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**FRACIONAMENTO DO FÓSFORO EM SEDIMENTOS DE  
RESERVATÓRIOS TROPICAIS SEMIÁRIDOS**

Natal – RN  
2017

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Dissertação apresentada ao Programa de Pós-graduação  
*stricto sensu* em Engenharia Sanitária, da Universidade  
Federal do Rio Grande do Norte, como requisito parcial  
à obtenção do título de Mestre em Engenharia  
Sanitária.

Orientadora: Prof<sup>a</sup> Dr<sup>a</sup> Vanessa Becker  
Coorientadora: Dr<sup>a</sup> Fabiana Araújo

Natal – RN

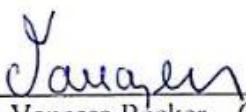
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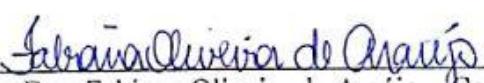
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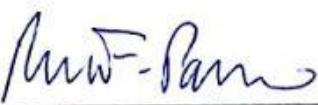
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## **Sumário**

Listas de Figuras .....	9
Lista de Tabelas .....	10
Apresentação .....	11
Abstract.....	13
Resumo .....	14
1. Introduction .....	13
2. Material and Methods.....	15
2.1. Study Area .....	15
2.2. Sediment Sampling .....	18
2.3. Phosphorus Fractionation .....	18
3. Results .....	20
4. Discussion .....	24
5. Conclusions .....	28
6. References .....	28

## **Listas de Figuras**

Fig. 1. Location of the Cruzeta and Gargalheiras reservoirs in the Northeast of Brazil. ....	16
Fig. 2. Phosphorus Fractionation Scheme Modified from Paludan and Jensen (1995) modified by Lürling (personal communication). *BD= bicarbonate-buffered dithionite... .....	19
Fig. 3. Amount of organic or inorganic phosphorus per depth range in Gargalheiras (a) and Cruzeta (b) sediment.....	21
Fig. 4. Fractions of a) Soluble Reactive Phosphorus (SRP) and b) Non-reactive Phosphorus (NRP) per depth range in the sediment for Gargalheiras Reservoir.....	22
Fig. 5. Relative values of a) Soluble Reactive Phosphorus (SRP) and b) Non-reactive Phosphorus (NRP) per depth range in the sediment for Gargalheiras Reservoir .....	22
Fig. 6. Fractions of a) Soluble Reactive Phosphorus (SRP) and b) Non-reactive Phosphorus (NRP) per depth range in the sediment for Cruzeta Reservoir.....	23
Fig. 7. Relative values of a) Soluble Reactive Phosphorus (SRP) and b) Non-reactive Phosphorus (NRP) per depth range in the sediment for Cruzeta Reservoir .....	23
Fig. 8. Amount of available and non-available phosphorus in each depth of the sediment for a) Gargalheiras and b) Cruzeta. ....	24

## **Lista de Tabelas**

Table 1- Water conditions (minimum, maximum, average and standard derivation) in the Gargalheiras and Cruzeta reservoirs at the sampling point near the dam during the period from May 2015 to June 2016 (Cavalcante et al., submitted).....	17
Table 2 - Organic Matter Content in sediment of Gargalheiras and Cruzeta Reservoirs....	21
Table 3 - Literature data of concentration ( $\text{mg kg}^{-1}$ ) of P-fractions in lake sediments.....	26

## Apresentação

A proposta deste trabalho refere-se a uma investigação sobre reservatórios localizados na região semiárida brasileira, com um déficit hídrico quantitativo, que vêm apresentando problemas de eutrofização ao longo das décadas. Uma das principais consequências da eutrofização, que pode ser definida como o enriquecimento de corpos hídricos por nutrientes, é o surgimento de cianobactérias, quem podem provocar sérios danos aos corpos hídricos, como a dificuldade do tratamento da água (caso o ambiente seja fonte de abastecimento), diminuição drástica da biodiversidade e até problemas de saúde pública, já que as cianobactérias são potencialmente tóxicas.

Apesar de ser um processo natural, a eutrofização é intensificada por diversas atividades antrópicas. Por isso, o meio mais eficiente para garantir a água em quantidade e qualidade suficientes, é a prevenção da poluição, especialmente a eliminação de fontes externas de nutrientes, como fósforo e nitrogênio. O controle das cargas concentram-se principalmente no fósforo, já que é limitante para o crescimento dos produtores primários (como cianobactérias) e possui o controle um pouco mais fácil que o nitrogênio. Porém, em ambientes eutróficos, pode haver a necessidade de mitigação, uma vez que a eliminação de fontes pode não ser suficiente para a restauração do ambiente. A capacidade de acumulação de fósforo no sedimento de corpos hídricos durante períodos chuvosos, onde há um maior carreamento de nutrientes da bacia de um corpo hídrico é um dos motivos para a ineficiência na melhoria da qualidade da água quando são eliminadas as fontes externas de fósforo. Isso porque, o fósforo acumulado no sedimento pode continuar sendo liberado para a coluna d'água, alimentando o sistema.

As várias formas em que fósforo (P) ocorrem no sedimento (fracionamento de P) têm recebido considerável atenção durante as últimas décadas e muitas extrações químicas dessas formas têm sido desenvolvidas. Isso porque a quantificação das formas de fósforo no sedimento, bem como a determinação do potencial de disponibilidade (potencial de aproveitamento pelos produtores primários), é de suma importância para planos de restauração de reservatórios, através da aplicação de produtos utilizado em técnicas de geoengenharia.

O fósforo é geralmente dividido em fósforo orgânico, que representa vários compostos ligados a organismos ou moléculas orgânicas dissolvidas, e inorgânico, associados com ferro, alumínio, óxidos e hidróxidos de cálcio, manganês e argilas

minerais. Há ainda uma distinção entre as formas que leva em consideração a mobilidade: fósforo móvel e imóvel. A fração móvel pode ser facilmente liberada do sedimento para a água com mudanças da condição ambiental.

Os reservatórios do semiárido brasileiro são geralmente rasos, com grande variação do nível d'água, devido aos prolongados períodos de estiagem. Os estudos sobre as cargas internas de fósforo em corpos hídricos do semiárido são escassos e o potencial de liberação desconhecido. Porém, algumas características da região são propícias à liberação, como: as baixas profundidades dos reservatórios que facilitam a ressuspensão do sedimento pela ação dos ventos e a elevada temperatura, que pode acelerar reações de decomposição de matéria orgânica e ressolubilização do fósforo e ainda provocar estratificação da coluna d'água, podendo assim, haver anoxia próximo ao sedimento, o que propicia a liberação do fósforo do sedimento.

Dessa forma, o objetivo desse trabalho foi verificar a formas de fósforo presentes no sedimento, bem como quantificar o fósforo potencialmente disponível para os produtores primários, a fim de avaliar a contribuição das cargas de fósforo dos sedimentos para a alimentação da eutrofização em sistemas na região semiárida.

