlier, P<sub>FeAl</sub> is readily available under anoxic conditions, usually found in the eutrophic reservoirs. It is well established that most reservoirs in Ceará state present this condition in the hypolimnium. Therefore, P<sub>FeAl</sub> can be considered an easily available fraction for internal recharge. R#1, the most upstream reservoir of the watershed, had the highest potential of internal recharge of P, followed by R#7, the most downstream reservoir of the watershed. The newer reservoirs (R#4 and R#5) presented a lower potential for internal recharge, as would be expected. Contrary to this trend, R#3, considered an old reservoir, displayed a low potential for internal recharge.

Table 5 – Summary of sediment characteristics of upper profile in stages one and two in seven reservoirs in Ceará state in 2016

| Reservoir | Situation | Age (years) | Point | Predominant fraction of P <sub>i</sub> (%P <sub>T</sub> ) | P <sub>O</sub> (% P <sub>T</sub> ) | P <sub>i</sub> (% P <sub>T</sub> ) | P <sub>T</sub> (mg.kg <sup>-1</sup> ) |
|-----------|-----------|-------------|-------|---|------------------------------------|------------------------------------|---------------------------------------|
| R#1       | Dry       | 20          | A     | P <sub>FeAl</sub> - 58%                                   | 0                                  | 100%                               | 940.1                                 |
|           |           |             | B     | P <sub>FeAl</sub> - 37%                                   | 39%                                | 61%                                | 677.6                                 |
| R#2       | Wet       | 12          | A     | P <sub>FeAl</sub> - 15%                                   | 57%                                | 43%                                | 499.9                                 |
|           |           |             | B     | P <sub>FeAl</sub> - 20%                                   | 58%                                | 42%                                | 618.6                                 |
|           |           |             | C     | P <sub>FeAl</sub> - 14%                                   | 67%                                | 33%                                | 467.7                                 |
| R#3       | Wet       | 17          | A     | P <sub>Ca</sub> - 33%                                     | 30%                                | 70%                                | 524.0                                 |
|           |           |             | B     | P <sub>Ca</sub> - 22%                                     | 47%                                | 53%                                | 446.8                                 |
|           |           |             | C     | P <sub>FeAl</sub> - 12%<br>P <sub>Ca</sub> - 12%          | 64%                                | 36%                                | 560.4                                 |
| R#4       | Wet       | 3           | A     | P <sub>Re</sub> - 73%                                     | 9%                                 | 91%                                | 396.3                                 |
|           |           |             | B     | P <sub>Re</sub> - 71%                                     | 5%                                 | 95%                                | 398.1                                 |
| R#5       | Wet       | 2           | A     | P <sub>FeAl</sub> - 12%<br>P <sub>Re</sub> - 12%          | 63%                                | 37%                                | 551.6                                 |
|           |           |             | B     | P <sub>Re</sub> - 50%                                     | 25%                                | 75%                                | 658.9                                 |
| R#6       | Dry       | 8           | A     | P <sub>FeAl</sub> - 22%                                   | 52%                                | 48%                                | 772.5                                 |
|           |           |             | B     | P <sub>Ca</sub> - 61%                                     | 3%                                 | 97%                                | 694.2                                 |
| R#7       | Dry       | 8           | A     | P <sub>FeAl</sub> - 23%                                   | 51%                                | 49%                                | 815.5                                 |

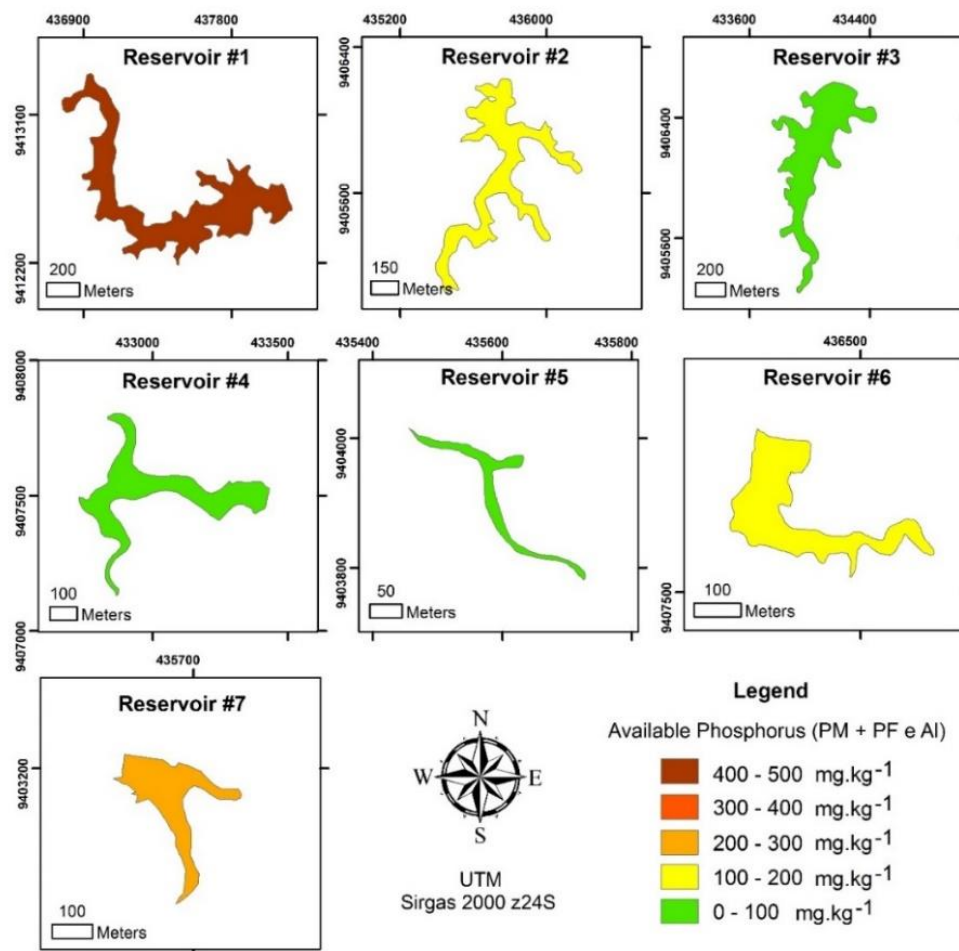
Source: Autor (2017).

Figure 6 – Sediment characteristics, phosphorus fractions and total phosphorus in upper profile determined in reservoirs during both samplings in 2016



Source: Autor (2017).

Figure 7 – Scale of available phosphorus in the reservoirs during both stages of sampling in 2016.



Source: Autor (2017).

