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Phosphorus dynamics in the water of tropical semiarid reservoirs in a prolonged drought period

Dinâmica do fósforo na água de reservatórios tropicais semiáridos em um período de seca prolongada

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Abstract: Aim: To verify the vertical distribution of phosphorus in the water and to identify the predominant forms of P in the water column for understand the phosphorus dynamics in tropical semiarid reservoirs during a prolonged drought period. **Methods:** Two reservoirs from the semiarid region of Rio Grande do Norte were analysed during the period from May 2015 to June 2016. Were analysed: Suspended solids (SS), chlorophyll a (Chl-a), dissolved oxygen (OD) and temperature. Vertical profiles were plotted for total phosphorus (PT), total dissolved phosphorus (PTD), particulate phosphorus (PP), dissolved organic phosphorus (POD) and soluble reactive phosphorus (FRS). **Results:** The phosphorus values distributed in the water column were high for both reservoirs, presenting the highest values during the periods with lower depth. Gargalheiras presented greater predominance of PT and PP, while Cruzeta had the highest values of FRS. Chl-a and SS values were also consistent with phosphorus values: Chl-a was higher in Gargalheiras, while SS, mainly inorganic, were higher in Cruzeta. Gargalheiras presented anoxic conditions close to the sediment from May 2015 to December 2015, which may induce the release of phosphorus from the sediment to the water column. Values that are too high during the shallower months, especially in Cruzeta, may have been influenced by the release of P from sediment through wind resuspension. **Conclusions:** The amounts and predominant types of phosphorus in the water column are of great importance to understand the phosphorus dynamics and will support restoration plans for the studied environments. In this study it was possible to verify that the reservoirs are susceptible to the release of P from the sediment due to the environmental conditions, mainly low depths, resuspension of the wind and anoxia in the hypolimnion.

Keywords: phosphorus forms in the water; prolonged drought; internal loading.

Resumo: Objetivo: Verificar a distribuição vertical do fósforo na água e identificar as formas predominantes de P na coluna d'água, para entender a dinâmica do fósforo em reservatórios semiáridos tropicais em um período de seca prolongada. **Métodos:** Foram analisados dois reservatórios da região semiárida do Rio Grande do Norte, durante o período de Maio de 2015 a Junho de 2016. Foram analisados: sólidos suspensos (SS), clorofila-a (Chl-a), oxigênio dissolvido (OD) e temperatura. Perfis verticais foram traçados para fósforo total (PT), fósforo total dissolvido (PTD), fósforo particulado (PP), fósforo orgânico dissolvido (POD) e fósforo reativo solúvel (FRS). **Resultados**: Os valores de fósforo distribuídos na coluna d'água foram elevados para ambos os reservatórios, apresentando os maiores valores durante os períodos com menor profundidade. Gargalheiras apresentou maior predominância de PT e PP, enquanto Cruzeta apresentou os maiores valores de FRS. Os valores de Chl-a e SS também foram condizentes com os valores de fósforo: a Chl-a foi maior em Gargalheiras, enquanto os SS, principalmente inorgânicos, foram maiores em Cruzeta. Gargalheiras apresentou condições anóxicas próximo ao sedimento de maio de 2015 a dezembro de 2015, o que pode induzir a liberação de fósforo do sedimento para a coluna d'água. Valores demasiadamente elevados durante os meses mais rasos, principalmente em Cruzeta, podem ter sofrido influência da liberação de P do sedimento através da ressuspensão pelo vento. **Conclusões:** As quantidades e os tipos predominantes de fósforo na coluna de água são de grande importância para entender a dinâmica do fósforo e apoiarão planos de restauração para os ambientes estudados. Neste estudo foi possível verificar que os reservatórios são suscetíveis à liberação de P do sedimento devido às condições ambientais, principalmente profundidades baixas, ressuspensão do vento e anoxia no hipolímnio.

Palavras-chave: formas de fósforo na água; seca prolongada; fertilização interna.

1. Introduction

Eutrophication has been defined as the nutrient enrichment of waters which results in increased production and growth of algae and macrophytes, unbalancing the ecosystem diversity and causing the degeneration of water quality (Dodds et al., 2009). Phosphorus (P) and nitrogen (N) are main causes of this problem. Thus, the attention has focused on the role of this nutrients in controlling algal growth (Schindler et al., 1973). More specifically, the control of eutrophication is mainly focused on phosphorus, as it can be decreased more easily to limit algal growth (Smith & Schindler, 2009).

Phosphorus is considered a limiting nutrient and is present in freshwater systems in forms: soluble reactive phosphorus (SRP), dissolved organic phosphorus (DOP), and particulate phosphorus (PP) (Teubner et al., 2003). The sum of soluble reactive phosphorus (SRP) and dissolved organic phosphorus (DOP) is the total dissolved phosphorus (TDP). The sum of the total dissolved phosphorus (TDP) and particulate phosphorus (PP) is the total phosphorus (TP). Most studies have reported the P concentrations as TP and SRP, due to the easy measurement. SRP is the primary dissolved form of phosphorus and is readily available to algae and aquatic plants (Golterman, 2004). PP can be seen as a key parameter in P limited ecosystems, because it is a function of total biomass, but, the PP is associated to other fraction of P in water (SRP and DOP) (Teubner et al., 2003). Thus, the determination of P forms in water is important to understand their dynamics and relationships with other components of the aquatic system, such as phytoplankton, macrophytes and sediment, and understand the implications in the water quality.