## PHOSPHORUS FRACTIONATION IN SEDIMENTS OF TROPICAL SEMI-ARID RESERVOIRS

**Abstract:** The reduction of external loads of phosphorus (P) is the main action to promote the reduction of eutrophication in lakes. However, the elimination of these sources is not always sufficient for the recovery. This occurs because the phosphorus can be accumulated in the sediment and can be released for long time. Thus, to restore a lake, is necessary also to reduce the internal loading. For this, is important to know the composition of phosphorus in the sediment, for to evaluate the phosphorus availability potential, important data for restoration plans of eutrophic systems. In this study, the forms of phosphorus in the sediment of two reservoirs in the semi-arid tropical region was investigated. The determination of the forms of phosphorus was evaluated by fractionation, sorting out the forms in loosely sorbed P (P-Water), reductant soluble P (P-BD), metal oxide bound P (P-NaOH), P bound to organic matter (P-Humic), calcium bound P (P-HCl) and residual P (P-residual). The sediment was collected in September 2016 and sliced *in situ* every 2 cm from surface to 10 cm. The amount of P forms in the sediment varied of 5 mg.kg<sup>-1</sup> to 349 mg.kg<sup>-1</sup> for Gargalheiras reservoir. While in Cruzeta reservoir the forms varied of 12 mg.kg<sup>-1</sup> to 371 mg.kg<sup>-1</sup>. Despite the variation of amount between the depths and the reservoirs, in general, the range of fractions in Gargalheiras and Cruzeta, was: P-BD > P-NaOH > P-HCl > P-water > P-Residual > P-Humic. In both reservoirs the predominant form was BD followed by NaOH and HCl. The first two forms are available forms and are released easily, becoming it bioavailable for phytoplankton growth.

**Key-Words:** Phosphorus, Sediment, Fractionation, Availability of Phosphorus.

## **FRACIONAMENTO DO FÓSFORO EM SEDIMENTOS DE RESERVATÓRIOS TROPICIAS SEMIÁRIDOS**

**Resumo:** A redução das cargas externas de fósforo (P) é a principal ação para promover a redução da eutrofização em lagos. Entretanto, a eliminação dessas fontes nem sempre é suficiente para a recuperação. Isto ocorre porque o fósforo pode ser acumulado no sedimento e pode ser liberado por um longo período. Então, para restaurar um lago, é necessário também reduzir as cargas internas. Para isso, é importante conhecer a composição de fósforo no sedimento, para avaliar o potencial de disponibilidade do fósforo, importante dado em plano de restauração de sistemas eutróficos. Neste estudo, foram investigadas as formas de fósforo no sedimento de dois reservatórios na região tropical semiárida. A determinação das formas de fósforo foi realizada através do fracionamento, classificando as formas em P fracamente sorvido (P-water), P solúvel reduzido (P-BD), óxido metálico ligado à P (P-NaOH), P ligado a matéria orgânica (P-humic), cálcio ligado à P (P-HCl) e P residual (P-residual). O sedimento foi coletado em setembro de 2016, sendo fatiado *in situ*, a cada 2 cm, da superfície até 10 cm. A quantidade das formas de P no sedimento variaram de 5 mg.kg<sup>-1</sup> à 349 mg.kg<sup>-1</sup> para o reservatório Gargalheiras. Enquanto no reservatório Cruzeta as formas variaram de 12 mg.kg<sup>-1</sup> à 371 mg.kg<sup>-1</sup>. Apesar da variação da quantidade entre as profundidades e entre os reservatórios, em geral, a variação das frações em Gargalheiras e Cruzeta foi: P-BD > P-NaOH > P-HCl > P-water > P-Residual > P-Humic. Em ambos os reservatórios, a forma predominante foi P-BD seguida por NaOH e HCl. As duas primeiras formas são disponíveis e facilmente liberadas, tornando-se biodisponíveis para o crescimento fitoplanctônico.

**Palavras-Chave:** Fósforo, Sedimento, Fracionamento, Disponibilidade de Fósforo.

## 1. Introduction

Eutrophication is a global problem and an important cause of deterioration of the aquatic ecosystems, which results in economic losses and biodiversity (Dodds et al., 2009). The main symptom of eutrophication is a massive cyanobacterial blooms, which can directly affect human health. Blooms may cause high turbidity, anoxia, fish kills, and produce food web alterations causing foul odors, and they may contain various potent toxins (Carpenter et al., 1998; Codd et al., 2005; Dittmann e Wiegand, 2006; Paerl e Otten, 2013). In order to reverse eutrophication of lakes, many efforts have been employed for to reduce the external load of phosphorus (P) (Søndergaard et al., 2003), because this nutrient is a limiting nutrient that sustains primary productivity and has been recognized as a key factor responsible for eutrophication in lakes (Schindler et al., 1973).

The external sources are main causes for the contribution of phosphorus in these systems. The external sources can be point or non-point, such as effluents and soil leaching. However, there are also internal sources from the system itself such as aquatic plants, algal and sediments (Kaiserli et al., 2002). The phosphorus can be accumulated in the sediment of the water bodies during periods of high load and can be released to the water column during a long time, damaging the quality of the water and preventing improvement, even after reducing the external loads of P (Granéli, 1999). Thus, this process functions such as a mechanism of internal fertilization, acting as a new source of pollutant for the water (Lijklema et al., 1994; Wu et al., 2001).

The knowledge about the total phosphorus concentration in the sediment is not sufficient for predicting the potential of internal fertilization of the sediment. It is necessary to know the composition of phosphorus in the sediment in order to evaluate the phosphorus availability, because the fraction of available phosphorus is an important parameter for predicting the future internal P-loading (Kaiserli et al., 2002). The phosphorus content in sediments depends on the sediment composition, the sedimentation rate, the physicochemical conditions and the extent of diagenetic processes (Gonsiorczyk et al., 1998).

The forms in which P occurs in the sediment has received considerable attention during the last decades and many chemical sequential extractions have been developed (Williams et al. 1971; Paludan and Jensen 1995; Wang et al. 2013). Extraction methods provide information on the mobility potential of P species and allows to evaluate the origin of sedimented P (Horowitz 1991; Wang et al. 2013). Moreover, in terms of potential

bioavailability, the extracted fractions can be characterized as the loosely sorbed P (Water-P), the reductant soluble P (BD-P), the metal oxide bound P (NaOH-P) and the calcium bound P (HCl-P) (Kaiserli et al., 2002; Zhou et al., 2005).