## 5 CONCLUSIONS

Bottom sediments of seven reservoirs in the semiarid Northeast region of Brazil were investigated regarding their phosphorus content and the distribution of the various fractions. Special attention was given to the phosphorous internal loading potential. The easily available  $P_M$  fractions only accounted for a maximum of 6 % of the total phosphorus in the sediment.  $P_I$  predominated in most of the sediment samples, and the predominant  $P_I$  fraction was  $P_{FeAl}$ , which is considered reactive and available mainly in situations of low redox potential, condition commonly found in the region.

Organic phosphorus did not appear to have any relation with the other P forms and organic matter, and no trend was observed. In some reservoirs, the highest P concentrations were observed in the upper layers, indicating an increase in phosphorus accumulation in recent years, increasing the potential for internal recharge.

The trend of decreasing P as a function of depth was not present in all reservoirs studied. However, this may be attributed to the low depth of sediment collected in four of the seven reservoirs. It is important to note that the same fraction of phosphorus does not always dominate the longitudinal extent of the reservoir. The reservoirs that were completely dry appeared to have a greater concentration of P than the reservoirs with water stored. The P dissolved in the water, especially from the upper layers, may be an explanation, but a further research is necessary for support this hypothesis.

Of the seven reservoirs investigated, R#1 had the greatest potential of internal phosphorus loading. Whereas R#3 and R#4 are the ones with the lowest potential for interference with the water quality.

The location and the age of the reservoir in the watershed also may contribute to phosphorus in the bottom of the reservoir. R#1, located further downstream of the watershed and one of the oldest, presented higher concentrations of P than the other reservoirs in this study. The elevation and location of the sampling point, lacustrine, transition or riverine zone can influence the concentrations and the predominant form of P.

## **6 ACKNOWLEDGEMENTS**

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## Exchange of phosphorus between sediments and water in tropical semiarid reservoirs

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José Capelo-Neto<sup>a</sup>

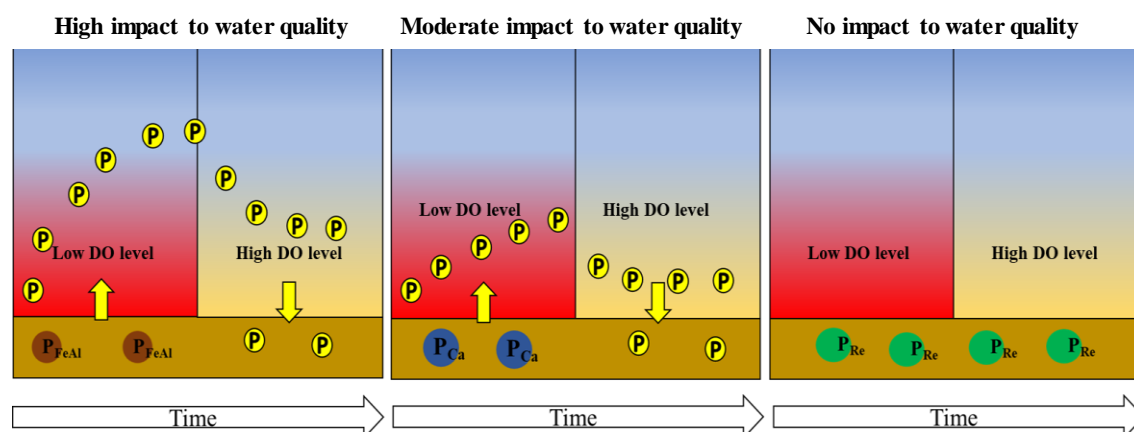
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### Graphical abstract



### Highlights

- Sediments rich in iron and aluminum promote phosphorus release to the water;
- Phosphorus release is proportional to reservoir age;
- Release and settling rates are well described by zero- and first-order models;
- Reservoirs with higher release rates present lower settling rates.

**Abstract**

Sediment plays an important role in nutrient dynamics in reservoirs, especially due to the negative effects of internal phosphorus (P) loading. This study investigated P dynamics at the sediment-water interface in three tropical semiarid reservoirs located in the Brazilian Northeast. Sequential chemical fractionation of the sediment phosphorus, in addition to simulation of the hypolimnion of the reservoirs in controlled laboratory conditions were performed to study the effect of P fractions on phosphorus exchange dynamics during anoxic and oxic stages. The results revealed that the older the reservoir, the higher the concentration of P bounded to iron and aluminum, which was responsible for up to about 10-fold increase in the concentration of P in the water column during anoxic conditions. After aeration, P concentration decreased but did not return to its initial condition. Contrastingly, the most recently constructed reservoir showed dominance of unavailable P fraction and the lowest concentration of P in the sediment, resulting in no potential impact to water quality. Phosphorus release and settling rates were well described by zero- and first-order models, respectively. Reservoirs with high availability of P not only released more phosphorus, but also presented a lower settling rate, resulting in higher potential impacts to water quality. The models proposed here can be used to simulate the exchange rates of P in tropical semiarid reservoirs.

**Keywords:** Bottom sediments; eutrophication; internal load; mathematical modeling; phosphorus availability.

## 7 INTRODUCTION

The influx of nutrients such as nitrogen (N) and phosphorus (P) significantly contributes to freshwater eutrophication. Additionally, it has been demonstrated that bottom sediment can have a major influence on water quality deterioration because of nutrient release, especially P (BAKER *et al.*, 2014; CHEN *et al.*, 2018; JARVIE *et al.*, 2017; KANE *et al.*, 2014; MICHALAK *et al.*, 2013). The increase in P concentration can, amongst other problems, favor the formation of potentially toxic harmful algal blooms (HABs), increasing biomass, turbidity, and the risks associated with toxic or noxious secondary metabolites. HABs represent a significant challenge to water treatment, increasing the economic burden to water utilities as filter run time is decreased and additional chemicals are needed (HE *et al.*, 2016). The problem of P release is potentialized by the fact that the phosphorus content in sediments is very persistent and P can be released from as deep as 20 cm (SØNDERGAARD; JENSEN; JEPPESEN, 2003). In order to assess this problem, the potential for P release to the water column needs to be determined. This can be achieved by sequential chemical fractionation of the inorganic phosphorus (IP) of the reservoir bottom sediment, since P fractions behave differently under different water conditions (CONG *et al.*, 2014). According to Rydin (2000), IP can be fractionated into:

- a) Mobile P ( $P_M$ ): the soluble fraction that can be considered readily available for release into the water column;
- b) P linked to iron and aluminum ( $P_{FeAl}$ ): a fraction only available under anoxic conditions;
- c) Calcium-bound phosphorus ( $P_{Ca}$ ): considered very difficult for release;
- d) Residual phosphorus ( $P_{Re}$ ): considered unavailable for release.