When nutrients enter in low-enriched systems, they are rapidly captured by phytoplankton, as they are required for the primary production of the ecosystem (Wetzel, 2001). After lysis and death of phytoplankton, large amounts of the incorporated phosphorus will be released as inorganic P, while small amounts are not mineralized and are incorporated into the sediment as org-P; the dissolved nutrients are again incorporated by the phytoplankton, and again a small part does to the sediment; process that occurs several times, which makes the amount stored in the sediment considerable (Golterman, 2004). The cycling of P is not limited to phytoplankton. The phosphate also enter in the sediment in inorganic forms, entering the lakes as a result of erosion or leaching, can be mainly adsorbed on iron, aluminium and calcium hydroxides. These inorganic compounds are also formed in the sediment, where the mineralization processes still continue to break organic forms of P (Golterman, 2004).

To reverse the process of eutrophication in lakes is essential a significant reduction in external nutrient loading, but not necessarily sufficient. Internal loading, by means of biomass cycling, sediment P release (through the influence of OD, temperature, pH, wind resuspension), organism activities, and other mechanisms, can introduce more nutrients to the lake than external loading in some times of the year; therefore require considerable attention (Cooke et al., 2005). The release of P from the sediment, in special, is an important process, because the release of phosphorus from the sediment can be so intense and persistent that its prevents any improvement in water quality for a considerable period after the reduction of external loading (Granéli, 1999; Søndergaard et al., 2013).

In the Brazilian semiarid region, the reservoirs have multiple uses, such as water supply for domestic use and drinking (mainly), irrigation and animal consumption. However, many reservoirs suffer negative impacts in water quality caused by human activities and the natural conditions of the region (Barbosa et al., 2012). The non-point sources of pollution, such as agriculture and livestock, are relevant for the aquatic systems of the semiarid region. They are often the main external source of nutrients arriving in the reservoirs during the rainy seasons through leaching of the soil (Oliveira, 2012; Medeiros et al., 2015). This is because, in semiarid regions, diffuse pollution of water sources may be high due to peculiar natural conditions of the region, notably shallow soils with little coverage due to characteristic vegetation (Oyama & Nobre, 2004). During the drought periods, the external loading of nutrients is very low in some reservoirs of the semiarid region, however, the concentrations of nutrients, mainly phosphorus, remains usually high . This may be due to the increase of the water retention time in the reservoirs which concentrates the nutrients in the system (Braga et al., 2015). Also, drought periods make reservoirs more susceptible to environmental factors, such as high temperatures and very low depths, which may influence phosphorus release from the sediment.

Thus, the study's aim is to verify the vertical distribution of phosphorus in the water and identify the predominant forms of P in water column during drought periods, to understand the dynamics of phosphorus in tropical semiarid reservoirs in a prolonged drought period.

2. Material and Methods

2.1. Study area

Gargalheiras and Cruzeta reservoirs (Figure 1) were formed by the damming of the river Acauã (in 1959) and the São José Creek (in 1929) respectively; both belong to the Piranhas-Assu river watershed.

The Gargalheiras reservoir is located in Acari city, in the semiarid region of the state of Rio Grande do Norte. The reservoir has a maximum capacity of 44 million m^3 (SEMARH, 2016). In the studied period, the depths of the reservoir were very low, varying from 7 m in May 2015, to 1.5 m in March 2016 and returning to 6m in April 2016.

The Cruzeta reservoir is located in the municipality of the same name, also in Rio Grande do Norte, and its maximum capacity is 23 million m^3. Both reservoirs serve multiple uses including human water supply. The variation of the depth of the Cruzeta reservoir was 2.5 m at the start of this study to 0.5 m in February 2016 and increasing to 2 m in March 2016.

The climate of the region is tropical semiarid with an average temperature higher than 25 °C and an evaporation rate of 1500 to 2000 mm.year^{-1} (SEMARH, 2016). This study was conducted