The fraction loosely sorbed P (water-P) is a form more bioavailable or immediately available (the form more labile) and also corresponds the phosphorus in the interstitial water (Fytianos e Kotzakioti, 2005; Kaiserli et al., 2002). The fraction reductant soluble P (BD-P) is associated with phosphorus bounded iron and manganese. This phosphorus form is more mobile because its adsorption and sorption are controlled by redox conditions, therefore it can be released under anoxic condition. The release occurs with the reduction and dissolution of the iron hydroxide ( $\text{FeOH}_3$ ), when the sediment surface is in anoxia (Amirbahman et al., 2013). The iron hydroxide has a strong capacity to adsorb the inorganic phosphate in the water column and in the aerobic sediments. However, when the iron III is reduced to iron II, in anoxic environment, the iron and the P adsorbed are released, becoming bioavailable (Lake et al., 2007). The metal oxide bound P (NaOH-P) is the form of P associated with aluminum oxides, and can be also released in anoxic conditions, of similar form of BD-P, which is exchangeable again with  $\text{OH}^-$  and inorganic P compounds soluble in bases (Kozerski e Kleeberg, 1998). This form could have an organic part and it may also have a part that is bound to humic acids, called humic-P, separated of the NaOH-P by acidification (Paludan e Jensen, 1995). The form calcium bound P (HCl-P) is associated with calcium, apatite and carbonates, and can be released when the pH of the environmental is acid (Gonsiorczyk et al., 1998; Jin et al., 2006b; Kim et al., 2003). In sequential scheme could have too others forms more refractory, called residual-P, more difficult to release.

The manipulation of biogeochemical processes using materials to achieve a desired chemical and/or ecological response has been termed geo-engineering in lakes, and is becoming a commonly considered eutrophication management tool (Spears et al., 2014). The techniques of geo-engineering it targets the control of P (in lake, sediment and water sources), thus, the quantification of the P forms in the sediment and its mobility are important information for the control of internal loading in restoration projects of lakes (Jensen, Reitzel and Egemose 2015; Reitzel et al. 2003; Waajen et al. 2015a, 2015b).

In the semi-arid regions, the diffuse pollution, mainly due to activities such as agriculture and livestock, usually is the main source of nutrients for the reservoirs due the human action. Also contribute the region characteristics, such as: shallow soils with little cover, sparse vegetation (Oyama e Nobre, 2004), long periods of shortage of precipitation,

intermittence of rivers, high rates of evaporation and also intense rains that occur in concentrated form in a few months of the year (Barbosa et al., 2012; Costa et al., 2009). This promotes greater erosion and increases the potential of carrying nutrients to water bodies (Haregeweyn et al., 2008) and intensifies the accumulation and concentration of nutrients, making these systems considerably more vulnerable to eutrophication than reservoir in more humid areas (Barbosa et al., 2012; Costa et al., 2009).

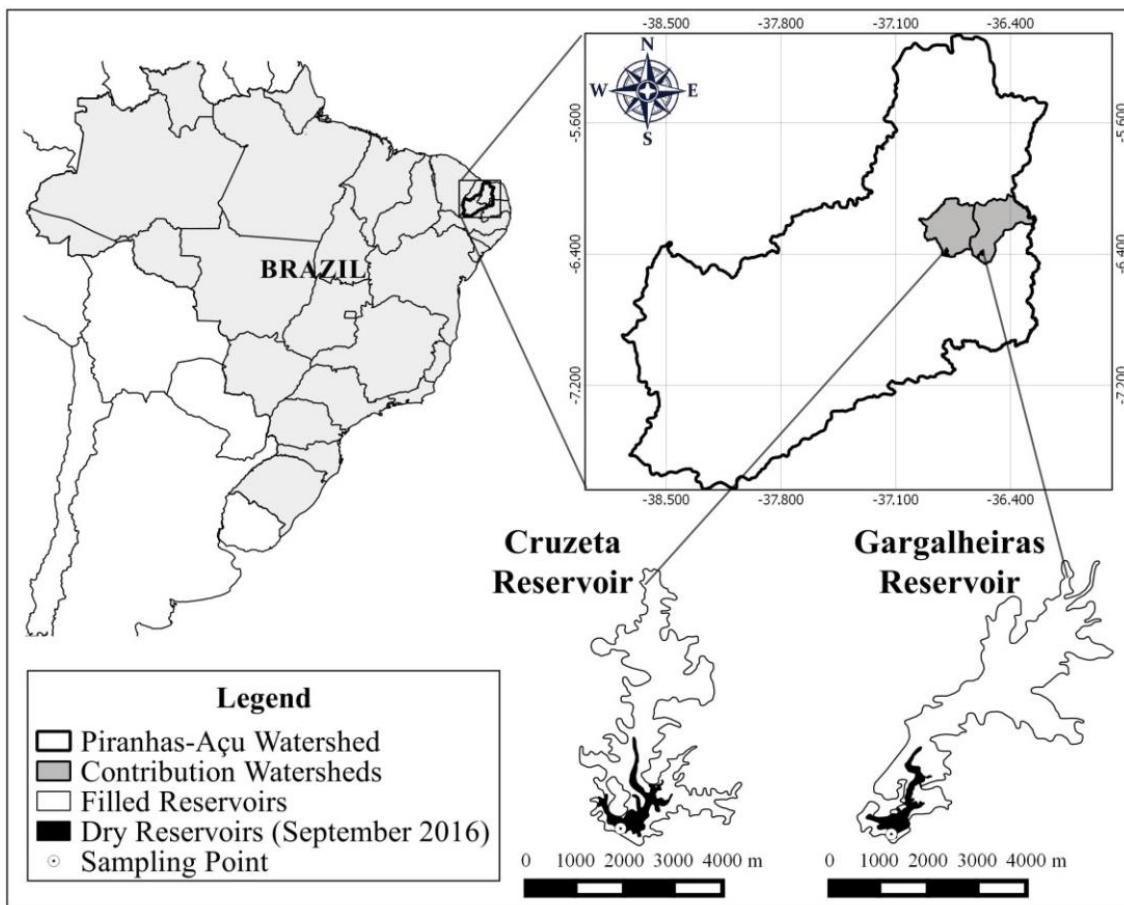
The high water temperatures in semi-arid regions, is responsible accelerate the reactions of decomposition and for forming stratification in the water column (Dantas et al., 2008), leading to a condition of anoxia near the sediment. Furthmore, the semi-arid reservoirs are generally shallow, with high variation of the water level, due to the prolonged periods of drought (Barbosa et al., 2012), thus the low depth facilitates the resuspension of the sediment by the action of the winds. These factors may influence the release of P from the sediment to water column. However, the potential release potential of phosphorus is unknown in semi-arid, because there are no studies on the internal phosphorus loading of water bodies of region.

So, the aim of this study was to verify the forms of phosphorus present in the sediment, to quantify the potential phosphorus available to the primary producers, in order to evaluate the contribution of the phosphorus loads of the sediments to the feeding of eutrophication in systems in the semi-arid region.

## **2. Material and Methods**

### **2.1. Study Area**

The study was developed in two eutrophic shallow reservoirs, Gargalheiras and Cruzeta, located in the Piranhas-Açu watershed in the tropical semi-arid region of Rio Grande do Norte state, northeast of Brazil (Figure 1). The region climate is classified, for Köppen's classification, as tropical semi-arid BS'h' (Alvares et al., 2014). The climate is warm of low latitude with an average rainfall of  $550 \text{ mm.year}^{-1}$  characterized by a rainy season between February and June. The region is experiencing an extreme drought during four years (2012 to 2016) that led to a continuous decrease in volume and consequently the surface area (Figure 1) of the reservoirs in region.