The dynamics of phosphorus exchange across the sediment-water interface has been discussed by many authors (BEUTEL *et al.*, 2008; CHAPRA, S. C.; CANALE, 1991; CHEN *et al.*, 2018; LARSEN *et al.*, 1979; RULEY, J. E.; RUSCH, 2004). However, because of the complexities involved in phosphorus transport processes such as release, settling and burial, there is no general model or theory describing P exchange between water and sediments. Firstly, the above-mentioned phosphorus fractionation varies considerably among different lakes and reservoirs. Secondly, the impact of P fractions on the exchange rates is still not completely understood. Thirdly, there are other factors that also affect the exchange rates such as pH, dissolved oxygen and algae

concentration in the water column. Therefore, studies are still needed to elucidate the dynamics of phosphorus exchange across the sediment-water interface.

In tropical semiarid regions, like the Brazilian Northeast, very dense networks with thousands of surface water reservoirs have been built (CAMPOS *et al.*, 2016). However, these reservoirs not only face sediment deposition (LIMA NETO; WIEGAND; ARAÚJO, 2011), but also present nutrient-enriched sediments ((BRAGA *et al.*, 2019). Thus, internal P loads are expected to affect significantly the water quality of these reservoirs, as the high water temperature accelerates reaction kinetics and promotes chemical stratification in the water column (DANTAS *et al.*, 2008), resulting in anoxic conditions near the bottom sediment. Moreover, these reservoirs are usually shallow and present high water level variation as a result of recurrent droughts (BARBOSA *et al.*, 2012). These factors perpetuate eutrophication of the reservoirs and HAB formation, which impact significantly water treatment (CAPELO-NETO; SILVA BUARQUE, 2016; PESTANA *et al.*, 2019), requiring in some cases in-lake techniques such as artificial aeration to minimize the impacts to water quality (PACHECO; LIMA NETO, 2017).

A recent study carried out by Cavalcante *et al.* (2018) evaluated the potential contribution of P loads from sediments of reservoirs in the State of Rio Grande do Norte, Brazilian semiarid. The results revealed high amounts of soluble form of P in the sediments and concluded that, in such reservoirs, P is easily available, thereby enhancing eutrophication and phytoplankton growth. Hence, when the hypolimnion of a tropical semiarid reservoir remains anoxic even for a short period, one would expect a significant release of P to the water column, which may or may not return completely to sediment after aerobic conditions are re-established. Furthermore, how different fractions of P will contribute to water column concentration under this scenario is still an open question.

The hypothesis raised in this paper is that by knowing the distribution of the P fractions in the bottom sediment, it would be possible to assess the P exchange potential in different tropical semiarid reservoirs. Therefore, this study had as objectives to identify the IP fractions of the bottom sediments of reservoirs located in the State of Ceará, Brazilian semiarid, and to investigate P exchange dynamics between sediments and water under aerobic and anoxic conditions using replicate experimental chambers and mathematical modelling. To the authors' knowledge, this is the first study investigating P transference at the water-sediment interface in tropical semiarid reservoirs.

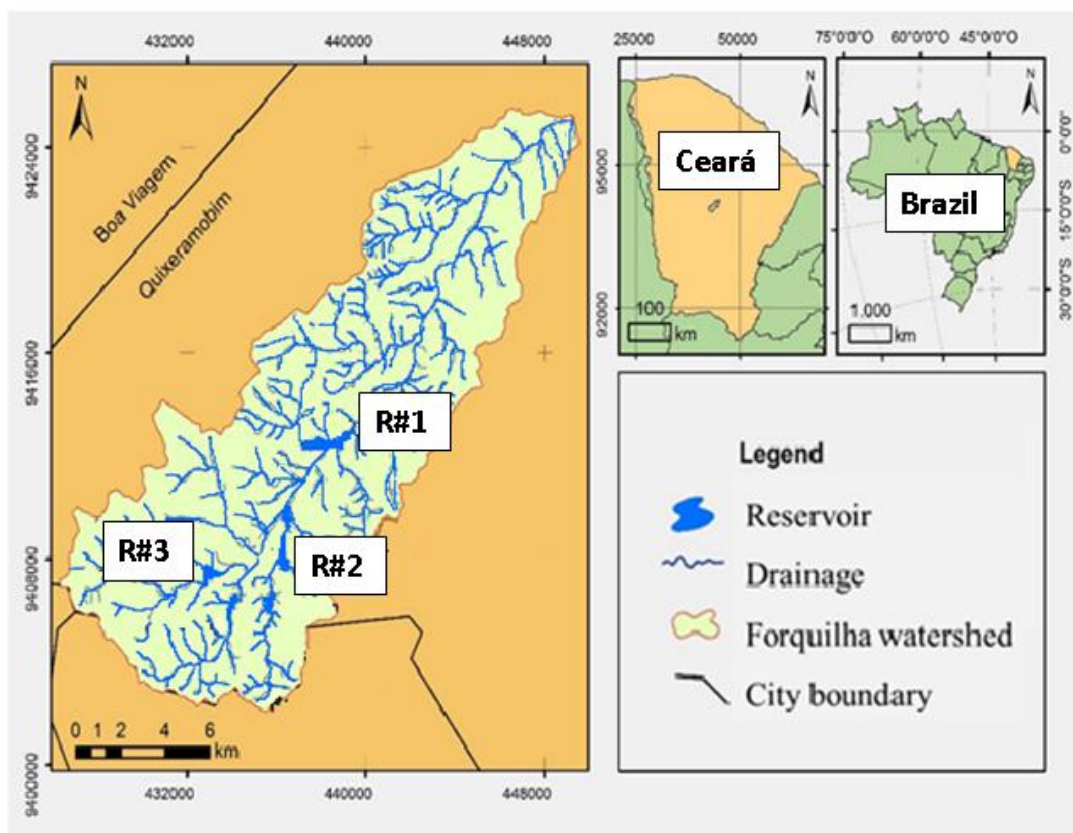


## 8 MATERIALS AND METHODS

### 8.1 Study site and sediment sampling

Water scarcity and water quality are particularly pressing issue in the arid and semiarid regions of the world. The semiarid region of Northeastern Brazil provides the ideal study ground for drinking water reservoirs that undergo periodical drought-and-refill cycles. The selected study area is located in the central region of the State of Ceará, in the experimental watershed of Forquilha River. This region encompasses a geomorphological diversity representative of the crystalline area of the Brazilian semiarid. The experimental watershed has an area of 221 km<sup>2</sup> and an average elevation of 315 m. The vegetation is shrub-like, heavily degraded due to the widespread practice of fires for the preparation of areas for agricultural purposes. Preceding this study, the selected area experienced five years of precipitation below the historical average. This situation was confirmed in the field surveys, when most of the reservoirs were completely dry. Three reservoirs with capacities of about 1.0 hm<sup>3</sup> (R#1, R#2, and R#3) were selected due to their respective ages and distribution within the watershed (see Figure 8 and Table 6). The sediment sampling was carried out in the lacustrine zone of these reservoirs. The surface layer of the sediment was collected at a depth of approximately 5 cm with the aid of a sediment trap.