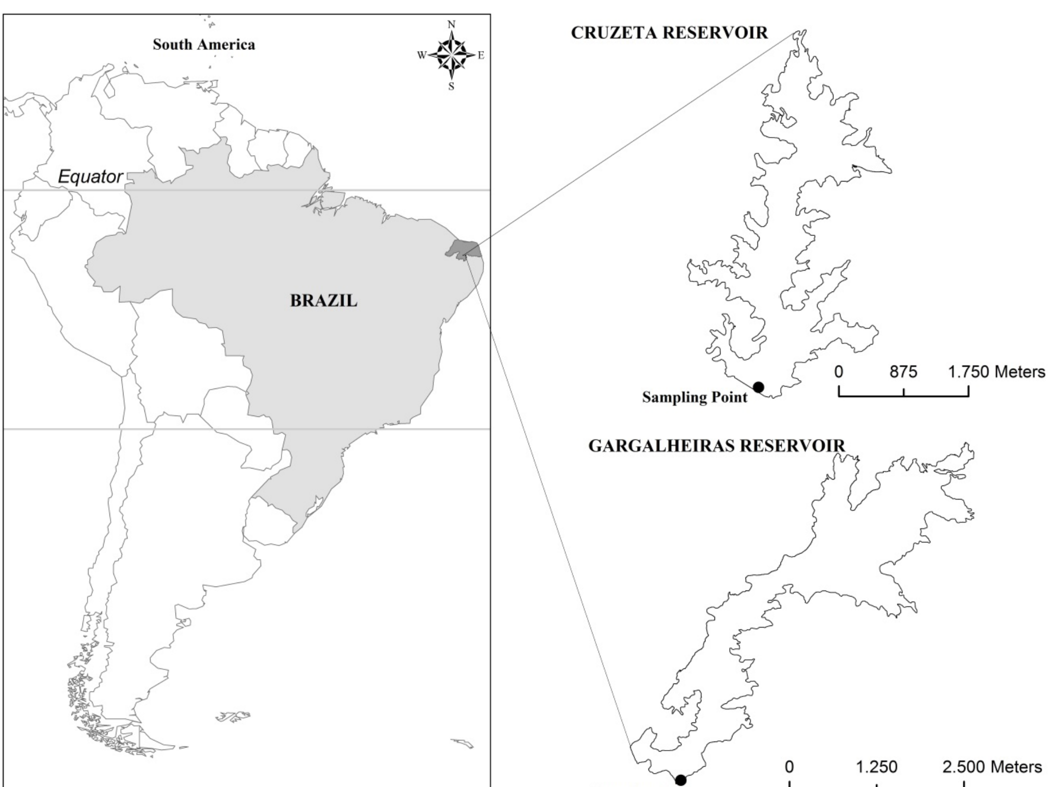

Figure 1. Location of the Gargalheiras and Cruzeta reservoirs and the sampling points near their respective dams.

from May 2015 to June 2016, comprising part of a prolonged drought period that started in 2012.

2.2. Samplings

Water samples were collected at station points near the dam (Figure 1). The point was chosen because, in the sampling period, the volume of the reservoir was very low and the surface area very small and so there was water only near the dam. Moreover, near to the dam there is greater depth and the greater accumulation of sediments. Another reason that makes the important point is that in it there is water catchment for human supply. Water temperature and dissolved oxygen were measured at 0.5 meter increments from the surface of the reservoir to the bottom, using an oxygen probe (Instrutherm MO-900). The vertical profile was defined by measuring the DO and temperature data of the water.

Based on the DO and the temperature vertical profiles, two integrated samples of the epilimnion and the hypolimnion were collected with a Van Dorn bottle for further analysis of suspended solids and chlorophyll-a (the latter was measured for epilimnion only). Samples were also collected every 0.5 m of the depth, using a Van Dorn bottle, to analyse the distribution of P in the water column.

The samples were stored in polyethylene bottles, previously washed with 10% HCl and deionized water, and packed in iceboxes during transport to the laboratory.

2.3. Analyses of the samples

The concentration of total suspended solids was determined through gravimetry after drying the filters at 105 °C. The concentration of Inorganic Suspended Solids (ISS) was measured after ignition in a muffle furnace at 550 ° C for 3h (APHA, 2005). The Organic Suspended Solids (OSS) were determined by calculating the difference between the concentration of total suspended solids and inorganic suspended solids. The concentration of chlorophyll-ɑ was measured through spectrophotometry by extraction with 96% ethanol (Jespersen & Christoffersen, 1987).

Concentrations were determined for Soluble Reactive Phosphorus (SRP) (the most bioavailable form), Total Dissolved Phosphorus (TDP), Organic Dissolved Phosphorus (ODP), Total Phosphorus (TP) and Particulate Phosphorus (PP) (incorporated in the biota).

TP and TDP were measured through colorimetric analysis (Murphy & Riley, 1962) after the digestion of the samples (Valderrama, 1981). The SRP was also obtained by means of the colorimetric method (Murphy & Riley, 1962). The ODP and the PP were determined by calculating the differences TDP-SRP and TP-TDP, respectively. The samples for the analysis of SRP and TDP were filtered on glass fibre membranes (0.45 μm).

2.4. Data analysis

The historical data series (1963-2013) of precipitation was provided by the Agricultural Research Company of Rio Grande do Norte (EMPARN, 2016) and the volumetric variation data was provided by the Secretariat of Environment and Water Resources of Rio Grande do Norte (SEMARH, 2016).

The vertical profiles of DO, temperature, and phosphorus types in the water column were elaborated. The data were divided into two periods, before and after rainfall events, and then mosaics of these periods were produced.