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

The Cruzeta reservoir has a maximum storage capacity of 35 million m<sup>3</sup> and a maximum depth of 14.5 m near the dam. In September of 2016, month of sampling of the sediment, the volume, provided by the Secretary of Water resources of the State of Rio Grande do Norte (SEMARH), was of 89,593m<sup>3</sup>, which corresponds to 0.38% of the maximum capacity, and your depth near the dam was only 0.8 m. The Gargalheiras reservoir, located in Acari city, has a maximum capacity of 44.4 million m<sup>3</sup> and maximum depth of 26.5 m. In September the volume, also provided by SEMARH, was of 516,251m<sup>3</sup>, 1.1% of the maximum, and depth of 6 m. Both reservoirs have multiple uses such as human supply (priority use), irrigation, fishing, recreation and animal watering.

The soil of the watershed of contribution of Gargalheiras is classified as Litholic Neosoils (Figure 1), for Brazilian classification, fulfilled by Brazilian Company of Agricultural Research (EMBRAPA), a shallow soil, poorly developed, with predominance of the source material, associated with relief more slope and with contents of phosphorus naturally low. While the soil of the watershed of contribution of Cruzeta is classified, for Brazilian classification, as Chromic Luvisol (Figure 1), a shallow soil with high base

saturation and concentration of clay of high cations exchange capacity.

Characteristics of the water column of the reservoirs were measured in a monitoring during May 2015 to June 2016 (Cavalcante et al., submitted), before sediment sampling (Table 1). Both reservoirs presented values of total phosphorus (TP) and chlorophyll (*chl-a*) above of the limit to be considered eutrophic, of 50 mg.L<sup>-1</sup> for TP and 15 mg.L<sup>-1</sup> for Chl-*a*, according Thornton and Rast (1993). However, the concentration of TP and chl-a in Gargalheiras reservoir it has presented higher values than Cruzeta and there is a predominance of organic solids (OSS). The concentration of Soluble Reactive Phosphorus (SRP) and inorganic suspended solids is greater in Cruzeta. The dissolved oxygen (DO) in Gargalheiras varied of 0 to 8 mg.L<sup>-1</sup>, presenting anoxia in a few months, and Cruzeta had values ranging from 0.7 to 14, presenting a homogeneous and well aerated water column, but with a few months presenting hypoxia.

**Table 1-** Water conditions (minimum, maximum, average and standard derivation) in the Gargalheiras and Cruzeta reservoirs at the sampling point near the dam during the period from May 2015 to June 2016 (Cavalcante et al., submitted).

Parâmetro	Gargalheiras	Cruzeta
<b>DO (mg L<sup>-1</sup>)</b>	0 - 8 (3.09 ± 0.28)	0.37 – 14 (5.07 ± 0.44)
<b>ISS (mg L<sup>-1</sup>)</b>	2 – 260.83 (76.45 ± 19.43)	3 – 317.5 (81.73 ± 28.48)
<b>OSS (mg L<sup>-1</sup>)</b>	12.75 – 254.20 (80.18 ± 20.33)	3.89 - 570 (86.72 ± 41.89)
<b>SRP (μg L<sup>-1</sup>)</b>	6.7 – 504.55 (106.29 ± 38.00)	65.17 – 467.5 (174.17 ± 32.75)
<b>TP (μg L<sup>-1</sup>)</b>	203.65 – 1853.33 (744.2951 ± 132.51)	169.6 - 3030 (559.88 ± 198.57)
<b>Chl-<i>a</i> (μg L<sup>-1</sup>)</b>	77.93 – 2960.132 (789.89 ± 210.65)	43.47 – 3369.31 (416.72 ± 238.71)

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

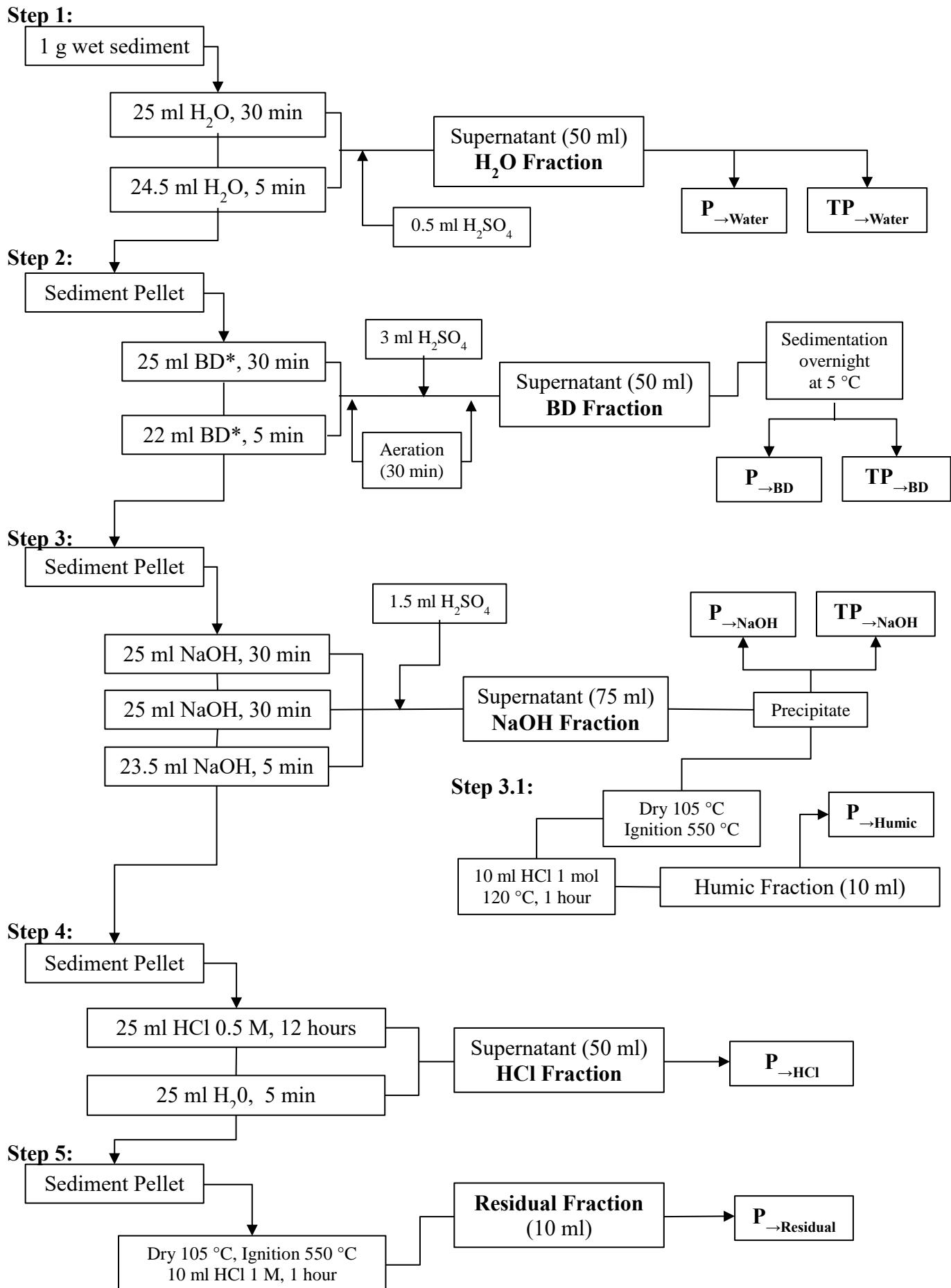
## 2.2 Sediment Sampling

The sediment samples used for the P fractionation were collected at the study site in September of 2016, using a manual Kajak corer with length of 50 cm and 7 cm of diameter. The sediment core was sliced by depth ranges in situ and separated in 0-2 cm, 2-4 cm, 4-6 cm, 6-8 cm and 8-10 cm. The samples were stored in polyethylene transparent containers and transported in a thermally insulated box with ice. At the laboratory the samples were kept refrigerated and maintained in the same containers until analysis.