Figure 8 – Selected reservoirs (R#1, R#2 and R#3) in the experimental watershed of Forquilha, in the State of Ceará, Brazilian semiarid.



Source: Autor (2018).

Table 6 – Coordinates of the sediment sampling points and ages of the studied reservoirs.

| Reservoir | Age (years) | Geo coordinates           |
|-----------|-------------|---------------------------|
| R#1       | 20          | 5°18'57" S<br>39°33'25" W |
| R#2       | 8           | 5°21'27" S<br>39°36'29" W |
| R#3       | 3           | 5°21'35" S<br>39°36'14" W |

Source: Autor (2018).

## 8.2 Extraction of P from sediment

Analysis of phosphorus in the sediment was performed before the P exchange simulation, in order to verify the sediment characteristic and thus to assess sediment-water interaction. Sediment's P extraction was carried out by sequential chemical fractionation of the inorganic phosphorus (IP) according to Rydin (2000), which consists of fractioning IP into mobile phosphorus ( $P_M$ ), iron-bound phosphorus ( $P_{FeAL}$ ), calcium-bound phosphorus ( $P_{Ca}$ ) and residual phosphorus ( $P_{Re}$ ). Total phosphorus ( $P_T$ ), which can

be subdivided into IP and organic phosphorus (OP), was also analyzed, and OP was obtained by subtracting TP from IP concentration:  $OP = TP - (P_M + P_{FeAl} + P_{Ca} + P_{Re})$ .

### 8.3 Water-sediment interface simulation

For the sediment-water interaction simulation, 25 g of sediment from the top 5-cm layer from each reservoir was grounded with a pestle and mortar and placed into sealed jars (microcosmos), in duplicate. In addition, the microcosmos were wrapped with aluminum foil to avoid oxygen generation by photosynthetic organisms (Figure 9). The sediment was then covered with 1600 mL of raw water from Gavião reservoir, the drinking water reservoir located at metropolitan region of Fortaleza (capital of Ceará State) with capacity of 33.3 hm<sup>3</sup>. The height of the water in the microcosmos (H) was 15 cm. Note that the use of Gavião reservoir's water was necessary because the studied reservoirs (R#1, R#2, and R#3) were completely dry at the time of the field surveys.

Water quality parameters (Table 7) were determined prior and during the experiment and included total phosphorus – TP and dissolved or soluble phosphorus – DP, dissolved oxygen – DO (YSI 55, USA), 254 nm absorbance (Spectrophotometer GENESYS 10S UV – VIS, USA), and pH (AN 2000, China). Absorbance at 254 nm was determined as an estimation of dissolved organic material in the water. All reagents used were of analytical grade.

Table 7 – Water quality parameters for the raw water added to the sediment containing jars in the sediment-water interface experiment

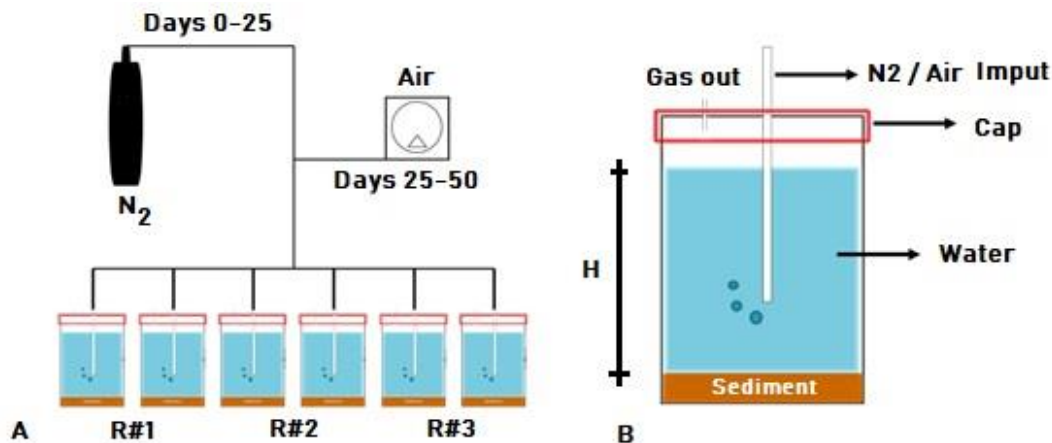
| Parameter                                       | Result |
|---|--------|
| Dissolved oxygen (mg L <sup>-1</sup> )          | 4.7    |
| 254 nm absorbance                               | 0.369  |
| pH  | 7.1    |
| Total phosphorus - TP (µg L <sup>-1</sup> )     | 197.5  |
| Dissolved phosphorus - DP (µg L <sup>-1</sup> ) | 56.4   |

Source: Autor (2018).

The microcosmos were submitted to anoxic followed by aerobic condition. In the anoxic phase, nitrogen (N<sub>2</sub>) was sparged gently in order to maintain DO below 0.5 mg.L<sup>-1</sup> for 25 days or until P concentrations in the water stabilized. The next stage consisted of gently sparging air in order to reach DO > 4 mg.L<sup>-1</sup>, maintained for 25 days or until P concentrations in the water stabilized. No resuspension of sediment occurred during

sparging. Change in P concentration was calculated based in the initial water concentration, considering the volume of the aliquot subtracted for analysis.

Figure 9 – Experimental setup for the sediment-water column interaction: (a) microcosms sparged initially with nitrogen and then with air; and (b) microcosms close up containing sediment, raw water and gas input/output details.



Source: Autor (2018).

#### 8.4 Phosphorus exchange model

Neglecting the inflow, outflow and atmospheric P exchange in the water column, the phosphorus balance equation of Ruley, J. E. and Rusch (2004) can be written as:

$$V \frac{dC}{dt} = k_r A - k_s A C \quad (1)$$

in which  $C$  ( $\text{g}\cdot\text{m}^{-3}$ ) is the concentration of total phosphorus or orthophosphate,  $A$  ( $\text{m}^2$ ) and  $V$  ( $\text{m}^3$ ) are the cross-sectional area and water volume of the experimental chambers (Fig. 2), respectively,  $k_r$  ( $\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ ) and  $k_s$  ( $\text{m}\cdot\text{day}^{-1}$ ) are the reaction coefficients to account for release and settling of phosphorus, respectively, and  $t$  is the elapsed time. Note that the above equation is equivalent to that proposed by Larsen *et al.* (1979). It is also important to mention that a one-compartment model was used here instead of the two-compartment model of Chapra and Canale (1991), for instance, as P burial was neglected under the present experimental conditions.

