

Phosphorus partitioning in sediments from a tropical reservoir during a strong period of drought

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Abstract Monitoring phosphorus (P) concentration in water and sediments in the Castanhão reservoir, under intensive aquaculture, in Northeastern Brazil showed internal process to dominate P cycling following a reduction of reservoir volume due to an extended drought period. A strong negative correlation between soluble reactive phosphorus in surface waters (SRPs) with the reservoir volume results from diminishing dilution capacity; bottom water SRP showed no significant correlation with volume and imply SRP remobilization to surface layers. Total suspended solids (TSS) showed a significant correlation with chlorophyll-*a*, suggesting change primary productivity following SRP enrichment of surface waters and living cells dominating the TSS. As a result, eutrophication, as established by a trophic state index, was triggered in the reservoir probably enforced by intensive fish farming effluents, whose nutrients accumulated in bottom waters and which became available due to breaking of the thermocline. Since low rainfall periods are typical of the semi-arid region and tend to be more frequent and stronger due to climate change, multiple use of reservoirs in NE Brazil should be reevaluated.

Keywords Geochemistry · Sediments · Aquaculture · Reservoir · Northeastern Brazil

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Introduction

Sediments are relevant to assess the nature and intensity of impacts to aquatic ecosystems due to permanent chemical exchanges with the water column. In a variety of aquatic ecosystems, sediments are major sinks of phosphorus (P), but under certain conditions, they can act as important P sources to the water column (Ding et al. 2015; Ni and Wang 2015), influencing water quality and phytoplankton populations (Tang et al. 2014). Sediments also influence the rate of the anthropogenic eutrophication process of lakes and reservoir (Sen et al. 2007). Therefore, the management of the trophic state of many aquatic environments should take into consideration the complex nature of the P fate in sediments (Heidenreich and Kleeberg 2003; Hupfer and Dollan 2003).

To understand the P cycle in a waterbody, it is important to quantify the amount stored in surface sediments that can become potentially bioavailable under given environmental conditions. Bioavailability will finally depend on the geochemical interactions between P and other sediment constituents (Wetzel 2001; Selig 2003; Yu et al. 2006; Redel et al. 2007). Phosphorus occurs in aquatic sediments under different forms, some strongly bound to sediment particles, while others mobilize easier to the water column following small changes in water chemistry (Rydin 2000; Smith et al. 2011; Ding et al. 2015). Therefore, estimating the internal regeneration capacity of P from sediments is fundamental to propose measures and assess the results of policies to conserve and support sustainable use of reservoirs, and consequently human activities depending on them.

The role of sediments in regulating eutrophication processes is more significant in lakes and reservoirs under semiarid climate. These are frequently of multiple uses and prone to long periods of low rainfall. Under such extreme conditions, eutrophication can be easily triggered due to emissions of P

from anthropogenic activities, such as aquaculture, and the low dilution volume and altered hydrochemistry during drought periods (Santos et al. 2016). The Castanhão reservoir is a typical example of this situation. This multiple-use reservoir stores the largest water volume (6.7 billion m³) in northeastern Brazil under semiarid climate. It harbors extensive fish farms producing about 18,000 t of fish per year and supports irrigated agriculture around its margins. As a result, large emissions of nutrients, in particular of P, reach the reservoir waters continuously. Avelino (2015) reported an annual load of P to the Castanhão reservoir of 1590 t, with 97.5 % being anthropogenic. Measurements of the fluvial P fluxes from its major tributary, the Jaguaribe River, to the reservoir indicate strong retentions of about 95 % of the total incoming fluxes of soluble reactive phosphorus (SRP), total phosphorus (TP), and particulate phosphorus (Part-P), increasing the impact of this large P load. Concentrations of these P forms in the water column suggest bottom sediments as the major sink of the total P flux to the reservoir (Molisani et al. 2013), but there is no information of the distribution and geochemical partitioning of P in the Castanhão reservoir sediments, hampering an evaluation of the effective impact of the anthropogenic P loads to the trophic state of the reservoir, since deposited P can easily regenerate to the water column and thus triggering eutrophication. This work, therefore, aims to fill this gap by characterizing P distribution and partitioning in bottom sediments from the Castanhão reservoir during a strong period of drought, when the reservoir volume decreased to about 33 % of its maximum, to evaluate the role of regenerated P as a major trigger of eutrophication in the water column. The extreme volume reduction will accelerate

the internal regeneration of the sedimentary phosphorus, supporting the development of eutrophication.

Materials and methods

Study area

The study took place in the Castanhão reservoir (latitude 5.50° S, longitude 38.47° W) in the Middle Jaguaribe River watershed, which is located entirely within the semiarid region in the State of Ceará, NE Brazil (Fig. 1). The semiarid climate of Northeastern Brazil features peculiarities resulting from the behavior of its regulating weather systems marked by irregularities in rainfall across time and space, with annual rainfall means commonly ranging from 400 to 1000 mm and average of 756.5 mm during the past 80 years (FUNCEME 2014). Rainfall occurs from January to May and is scarce from June to December. During the study period, monthly precipitation varied from 0 to 181 mm. Driest years were 2012, 2013, and 2014, with a mean annual rainfall of 302.3, 656.5, and 571.1 mm, respectively, significantly below the historical annual average. This extended drought period relates to a strong El Niño event.

The Castanhão reservoir flooded completely for the first time in 2004. The total storage capacity of the reservoir is 6.7 billion m³, and the normal operating capacity is 4.45 billion m³. The reservoir covers a flooded area of 325 km² and is 48 km in length, with a depth exceeding 50 m in some areas (DNOCS 2014). The categories of the World Commission on Dams (2000) classify the Castanhão as a large reservoir.