## 2.3 Phosphorus Fractionation

Before the fractionation, was measured the dry weight – to support the calculation of amount of phosphorus (in mg) per amount of sediment (in kg) – and the organic matter of the sediment, by kiln-drying and Loss of Ignition ( $550^{\circ}\text{C}$  for 3 hours). P fractions were determined using an adaptation of the sequential extraction method developed for Paludan and Jensen (1995) modified by Lürling (personal communication), in a five-step scheme (Figure 2). For sequential extraction 1 g of fresh (still moist) sediment was used, called pellet.

In this method, anoxic distilled water extracts readily available P, or the loosely sorbed P (P-Water). The oxygen was withdrawn from the water by nitrogen stripping. In step 2, bicarbonate-buffered dithionite (0.11 M) solution extracts inorganic P associated with reducible iron and manganese reductant soluble P (P-BD). The sodium hydroxide (1 M) in step 3 extracts inorganic associated with aluminum oxides and clay minerals - metal oxide bound P (P-NaOH), together is extracted the phosphorus associated with organic matter (P-Humic), that is separated of the P-NaOH by means of acidification with sulfuric acid. In extraction of P-BD, the supernatant was aerated to remove the excess of dithionite. When the removal was not complete, a white precipitate of sulfur formed in the sample after addition of sulfuric acid (Lukkari et al., 2007; Paludan e Jensen, 1995). In these cases, the original sample was aerated again and the precipitate was allowed to settle overnight, at  $5^{\circ}\text{C}$ , and the supernatant was taken for P analysis (Lukkari et al., 2007). Subsequently, hydrochloric acid (0.5 M) extracts calcium bound inorganic P (P-HCl) in the step 4. In the step 5, the hydrochloric acid (1 M) extracts form more refractory and less mobile (P-Residual).



**Fig. 2.** Phosphorus Fractionation Scheme Modified from Paludan and Jensen (1995) modified by Lürling (personal communication). \*BD= bicarbonate-buffered dithionite.

The analysis were made in triplicate for each sediment depth range. After extraction procedure, all supernatants samples were acidified by adding sulfuric acid ( $H_2SO_4$ , 2M) prior to P analysis. Soluble reactive phosphorus (SRP) was determined for all the samples, after filtration (0,45  $\mu m$ ) by Murphy and Riley (1962), and total dissolved phosphorus (TDP) was determined, after filtration (0,45  $\mu m$ ) for Water -P, BD-P and NaOH-P following the methods described by Valderrama (1981) and Murphy and Riley (1962). The difference between the total dissolved phosphorus (TDP) and soluble reactive phosphorus (SRP) result in the non-reactive phosphorus (NRP). Therefore, NRP was estimated for the forms P-Water, P-BD and P-NaOH. The non-reactive phosphorus is the organic part of the fractions.

Described above for quantification of SRP and TDP, measured the concentration in milligram per liter (mg/L). So, the dry weight was measured for later calculation of the amount of phosphorus, in milligram, per kilogram of sediment.

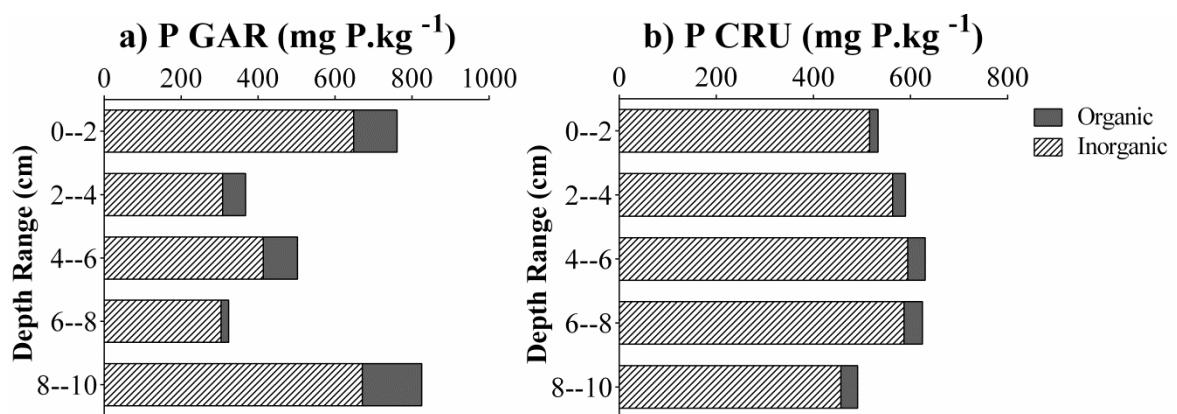
The most algae available forms of P are the loosely sorbed, reductant soluble and metal oxide-bound, can be easily released for water (Lürling e Oosterhout, 2013; Lürling e van Oosterhout, 2013; Zhu et al., 2013). So, the available phosphorus was determined by the sum of SRP of the forms P-Water, P-BD and P-NaOH. The non-available phosphorus was estimated by the sum of SRP of the forms P-Humic, P-HCl and P-Residual.

### **3. Results**

The organic matter content in Gargalheiras sediment showed higher values at surface and a slight reduction with increasing depth (Table 2). In contrast, Cruzeta sediment showed lower organic matter content at surface. Gargalheiras sediment also showed a higher concentration of phosphorus at surface and deeper layer than Cruzeta sediment (Figure 3). In general, the proportion of organic phosphorus was higher in Gargalheiras than Cruzeta sediment.