Thus, in order to model the behavior of TP and OP in the microcosms water, we assumed that only phosphorus release occurred during the anaerobic stage, while phosphorus settling occurred in the aerobic stage, resulting in the following analytical solutions for Eq. (1):

$$\text{Release (anoxic stage): } C = C_0 + 1/H(k_r t) \quad (2)$$

$$\text{Settling (oxic stage): } C = C_0 \exp [1/H(-k_s t)] \quad (3)$$

in which  $C_0$  ( $\text{g}\cdot\text{m}^{-3}$ ) is the initial concentration of total phosphorus or orthophosphate, and  $H$  ( $=V/A$ ) is the water depth in the chambers (see Figure 9).

## 8.5 Statistical tests

The correlation and ANOVA tests were performed in order to investigate the correlation and the differences between the data, respectively. The correlation was presented by  $R^2$  and the ANOVA by  $p$ .

# 9 RESULTS AND DISCUSSION

## 9.1 Sediments P analysis

Table 3 summarizes the results of sediment P analysis. Reservoir R#1 presented the highest values of  $P_T$  ( $998.72 \text{ mg}\cdot\text{kg}^{-1}$ ) and  $P_{\text{FeAl}}$  ( $567.43 \text{ mg}\cdot\text{kg}^{-1}$ , 57% of  $P_T$ ), indicating a high potential of P recharge to the water and HAB development, as Fe-P coupling mechanisms are responsible for the release of P from sediments (Chen *et al.*, 2018). In R#2,  $P_T$  was  $671.31 \text{ mg}\cdot\text{kg}^{-1}$  and the  $P_{\text{Ca}}$  predominated ( $421.90 \text{ mg}\cdot\text{kg}^{-1}$ ), representing 61% of  $P_T$ . As  $P_{\text{Ca}}$  can be considered inert and hardly available (RYDIN, 2000), this sediment should have moderate impact on this reservoir's trophic level. The lowest concentration of  $P_T$  was observed ( $302.91 \text{ mg}\cdot\text{kg}^{-1}$ ) in R#3, with the unavailable fraction ( $P_{\text{Re}}$ ) representing 68%. This indicates, also, that the sediment has little or no influence on water quality. Overall, the concentrations shown in Table 3 were lower than those reported by Cavalcante *et al.* (2018) in tropical semiarid reservoirs, but within the values obtained in other climatic regions (ROY; NGUYEN; WHITE, 2017; RYDIN, 2000; WANG *et al.*, 2006). Observing Table 6 Table 8, it can be inferred that age influences the concentration of P in the sediment, as well as in the dominant fraction of  $P_I$ , and consequently, the potential release of P. Reservoir R#1 (20 years) presented the highest concentrations of P in a readily available form, followed by R#2 (8 years) and R#3 (3 years), respectively. This result is consistent with Cavalcante *et al.* (2018), who reported higher P concentrations in older reservoirs (60 – 90 years).

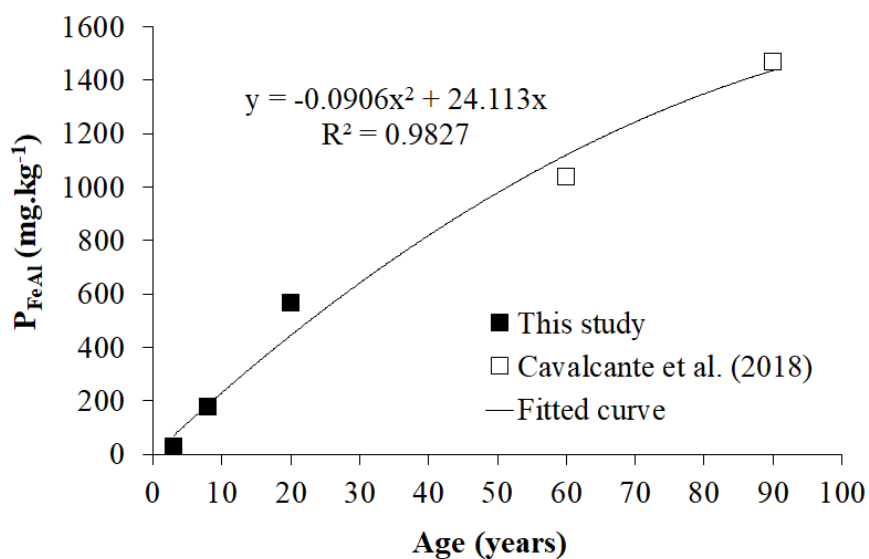
Figure 10 illustrates the effect of reservoir age on potentially mobile P concentrations in tropical semiarid reservoirs.

Table 8 – Concentration of P in the sediment, P forms, PI fractions and percentage in relation to the TP for each reservoir.

| Parameter                                | R#1        | % of TP | R#2    | % of TP | R#3    | % of TP |
|--|------------|---------|--------|---------|--------|---------|
| Depth(cm)                                | 0-5        | -       | 0-7    | -       | 0-5    | -       |
| pH                                       | 5.88       | -       | 6.03   | -       | 6.47   | -       |
| P <sub>T</sub> (mg.kg <sup>-1</sup> )    | 998.7<br>2 | -       | 694.2  | -       | 368.17 | -       |
| P <sub>M</sub> (mg.kg <sup>-1</sup> )    | 58.17      | 6%      | 11.96  | 2%      | 11.96  | 3%      |
| P <sub>FeAl</sub> (mg.kg <sup>-1</sup> ) | 567.4<br>3 | 57%     | 177.74 | 26%     | 28.18  | 8%      |
| P <sub>Ca</sub> (mg.kg <sup>-1</sup> )   | 329.4<br>7 | 33%     | 421.9  | 61%     | 13.76  | 4%      |
| P <sub>Re</sub> (mg.kg <sup>-1</sup> )   | 191.5<br>7 | 19%     | 59.71  | 9%      | 249.01 | 68%     |
| P <sub>I</sub> (mg.kg <sup>-1</sup> )    | 998.7<br>2 | 100%    | 671.31 | 97%     | 302.91 | 82%     |
| P <sub>O</sub> (mg.kg <sup>-1</sup> )    | 0          | 0%      | 20.83  | 3%      | 65.26  | 18%     |

Source: Autor (2017).

Figure 10 – Effect of reservoir age on the concentration of P linked to iron and aluminum, which is responsible to P release from anoxic sediments in tropical semiarid reservoirs.



Source: Autor (2019).