3. Results

The monthly rainfall was below the historical average in most of the studied months for both reservoirs (Figure 2). The accumulated rainfall during the studied period was 575 mm in Gargalheiras and 546 mm in Cruzeta, less than the historical average (658 mm in Gargalheiras and 755 mm in Cruzeta). In Gargalheiras reservoir, the precipitation was less than the historical average in 11 months tested and above the historical average in 3 months. The rain in these 3 months, mainly February and March, was important to subtly increase the volume accumulated in the reservoir. In Cruzeta the scenario is similar; 3 months of rain were above historical average, important to increase the reservoir level.

During the entire period, the volumes of the reservoirs remained at very low levels dropping sharply until the beginning of 2016. In January, February and March occurred rains that increased the level of the reservoirs of the region.

Vertical profiles of dissolved oxygen (DO) have shown several differences between the reservoirs (Figure 3). Gargalheiras, which has the greatest depth, presented chemical stratification, with anoxia near the sediment during May 2015 to December 2015. Whereas Cruzeta showed better mixing, nevertheless, with low DO values (minimum of 1 mg L^{-1}), in the beginning of 2015 and 2016. As expected, both reservoirs presented more thorough mixing during the driest and shallowest months, January 2016 to May 2016.

Neither of the reservoirs presented thermal stratification (Figure 4), except during the period that followed the rains (between April and May 2016) and mainly in Gargalheiras, when a variation of 6 °C in the water column along 6.4 m of depth was observed.

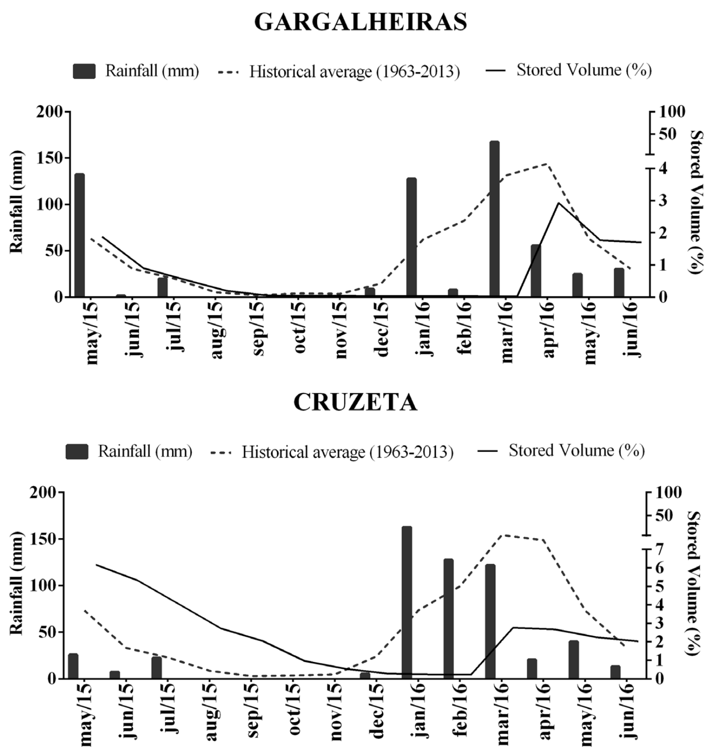

Figure 2. Monthly rainfall, historical average rainfall and stored volume of the Gargalheiras and Cruzeta reservoirs, from May/2015 to June/2016.

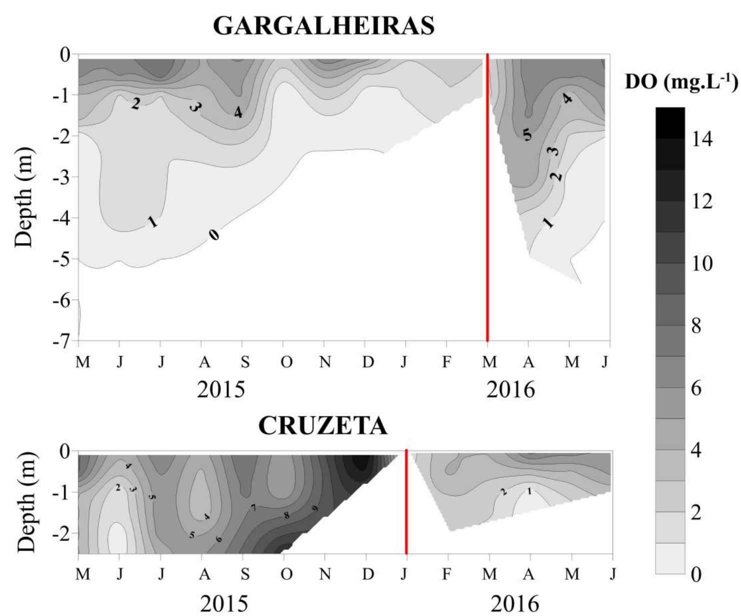

Figure 3. Vertical Profiles of dissolved oxygen (DO) of the reservoirs Gargalheiras and Cruzeta, in the period of May 2015 to June 2016. The red line is indicating the highest rainfall in the period, which contributed to the increase in water depth, as can be seen in the figure.