**Table 2** - Organic Matter Content in sediment of Gargalheiras and Cruzeta Reservoirs.

Depth (cm)	Gargalheiras	Cruzeta
0--2	5.8%	3.6%
2--4	5.7%	5.0%
4--6	5.7%	5.0%
6--8	5.6%	4.8%
8--10	5.5%	5.2%

**Fig. 3. Amount of organic or inorganic phosphorus per depth range in Gargalheiras (a) and Cruzeta (b) sediment.**

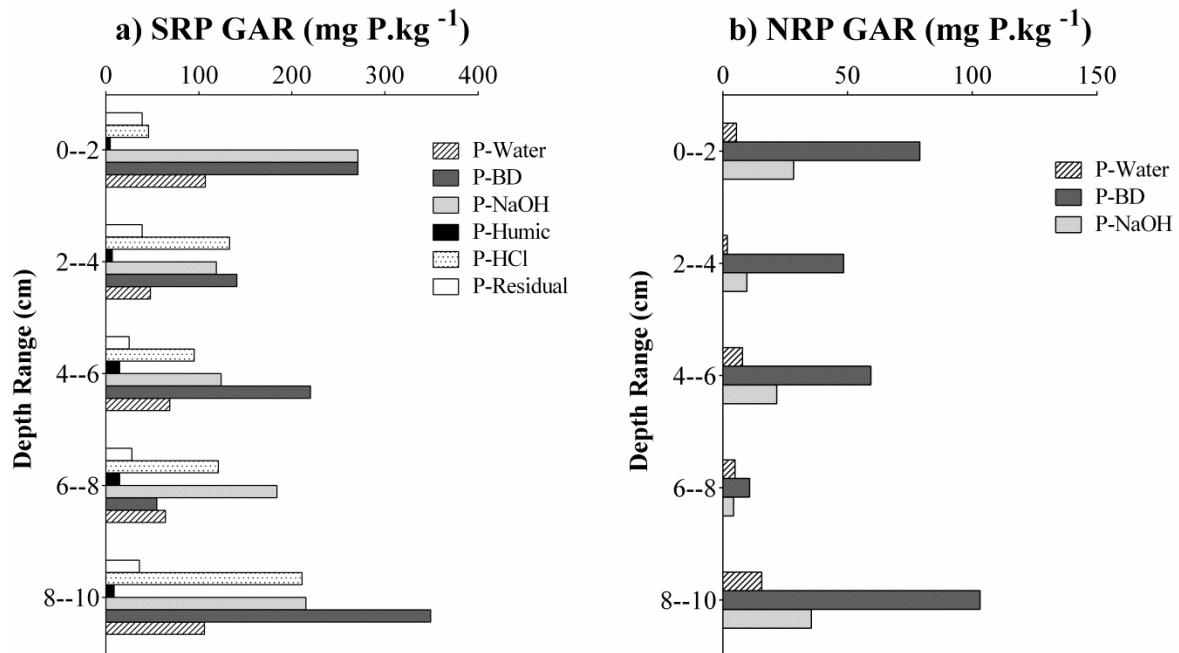
The amount of soluble reactive phosphorus (SRP) was greater than Non-Reactive Phosphorus (NRP) in all fractions (Figure 4). Whereas all forms, the minimum and maximum values of SRP contents in Gargalheiras were  $5 \text{ mg.kg}^{-1}$  and  $349 \text{ mg.kg}^{-1}$ , respectively (Figure 4a). While NRP contents ranged from  $2 \text{ mg.kg}^{-1}$  to  $103 \text{ mg.kg}^{-1}$  (Figure 4b). The range of amount of P fraction in 10 cm of the sediment were:  $349.50 \text{ mg.kg}^{-1}$  of P-water,  $1036 \text{ mg.kg}^{-1}$  of P-BD,  $913.18 \text{ mg.kg}^{-1}$  of P-NaOH,  $51.29 \text{ mg.kg}^{-1}$  of P-Humic,  $606.62 \text{ mg.kg}^{-1}$  of P-HCl and  $166.47 \text{ mg.kg}^{-1}$  of P-Residual.

Despite the variation between the depths, in general, the range of SRP fractions in decreasing order was: P-BD > P-NaOH > P-HCl > P-water > P-Residual > P-Humic (Figure 5a). The range of NRP fractions was: P-BD > P-NaOH > P-water (Figure 5b).

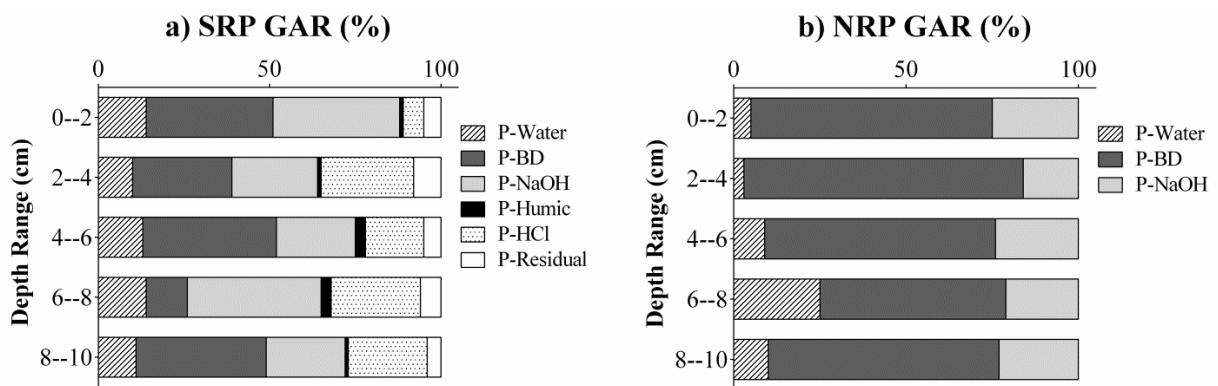
In Cruzeta, the amount of soluble reactive phosphorus (SRP) was too greater than non-reactive phosphorus (NRP). SRP contents in Cruzeta ranged from  $12 \text{ mg.kg}^{-1}$  to  $371 \text{ mg.kg}^{-1}$ . While NRP contents ranged from  $0 \text{ mg.kg}^{-1}$  to  $32 \text{ mg.kg}^{-1}$ . Adding the values of SRP of all slices, it is possible to obtain:  $345.72 \text{ mg.kg}^{-1}$  of P-water,  $1468.30 \text{ mg.kg}^{-1}$  of P-

BD, 902.30 mg.kg<sup>-1</sup> of P-NaOH, 128.36 mg.kg<sup>-1</sup> of P-Humic, 889.44 mg.kg<sup>-1</sup> of P-HCl and 209.49 mg.kg<sup>-1</sup> of P-Residual. These values corresponding to amount of P fractions in 10 cm of the sediment.