## 9.2 Water-sediment interface simulation

### 9.2.1 Phosphorus in water

The microcosms were run for approximately 50 days under identical ambient conditions. The average water temperature was 27°C and pH values during the two phases were  $7.3 \pm 0.4$  (n = 109, 5% RSD). In R#2, however, the pH values increased in the

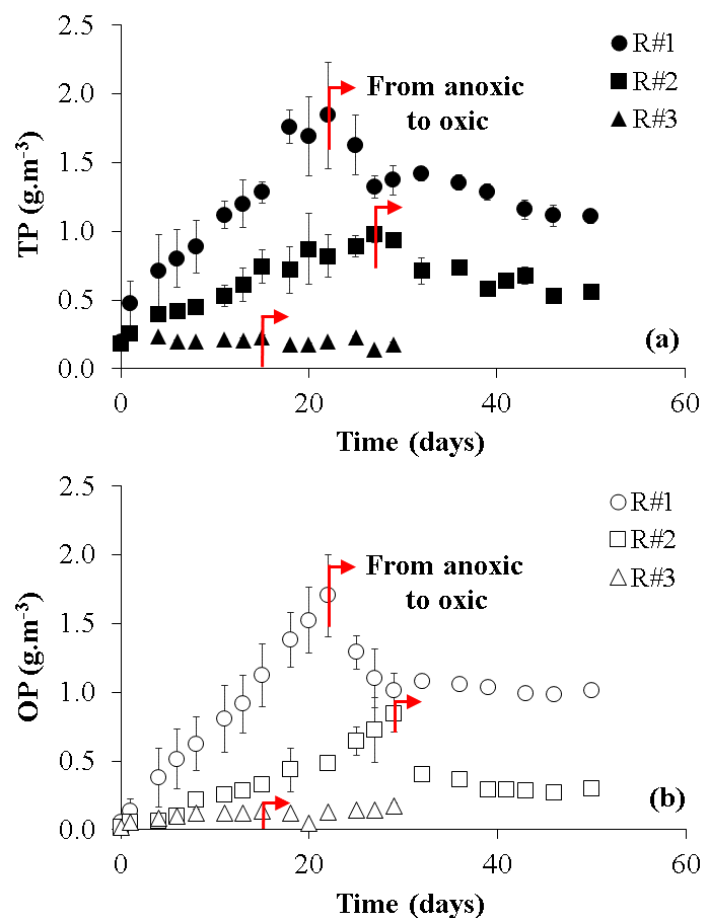
aerobic phase, as also observed by Jiang *et al.* (2006), where pH values were higher in jars with presence of oxygen. According to Beutel *et al.* (2008), the pH decay in the anoxic phase can be attenuated by the removal of CO<sub>2</sub> from the chamber water as result of nitrogen bubbling.

The dissolved oxygen (DO) in the anoxic phase was maintained at approximately 0.5 mg.L<sup>-1</sup>, while, in the aerated step, DO values were 4.3 ± 0.4 mg.L<sup>-1</sup> (n = 46, 9% RSD). In addition, the pH of the sediment did not appear to influence the pH of the superposed water, since the sediment presented a pH value of 5.88, while the pH values of the two jars of reservoir R#1 were 7.14 ± 0.14 (n = 33, 2% RSD). Nevertheless, the pH can influence the adsorption of P, as suggested by Wang *et al.* (2005).

After analysis of TP, OP and pH in the six chambers, ANOVA test showed no significant difference between P analyzes between the two jars representing the same reservoir (p > 0.05, α = 5%). However, it was possible to observe in each reservoir different behaviors in relation to the release of P to the water column during the anoxic and aerobic phases.

In the anoxic phase, the water in the microcosms containing sediment from reservoirs R#1 and R#2 presented increasing concentrations of P (R<sup>2</sup> > 0.90), while in the aerobic phase the concentration of P in the water decreased (R<sup>2</sup> < -0.79), as shown in Figure 11. In R#1, where the sediment has the greatest potential of influence in water quality due to high concentration of P<sub>FeAl</sub>, the P release was significantly higher (p < 0.05) than in the other reservoirs, presenting, after 22 days, 1.84 g.m<sup>-3</sup> of TP and 1.70 g.m<sup>-3</sup> of OP.

Figure 11 – Variation of total phosphorus and orthophosphate concentrations during the anoxic and oxic phases in the experimental chambers for each reservoir.



Source: Autor (2019).

According to Cong *et al.* (2014), iron-bond P is easily desorbed from the sediments and released into the underlying water. In the aerobic phase, TP and OP after 10 days were  $1.11$  and  $1.01$   $\text{g}\cdot\text{m}^{-3}$ , respectively, representing total settling of approximately 40% of TP and OP present in the water. Differently to what was observed here, Beutel *et al.*, (2008) found that the concentrations of Soluble Reactive Phosphorus (SRP), referred to in our study as orthophosphate (OP), practically returned to the initial conditions after aeration. In the anoxic phase developed by Beutel *et al.* (2008), the approximate amount of SRP released was  $0.25$   $\text{g}\cdot\text{m}^{-3}$ , practically the same amount returned to the sediment after aeration, while in R#1, the OP released was  $2.50$   $\text{g}\cdot\text{m}^{-3}$  and the precipitated was  $0.94$   $\text{g}\cdot\text{m}^{-3}$ , representing 38% reduction of P in the water column. Their experiments presented approximately  $0.30$   $\text{g}\cdot\text{m}^{-3}$  at the end of the anoxic phase but only  $0.05$   $\text{g}\cdot\text{m}^{-3}$  at the end of the aerobic phase. However, in this study the DO under



aerated conditions presented values of up to  $9 \text{ mg.L}^{-1}$ , whereas the conditions found in the Brazilian semiarid and in our microcosmos were about half of that.

In R#2 microcosmos, the concentration of TP and OP in the water after the end of the anoxic phase were  $0.93$  and  $0.84 \text{ g.m}^{-3}$  after 29 days, respectively. After 21 days of aeration, the concentration of TP found in water was  $0.52 \text{ g.m}^{-3}$ , and  $0.36 \text{ g.m}^{-3}$  of OP. Similar to what was found in the R#1 microcosmos, the concentration of P increased during nitrogen bubbling (when  $\text{DO} = 0.5 \text{ mg.L}^{-1}$ ), but it was about two times lower. This behavior can be explained by the different characteristics of the sediments in R#1 and R#2.

The predominant fraction of  $P_1$  in the sediment of R#2 is  $P_{Ca}$  ( $421.9 \text{ mg.kg}^{-1}$ , 61% of TP), which is considered inert and not easily available, and the fractions considered available,  $P_{FeAl} + P_M$ , presented a concentration in the sediment of  $189.7 \text{ mg.kg}^{-1}$ , representing 28% of the  $P_T$ , while in R#1 these fractions had a concentration of  $625.6 \text{ mg.kg}^{-1}$ , 300% greater than in R#2.