The values of P in Gargalheiras (Figure 5) and Cruzeta (Figure 6) were very high throughout the study period; mean values are presented in Table 1. TP in both reservoirs presented values above the standard limit for eutrophication (50 μg.L^{-1}) (Thornton & Rast, 1993).

The vertical profiles of P in Gargalheiras presented higher values during the months with

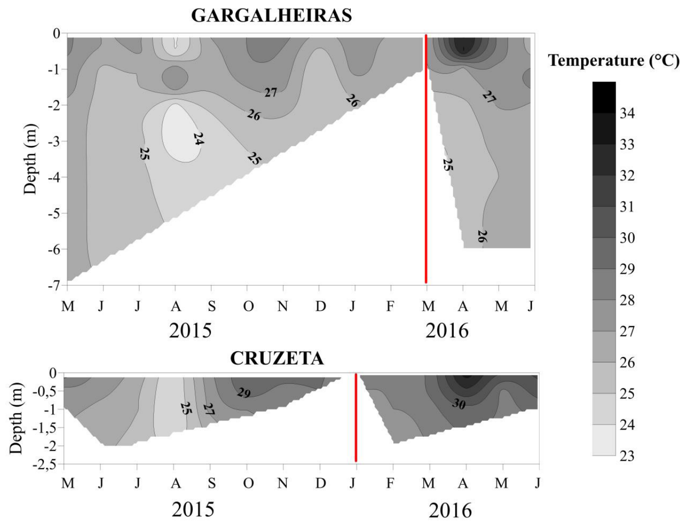

Figure 4. Vertical temperature profiles of Gargalheiras and Cruzeta reservoirs from May 2015 to June 2016. The red line is indicating the highest rainfall in the period, which contributed to the increase in water depth, as can be seen in the figure.

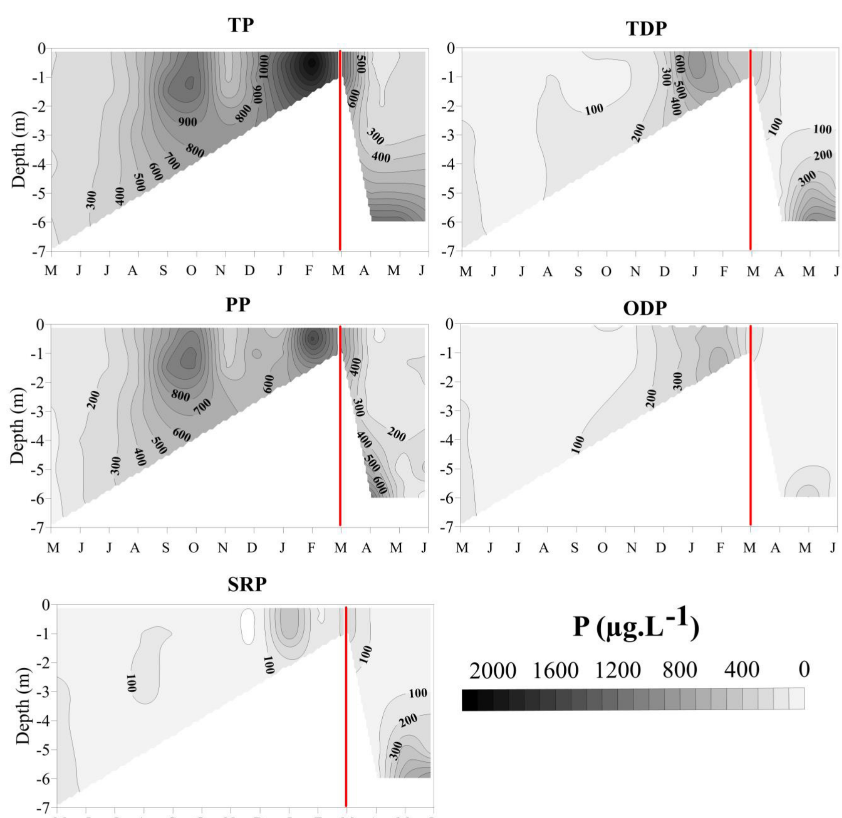

Figure 5. Total Phosphorus (TP), Total Dissolved Phosphorus (TDP), Particulate Phosphorus (PP), Dissolved Organic Phosphorus (ODP) and Soluble Reactive Phosphorus (SRP) in Gargalheiras reservoir from May 2015 to June 2016. The red line is indicating the highest rainfall in the period, which contributed to the increase in water depth, as can be seen in the figure.