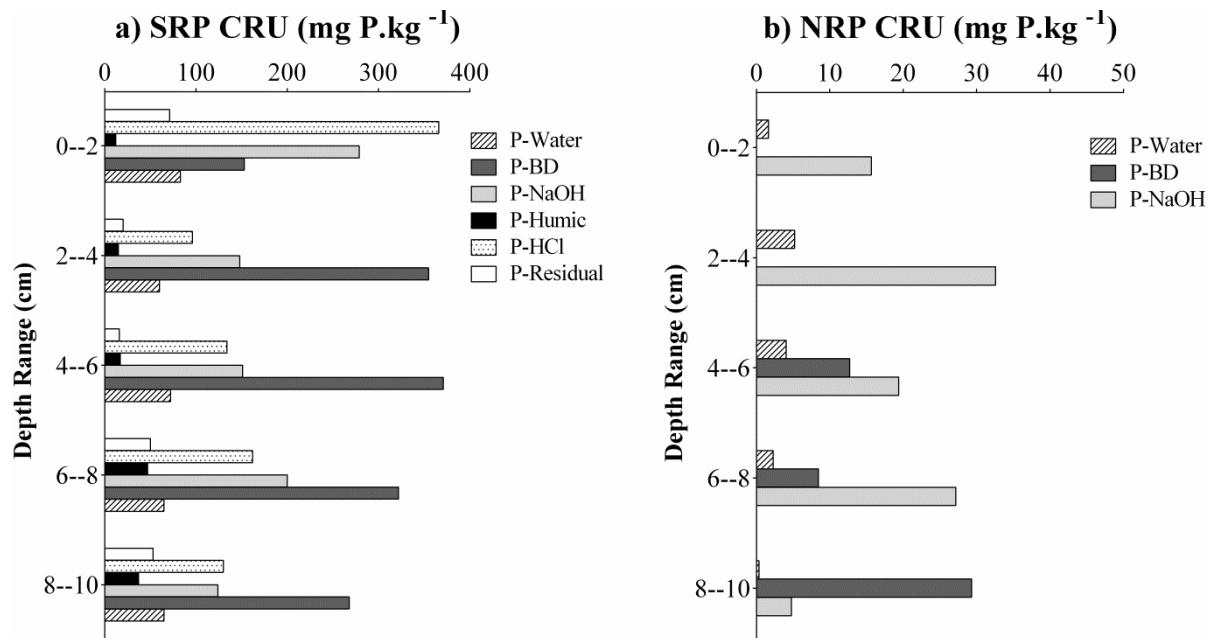
Despite the variation between the depths, in general, the range of SRP fractions in decreasing order was: P-BD > P-NaOH > P-HCl > P-water > P-Residual > P-Humic (Figure 7a). The range of NRP fractions was: P-NaOH > P-BD > P-Water (Figure 7b).



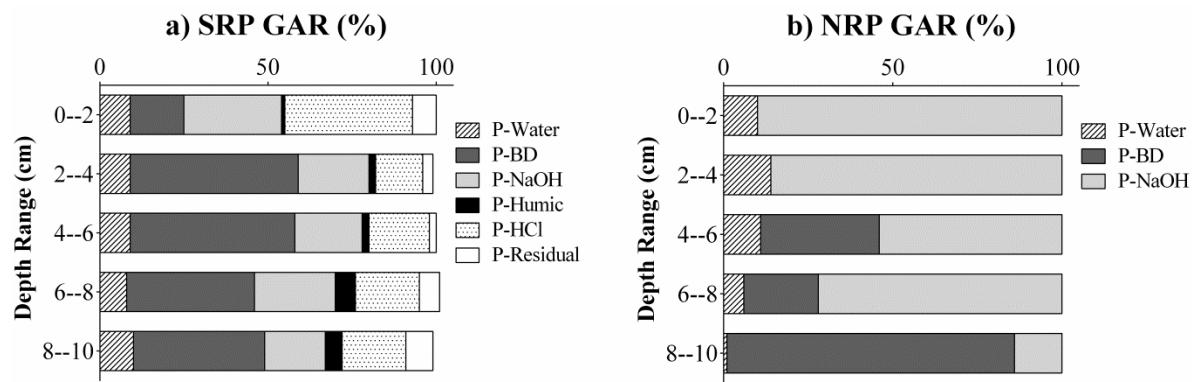
**Fig. 4.** Fractions of a) Soluble Reactive Phosphorus (SRP) and b) Non-reactive Phosphorus (NRP) per depth range in the sediment for Gargalheiras Reservoir.



**Fig. 5.** Relative values of a) Soluble Reactive Phosphorus (SRP) and b) Non-reactive Phosphorus (NRP) per depth range in the sediment for Gargalheiras Reservoir.

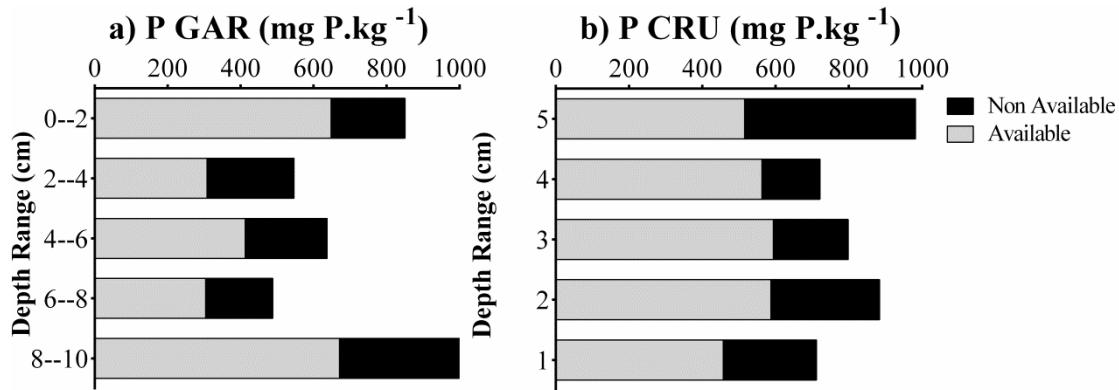


**Fig. 6.** Fractions of a) Soluble Reactive Phosphorus (SRP) and b) Non-reactive Phosphorus (NRP) per depth range in the sediment for Cruzeta Reservoir.



**Fig. 7.** Relative values of a) Soluble Reactive Phosphorus (SRP) and b) Non-reactive Phosphorus (NRP) per depth range in the sediment for Cruzeta Reservoir.

The total pool of P (all forms and the amounts in the all slices) in 10 cm of the sediment was  $3603.96 \mu\text{m.L}^{-1}$  in Gargalheiras and  $4096.22 \mu\text{m.L}^{-1}$  in Cruzeta. In terms of overall P availability both reservoirs presented a high amount of P (Figure 8). The total available P in Gargalheiras was  $2343.68 \text{ mg.kg}^{-1}$  and non-available was  $824.39 \text{ mg.kg}^{-1}$  of the surface up to 10 cm of depth. In Cruzeta, the total available P was  $2716 \text{ mg.kg}^{-1}$  and non-available P was  $1227.28 \text{ mg.kg}^{-1}$  of the surface up to 10 cm of depth.



**Fig. 8.** Amount of available and non-available phosphorus in each depth of the sediment for a) Gargalheiras and b) Cruzeta.

#### 4. Discussion

A far as concern, this study is the first work showing the concentration of the different P fractions in semi-arid sediments. Gargalheiras and Cruzeta reservoirs showed a higher content of phosphorus. This study showed that the amount of P in sediments of semi-arid regions are enough high in relation to others regions (Table 3) as Singapore, mainly MacRitchie Reservoir (Ting e Appan, 1996), Greece (Kaiserli et al., 2002) and China (Wang et al., 2006). In addition, the available phosphorus form is predominant in the two studied reservoirs. This means that most of the phosphorus in the sediment is bound to ions such as Fe, Al, Mn and weakly sorbed. These fractions are more easily released, mainly when anoxic conditions prevail at the sediment–water interface, becoming it available for phytoplankton growth.