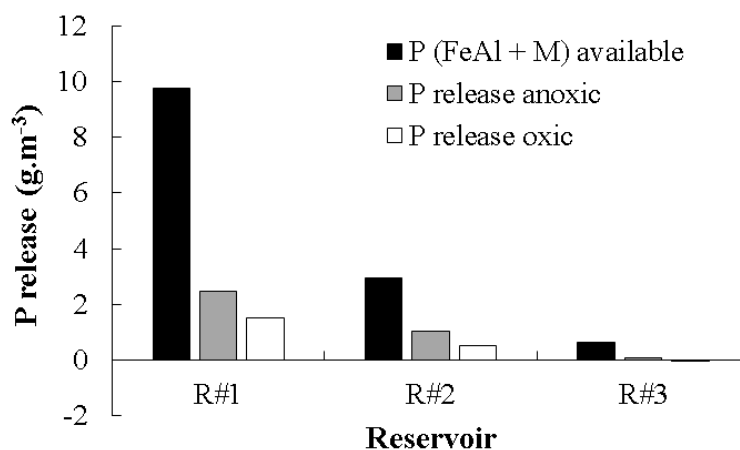
In R#3, the sediment had higher concentrations of  $P_{Re}$  ( $249.01 \text{ mg.kg}^{-1}$ ), fraction considered unavailable, representing 68% of the TP. Differently from the other reservoirs, the available fractions in the sediment represented only 11% of TP and therefore, the concentrations of TP in the water did not present a clear variation neither in the anoxic nor in the aerobic stages (Figure 11). The observed variations may be attributed to errors embedded in the analytical method.

According to Singleton and Little (2006), the aeration of the hypolimnion of a reservoir can be used as a recovery measure. In addition to preventing the release of P to the water column, this technique helps to precipitate it, thus improving water quality. However, the present study showed that this measure alone was not able to revert the release of P due to the anoxic condition. In the case of R#1, the sediment presented the capacity to increase the concentration of P in the water up to about ten times. This behavior was also observed by Wang *et al.* (2005), where phosphate sorption of the sediment was not completely reversible, concluding that the connection between the sediment particles and the sorbed phosphate can be firm.

Knowing the concentration of the available fractions of P,  $P_{FeAl}$  and  $P_M$  present in the sediment (25g of sediment superimposed by 1600 mL of water in each chamber) then the amount of P that could potentially be released to the water was calculated (Figure 12). Although R#1 presented higher release of P, it represented only 25% of that P available in the sediment, while R#2 and R#3 represented 35% and 12%, respectively. After the

aerated step of R#2, 51% of the P released to the water column was returned to the sediment, whereas in R#1, this represented only 39% of the P. The aeration of the water was responsible for the settling of  $0.96$  and  $0.53$   $\text{g}\cdot\text{m}^{-3}$  in R#1 and R#2, respectively. In the reservoir R#3, the sediment did not influence the supernatant water and the anoxic and aerobic stages apparently did not interfere with the release and settling of P (see Figure 12).

Figure 12 – Available phosphorus ( $\text{P}_{\text{FeAl}} + \text{P}_{\text{M}}$ ) present in 25g of sediment in 1600 mL compared to the concentration of total phosphorus released at the end of the anoxic and aerobic phases for each reservoir.



Source: Autor (2018).

### 9.2.2 P exchange rates

The fitting of the model (Eqs. 2 and 3) to the experimental data of TP and OP was performed, resulting in release coefficients  $k_r$  of 0.011 and 0.004  $\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$  and in settling coefficients  $k_s$  of 0.004 and 0.07  $\text{m}\cdot\text{day}^{-1}$  for reservoirs R#1 and R#2, respectively (see Table 9 and Figure 13, Figure 14). Note that the same  $k_r$  and  $k_s$  values were used for adjusting the data of TP and OP for each reservoir, resulting in coefficients of determination  $R^2$  ranging from 0.770 to 0.973 for TP and from 0.540 to 0.995 for OP, which indicates that the exchange rates between sediment and water were well represented by zero- and first-order models, respectively, as proposed by Larsen *et al.* (1979) and Ruley and Rusch (2004). This suggests that such models can be potentially used to simulate the release and settling of phosphorus in tropical semiarid reservoirs. It is also important to note that the adjusted values of phosphorus exchange rates obtained

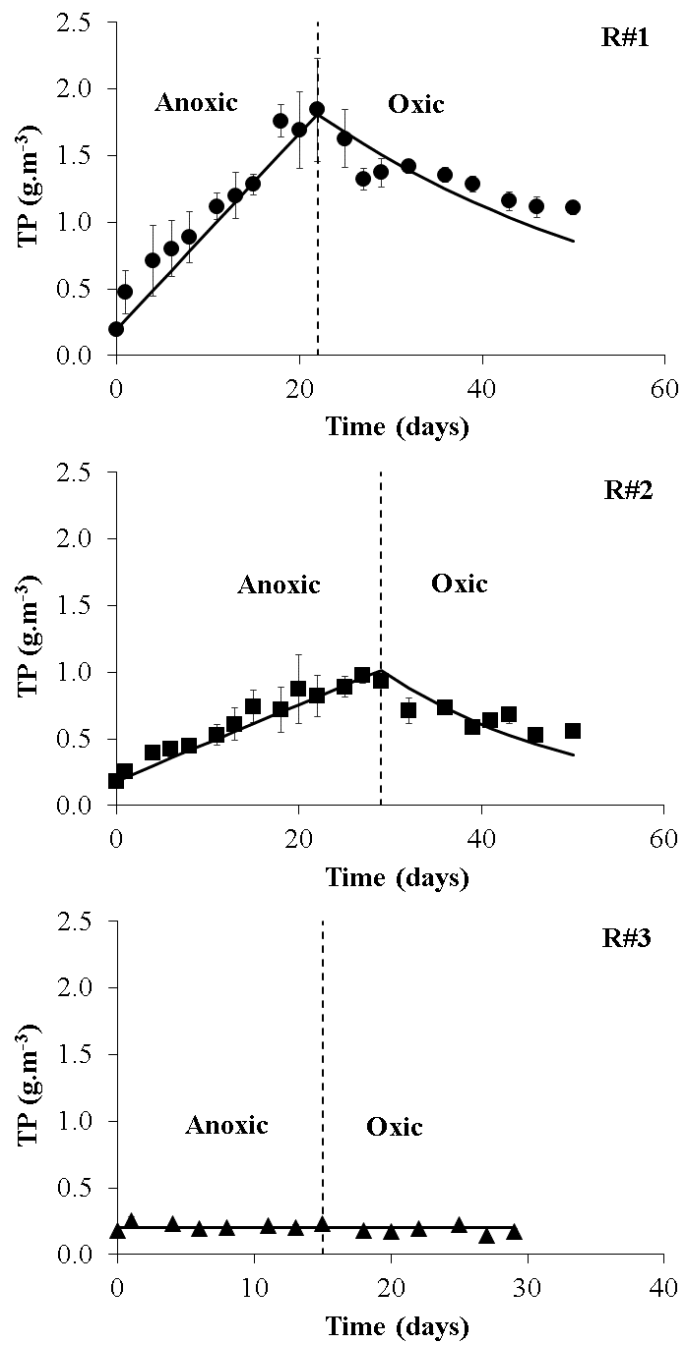
in the present study for R#1 and R#2 were lower than those summarized by Ruley and Rusch (2004). This probably occurred because here we avoided sediment resuspension and growth of photosynthetic organisms in the experimental chambers, potentially reducing the  $k_r$  and  $k_s$  values, respectively. Contrastingly to the above-mentioned trends for the anoxic and oxic stages in R#1 and R#2, the reservoir R#3 did not present any clear trend over time, and the  $k_r$  and  $k_s$  values were considered zero (see see Table 9 and Figure 13, Figure 14). Observe that the  $k_r$ -values decreased from R#1 to R#3, as the available P fractions in the sediment also decrease accordingly (see Figure 12). On the other hand, the  $k_s$ -values were higher for R#2, which suggests that reservoirs with high available P fractions, such as R#1, not only release more phosphorus, but also present a lower settling rate of P, resulting in higher impacts to water quality than R#2, while R#3 presented no potential impact to water quality.