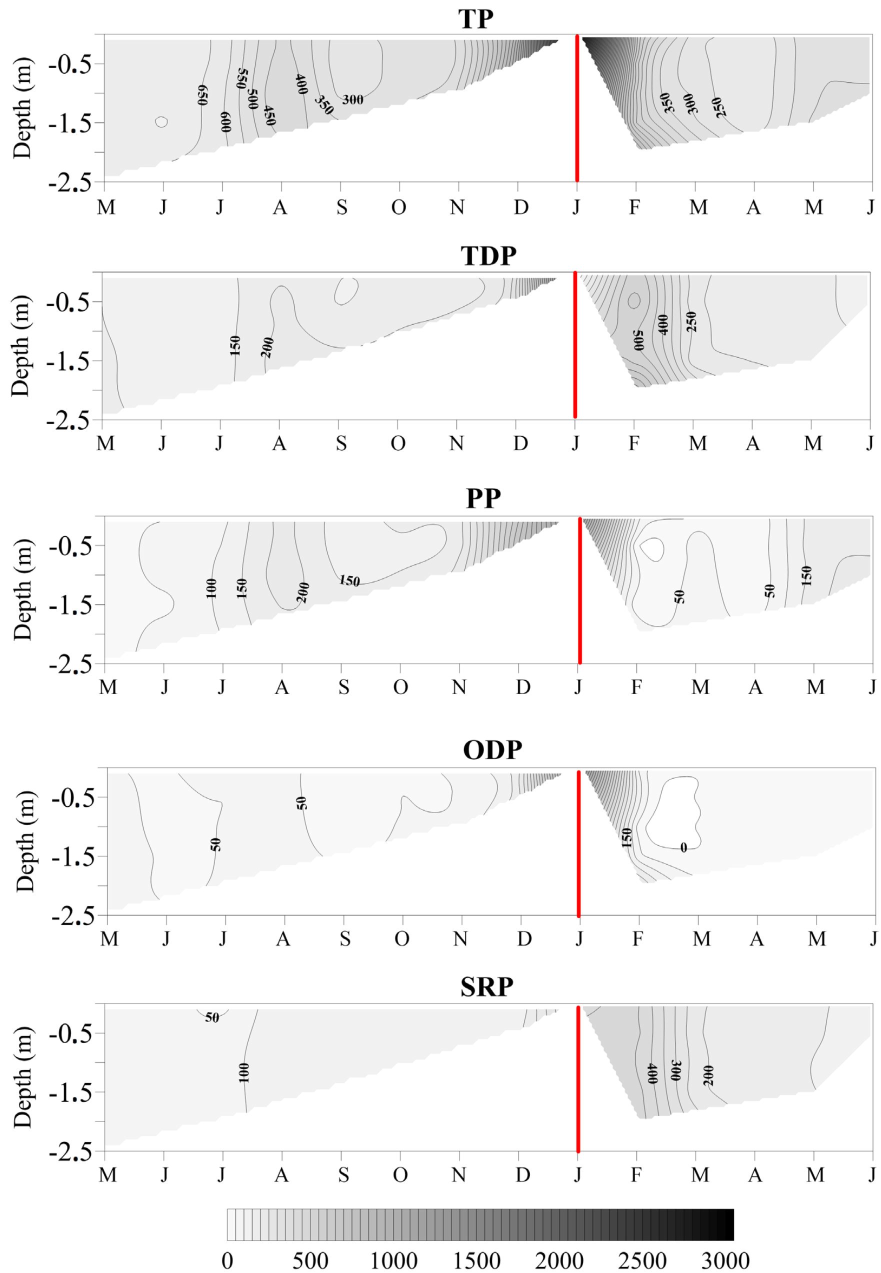

Figure 6. Total Phosphorus (TP), Total Dissolved Phosphorus (TDP), Particulate Phosphorus (PP), Organic Dissolved Phosphorus (ODP) and Soluble Reactive Phosphorus (SRP) in Cruzeta from May 2015 to June 2016. The red line is indicating the highest rainfall in the period, which contributed to the increase in water depth, as can be seen in the figure.

Table 1. Mean, maximum and minimum values of the phosphorus forms analysed in the water of the Gargalheiras and Cruzeta reservoirs from May 2015 to June 2016.

Phosphorus Forms	GARGALHEIRAS			CRUZETA		
	Min	Mean	Max	Min	Mean	Max
SRP ($\mu g.L^{-1}$)	6.71	106.29	504.55	65.17	174.17	467.5
ODP ($\mu g.L^{-1}$)	24.69	135.63	503.46	5.96	145.99	1317.48
PP ($\mu g.L^{-1}$)	96.45	502.3	1255.42	18.13	239.72	1286.67
TDP ($\mu g.L^{-1}$)	76.2	241.99	854.44	108	320.15	1743.33
TP ($\mu g.L^{-1}$)	203.65	744.3	1853.33	169.6	559.88	3030

SRP= Soluble Reactive Phosphorus, ODP= Organic Dissolved Phosphorus, PP= Particulate Phosphorus, TDP = Total Dissolved Phosphorus, TP = Total Phosphorus.

lower depths. However, posteriorly, when the heavy precipitation increased the depth of the reservoir, high concentrations of P were still observed at the bottom near the sediment.