The reductant soluble phosphorus (P-BD) was a form with higher predominance in the reservoirs. This form is usually the most common in several lakes, which has the greater amount (Table 3). The P-BD is related with oxides which may appear in sediments and represents the redox-sensitive P forms, mainly bound to Fe-hydroxides and Mn compounds. This fraction is considered as potentially mobile pool of P and is algal available (Kaiserli et al., 2002). It may be released from anoxic sediments and becomes an internal P source to water bodies, which suffer from occasional DO depletion (Kleeberg and Dudel, 1997), because the iron in the oxidized form has a strong binding capacity with phosphate, so, in anoxic conditions, the iron is reduced, releasing the phosphate for the water column.

Gargalheiras reservoir experienced anoxia in many months during May 2015 to June 2016 (Cavalcante et al., submitted), period prior to the sediment sample of this study. Associating the prevalence of the P-BD with the presence of anoxic conditions in interface water-sediment, is possible claim that in Gargalheiras reservoir there is a high possibility of has release of reductant soluble P (P-BD), during the periods with anoxic conditions.

The Cruzeta reservoir did not present anoxia at the bottom, during the period of May 2015 to June 2016, but presented hypoxia in a few months and in most months the reservoir presented a homogeneous water column (Cavalcante et al., submitted). So, despite the predominance of P-BD, in Cruzeta reservoir there is less possibility of released P bound Fe and Mn. However, the Cruzeta Reservoir has a high inorganic turbidity, caused by high values of SRP and inorganic solids (Braga et al., 2015; Medeiros et al., 2015; Cavalcante et.al, submitted), which presented average of  $174.17 \mu\text{g.L}^{-1}$  and  $81.73 \text{ mg.L}^{-1}$ , respectively, during May 2015 to June 2016 (Cavalcante et al., submitted), a period prior to sediment sampling. This can be explained by the shallower conditions (depths < 2m) during the drought which enhance sediment resuspension by the wind (Cavalcante et al., submitted).

The resuspension does not necessarily lead to increased release of phosphorus; this is because the overall process depends on the actual equilibrium conditions between sediment and water (Søndergaard et al., 1992). But, in some lakes it has been shown that resuspension increases release rates (Fan et al., 2001; Søndergaard et al., 1993). Thus, the resuspension by wind can de releasing P of the sediment and probably, the high amount of SRP in the water has a contribution of P of the sediment. It is not possible to say with certainty which form of phosphorus is released through resuspension, however, the P-water, that is the form more labile (Fytianos e Kotzakioti, 2005; Kaiserli et al., 2002; Paludan e Jensen, 1995), can be easily released with a physical alteration of the system caused by resuspension.

The P-NaOH was the second predominant form in both reservoirs. This fraction includes dissolved reactive phosphorus sorbed to clay minerals, oxides of Al and organic P (Paludan e Jensen, 1995). This form also could be released when anoxic conditions prevail in the sediment–water interface (Ting e Appan, 1996), similar to the release of P-BD. Then, P-NaOH has the possibility of being released into the Gargalheiras reservoir, due to the presence of anoxic conditions. However, the P-BD is more mobile than P-NaOH, so, has more possibility of release than P-NaOH.

**Table 3** - Literature data of concentration ( $\text{mg kg}^{-1}$ ) of P-fractions in lake sediments.

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

\* Values roughly estimated from figure data

<sup>a</sup>(Ting e Appan, 1996) Sediment collected in the top 5 cm

<sup>b</sup>(Gonsiorczyk et al., 1998) Sediment collected superficially

<sup>c</sup>(Kaiserli et al., 2002) Sediment collected superficially

<sup>d</sup>(Wang et al., 2006) Sediment collected in the top 30 cm

<sup>e</sup>(Rydin, 2000) Sediment collected in the top 15 cm

The P-HCl fraction corresponds to the phosphorus bonded to calcium, including apatite P and P bound to carbonates, and it was the third fraction predominant in both reservoirs. This form is considered as non-bioavailable and difficult to release, however, under weakly acidic conditions, it can be partly released (Jin et al., 2006b; Li et al., 2015). Nonetheless, the bottom water pH values from reservoirs of the semi-arid region are usually above pH 8, and they also present high alkalinity values being the highest values observed usually in the dry season (Huszar et al., 2000). So, the release of P-HCl is more difficult in semi-arid regions, mainly in periods of extreme drought, since water generally has alkaline conditions.

The pH also influence in release of P-BD and P-NaOH forms. High pH promotes the release of these forms, because the P biding capacity of iron and aluminum compounds as pH increase in the overlying water and the sediment, primarily due to the ligand exchange reactions in which hydroxide ions may replace orthophosphate (Jin et al., 2006a). Therefore, the release of these forms can also occur due to the high pH in both studied reservoirs.

In the semi-arid regions, mainly in drought periods, the reservoirs present high concentrations of algal biomass, indicative of accelerated eutrophication with possible cyanobacterial blooms (Barbosa et al., 2012; Braga et al., 2015). The release of P from the sediment, certainly contributes heavily to this problem, because the pool of P is very high. Therefore, the semi-arid reservoirs need for effective treatments to control eutrophication and mitigate the damage caused by cyanobacterial. The results of this work are very important to understand the dynamics of the sediment in semi-arid reservoirs, a region that has scarce data in this area.

The data of this study also are important because this information can be used in the restoration of the semi-arid reservoirs, by means the application of geoengineering techniques. Because the dosage of the products used in the techniques is based on estimates of the potential releasable phosphorus pool in water and sediment (Lürling e van Oosterhout, 2013). Many techniques can be employed in water bodies to reduce the eutrophication. The first step is to tackle direct input of nutrients (Cooke et al., 2005), but the internal P load can delay the recovery (Søndergaard et al., 1992). The technique, known as P-capping, can be used to control legacy P stores in sediments, through the application of products focusing on three types (1) aluminosilicate minerals (e.g., modified

zeolites), (2) existing catchment soils amended with natural materials (e.g., chitosan), and (3) mineral-based byproducts (Spears et al., 2014, 2013).

In summary, our results highlight the potential impact of the potentially high amounts of labile P in the sediment of semi-arid. We encourage after research's to apply the method we used to investigate a broader number of lake regarding P fractions and the future application of products for the restoration of semi-arid lakes.

## 5. Conclusions

The phosphorus buried in the sediment, accumulated over many years, is high in Gargalheiras and Cruzeta reservoirs, in relation to other regions (table 3). But, the amount of P does not showed distribution tendency of increase or decrease through with depth. In addition, the predominant forms in the sediment were available forms, mainly the form reductant soluble (P-BD), evidencing that the phosphorus can be released easily for the water column under anoxic conditions near the sediment, mainly in Gargalheiras reservoir, which presented this conditions in many periods. In Cruzeta reservoir, the predominance also is the P-BD form, but the reservoir presented in the last years depths very low (<2m), so the anoxic condition near the sediment are not common and frequent, as in Gargalherias. But, it is also susceptible to release, of the others forms such as P-water (the more labile), by the action of the wind, because its depth is currently very low.

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