Table 9 – Fitted P release and settling coefficients obtained in the present study compared with the ranges reported in the literature.

| <b>Parameter</b>                              | <b>R#1</b> | <b>R#2</b> | <b>R#3</b> | <b>Ruley and Rusch<br/>(2004)</b> |
|---|------------|------------|------------|-----------------------------------|
| $k_r$ (g.m <sup>-2</sup> .day <sup>-1</sup> ) | 0.011      | 0.004      | 0.000      | 0.019 – 0.046                     |
| $k_s$ (m.day <sup>-1</sup> )                  | 0.004      | 0.007      | 0.000      | 0.009 – 0.120                     |

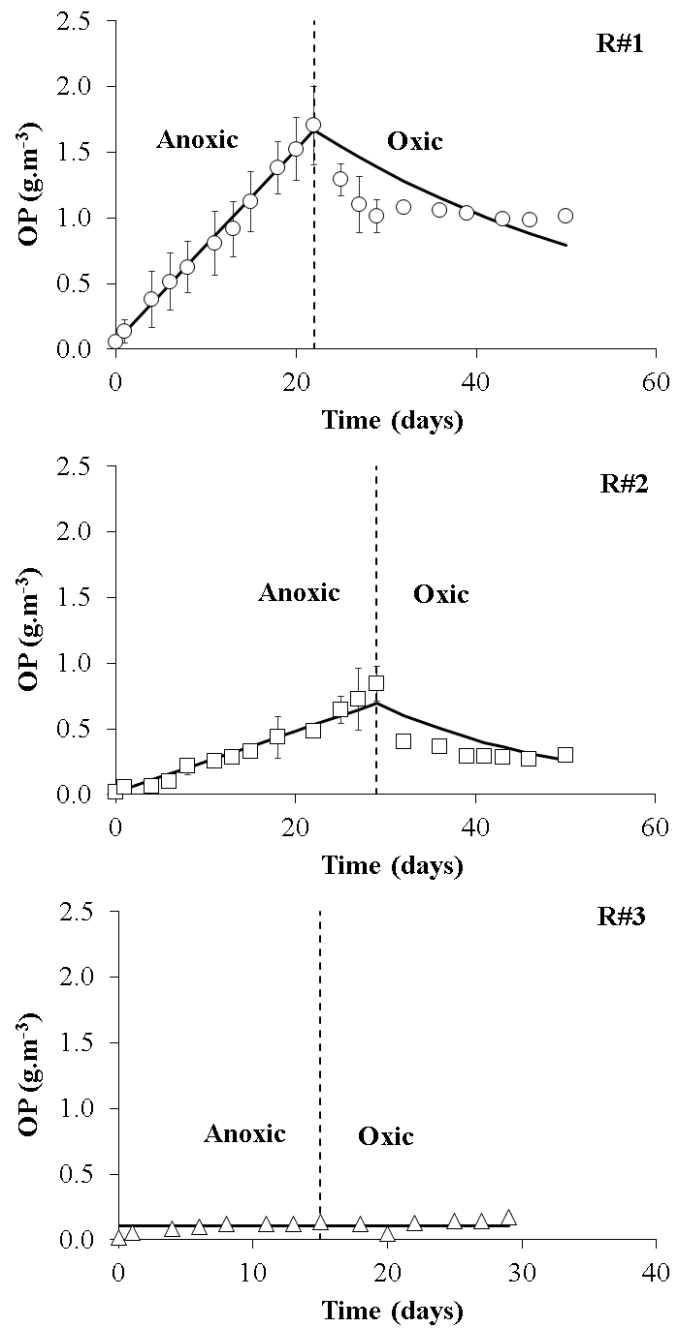
Source: Autor (2019).

Figure 13 – Fitting of the model to the experimental data of total phosphorus during the anoxic and oxic phases in the experimental chambers for each reservoir.



Source: Autor (2019).

Figure 14 – Fitting of the model to the experimental data of orthophosphate during the anoxic and oxic phases in the experimental chambers for each reservoir.



Source: Autor (2019).

## 10 CONCLUSIONS

The sediments of three reservoirs in the semiarid Northeast of Brazil were investigated regarding phosphorus content and the distribution of the various phosphorus fractions. Special attention was given to the phosphorus potential of release and settling in experimental chambers under anoxic and oxic conditions. It was found that the older the reservoir, the higher the concentration of P linked to iron and aluminum, which responded to up to about 10-fold increase in the concentration of P in the water column during anoxic conditions. After oxic conditions were met, P concentration in the chambers decreased but did not return to the initial condition. The results also indicated that the contribution of P from the sediment occurred mainly in the form of orthophosphate, which is linked directly with harmful algal blooms, and consequently with the elevation of the primary productivity of a water body. Contrastingly, the most recently constructed reservoir showed dominance of unavailable P fraction and the lowest concentration of P in the sediment, resulting in no potential impact to water quality. The release and settling rates of P between sediment and water were well represented by zero- and first-order models, respectively. Reservoirs with high available P fractions not only released more phosphorus, but also presented a lower settling rate, resulting in higher potential impacts to water quality. This study provided new findings regarding phosphorus dynamics at the sediment-water interface and new models and parameters that can be used to simulate the exchange rates of phosphorus in tropical semiarid reservoirs.

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