Phosphorus results have shown that the environments are very different. Total Phosphorus (TP) is composed of Particulate Phosphorus (PP) and Total Dissolved Phosphorus (TDP). In Gargalheiras, the predominant fraction of TP is the PP, while in Cruzeta it is TDP (Figure 7). The TDP is composed of Organic Dissolved Phosphorus (ODP) and Soluble Reactive Phosphorus (SRP). In Gargalheiras, TDP has more ODP than SRP and the opposite occurs in Cruzeta (Figure 7).

The concentrations of suspended solids did not show a pattern in either of the reservoirs (Figure 8). Gargalheiras presented a higher amount of Organic Suspended Solids (OSS) in 71% of the analysed

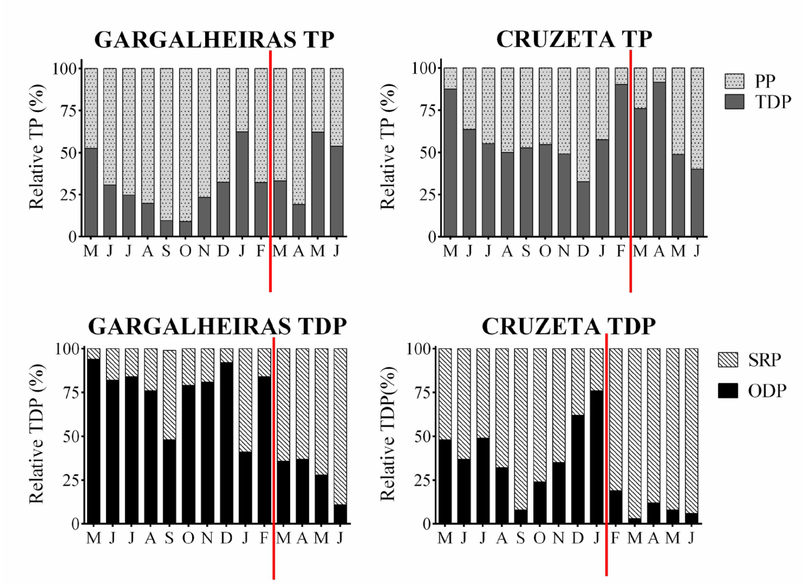

Figure 7. Relative Total phosphorus (TP) for Gargalheiras and Cruzeta, composed of the fractions of Particulate Phosphorus (PP) and Total Dissolved Phosphorus (TDP); and Relative Total Dissolved Phosphorus (TDP), composed of the fractions of Soluble Reactive Phosphorus (SRP) and Organic Dissolved phosphorus (ODP). The red line is indicating the highest rainfall in the period, which contributed to the increase in water depth, as can be seen in the figure.

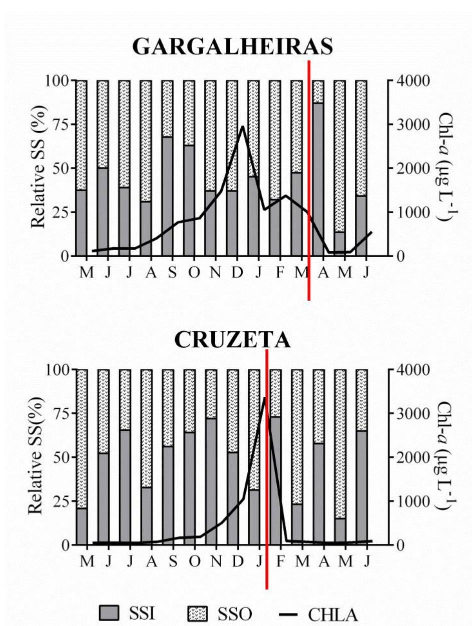

Figure 8. Concentrations of Inorganic Suspended Solids (ISS), Organic Suspended Solids (OSS), and Chlorophyll-a (Chl-a) in the Gargalheiras and Cruzeta reservoirs. The red line is indicating the highest rainfall in the period, which contributed to the increase in water depth, as can be seen in the figure.

months. While the amount of Inorganic Suspended Solids (ISS) was higher in Cruzeta during 64% of the studied months.

The concentration of chlorophyll-α was superior in Gargalheiras in most of the analysed months (Figure 8). However, both presented values higher than the standard limit for eutrophication (15 $\mu g.L^{-1}$) (Thornton & Rast, 1993).

4. Discussion

The results showed high concentrations of P in the water column in both reservoirs throughout the studied period. The P concentration in the whole water column increased as it became shallower.

Extreme drought periods cause large variations in water levels, which may cause changes in the physical, chemical and biological characteristics of aquatic environments (Moss, 2011). In the semiarid region of Rio Grande do Norte the drought started in 2012 and is still going at the time of writing.

The abrupt decrease in the volumes of both reservoirs greatly worsened the water quality, significantly increasing the amount of phosphorus and, consequently, the algal biomass (Naselli-Flores & Barone, 2005). The main input of this nutrient into aquatic environments of the semiarid region is diffuse pollution, reaching the water body through rainfall. In periods of no rain, there are no external inputs of nutrients (Naselli-Flores, 2003; Barbosa et al., 2012), so the increase in phosphorus in the water is mainly due to the amount of autochthonous nutrient that has been concentrated because of the decrease in water volume (Volohonsky et al., 1992).

During the analysed period (2015 to 2016), there were instances of rainfall that increased the volume of the reservoirs. This increase in volume is reflected in the decrease of phosphorus concentrations, mainly the total phosphorus, solids and chlorophyll-α, resulting from the large inflow of water into the reservoirs, providing an improvement in water quality (Arreghini et al., 2005). Despite this, there was an increase in the proportion of SRP observed in both reservoirs, emphasizing the importance of rainfall as a source of nutrient input to these environments due to the leaching of diffuse pollution. Therefore, the improvement is momentary since the high SRP values associated with the high temperatures of the region favour phytoplankton growth.

The data presented showed that the Gargalheiras and Cruzeta reservoirs are very different environments in terms of their composition of the P forms. In Gargalheiras we found a predominance of organic solids, in addition to higher values of chlorophyll, during most of the study period. Consequently, the predominant forms of phosphorus in this reservoir were PP and ODP. The lowest values of SRP concentration in the Gargalheiras reservoir were found in the periods with the highest concentration of algal biomass. This relationship is explained by the rapid capture of SRP by phytoplankton (Reynolds, 2006).

The Cruzeta reservoir had a unique behaviour for semiarid reservoirs as predominance of inorganic solids in this reservoir provided a high turbidity (Braga et al., 2015; Medeiros et al., 2015). In Cruzeta, Chl-a decreased while water volume reduced; this behaviour is contrary to many semiarid reservoirs. The high concentrations of SRP and inorganic solids, that caused inorganic turbidity, may have limited the algal growth by shading (Braga et al., 2015; Reynolds, 2006). The inorganic turbidity can be caused by resuspension of the sediment, through the action of the winds, since the reservoir presented low depths (<2.5 m) during the period of the study. A lower availability of light in the water column may lead to inhibition of phytoplankton growth as reported in other studies in the Brazilian semiarid region (Medeiros et al., 2015; Braga et al., 2015). As a result, the Cruzeta reservoir had lower values of chlorophyll, despite the high SRP concentration, compared to the Gargalheiras reservoir.

In addition, in some shallow lakes the wind mixing can control the variation in internal P loading (Jones & Welch, 1990), because the ressuspended solids from the sediment have particles bound to forms of phosphorus that can be released into the water. In a study in the lake Vest, Denmark, varying wind speed during seven days showed the highest values of suspended solids and total phosphorus in water were observed and showing that resuspension and increase of phosphorus in the water may be related (Søndergaard et al., 2003). This is a factor that may have influenced the high values of P during the driest months in both reservoirs. The solids values may also be an indication of resuspension. In both reservoirs, both organic and inorganic solids in the shallower months - in which the wind was able to mix the water column further and reach the sediment - increased, possibly indicating their resuspension and probably greater release of phosphorus. In Cruzeta, as mentioned previously, this situation was observed throughout the analyzed period because of its low depth.

However, the P release from the sediment occurs mainly due to anoxic conditions in the water-sediment interface. The reduction of iron hydroxide under anoxic conditions is the classic scenario in which phosphorus release from the sediment occurs (Amirbahman et al., 2003). Observing DO profiles, it was found that Gargalheiras presented anoxia in several months, while Cruzeta presented hypoxia some of the time. During the periods of anoxia in Gargalheiras, no higher values of SRP were recorded (the most bioavailable and mobile form of phosphorus) in the hypolimnion, which could indicate release of this nutrient from the sediment.

The temperature reflects many of the biologically mediated processes in the lake (Søndergaard et al., 2003) which includes stimulation of the mineralization of organic matter and the release of inorganic P (Bostrom & Pettersson, 1982). In April and May 2016, the water column of Gargalheiras exhibited thermal stratification. This is maybe because the rainy event occurred in March and April; there was a large influx of water which had a higher temperature than the water in the reservoir. Gargalheiras phosphorus data can prove this as the highest P values found in the bottom do not represent release from the sediment. This was the layer of water that was superficial in the month prior to the rains, and which was only superimposed by the new layer of water.

The quantities and the predominant types of phosphorus in the water column presented here are of great importance to understand the phosphorus dynamics and will support restoration plans for the studied environments. In this study was possible to verify that the reservoirs are susceptible to the release of P from the sediment due to its environmental conditions, mainly low depths, wind resuspension and anoxia in hypolimnion. But, the vertical distribution of P in the water column is not sufficient to verify if there is any release, or even the potential for the sediment to release P. Further studies are needed to understand the behaviour of P flow released according to environmental variables, such as composition and types of phosphorus in the sediment, in order to verify the mechanisms and variables that most influence the release.

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