Fig. 1 Study area and location of stations in the Castanhão reservoir, NE Brazil

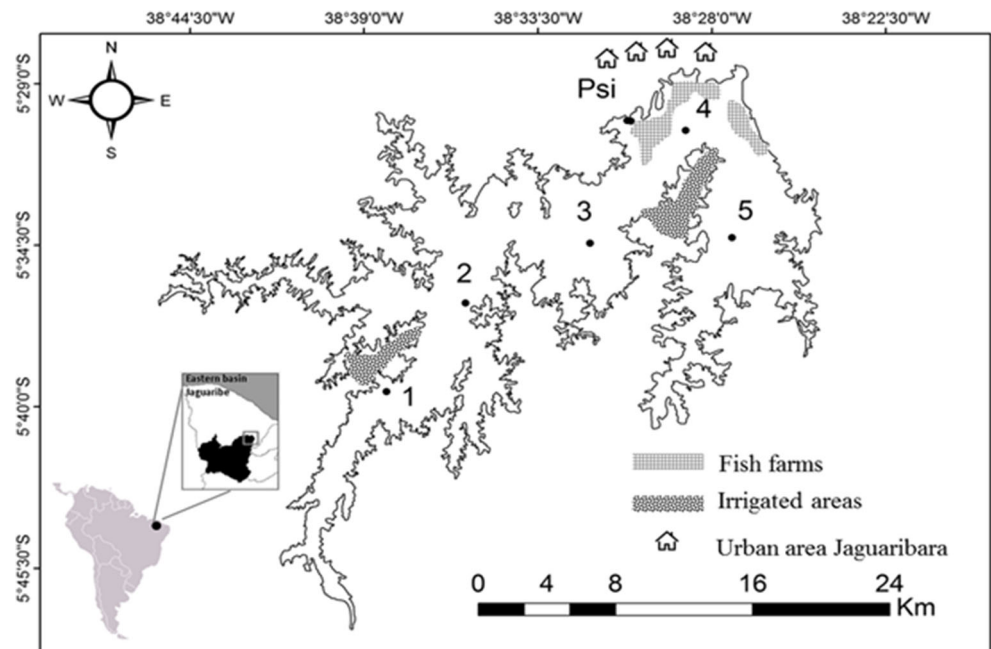


Figure 2 shows fluctuations in the water volume stored in the reservoir during the studied period. Water level fluctuations are determined primarily by the dam system operation. However, during the sampling period, there was a drastic reduction in the stored volume due to the prolonged absence of rain in the reservoir’s basin.

Sampling

Sampling occurred in January 2013, May 2013, and August 2014. Water quality was monitored in five stations (P1–P5) located along the reservoir (Fig. 1). In a typical fish (tilapia) farm, sampling occurred in November 2011, October 2012, and January 2013 in two stations within the area of cultivation (Psi, Fig. 1). The physical and chemical variables of the water column were obtained in situ. Dissolved oxygen with a YSI 556 MultiProbe System, pH using a portable Metrohn 826 pH meter and transparency with a Secchi disk. The water temperature was measured by a Compact-CTD JFE Advantech AST D687 model at intervals of 0.1 m from the surface to the bottom.

Water samples were collected using a Van Dorn bottle at the sub-subsurface (1 m deep) and at about 1 m from the bottom. For the analyses of soluble reactive phosphorus (SRP), samples were filtered immediately after collection through AP-40, 47-mm diameter, fiberglass filters, and frozen for later analysis. Filters were used to obtain the concentration of the total suspended solids in the water (TSS). Unfiltered samples were used for the determination of total P (TP). The chemical species were quantified in triplicate with final detection by spectrophotometry in the visible spectrum region

according to Valderrama (1981) for total P and Murphy and Riley (1962) for soluble reactive phosphorus.

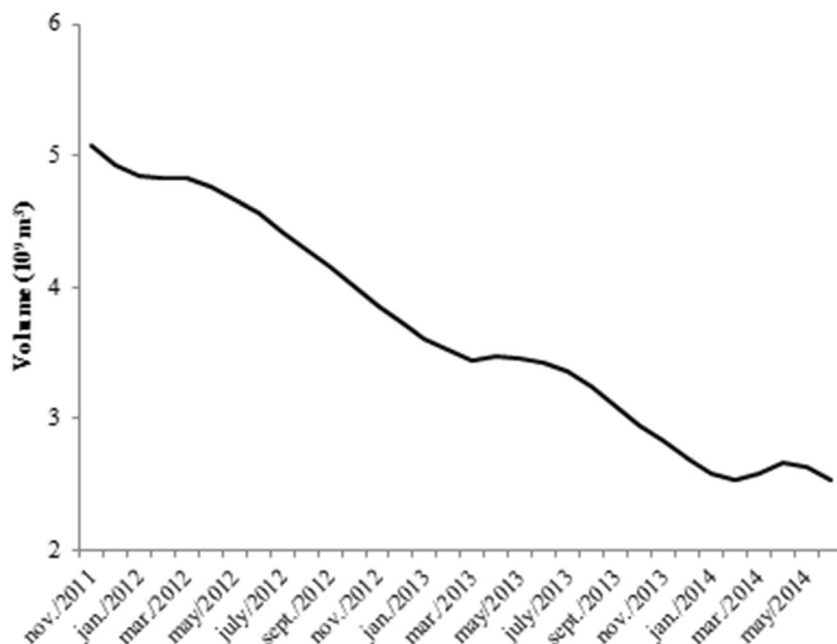
To quantify chlorophyll-*a* concentrations, filtered samples were stored frozen and transported to the laboratory where quantification was obtained in a spectrophotometer according to the ISO 10260 (1992) protocol.

The trophic state of the reservoir was estimated using the trophic state index (TSI_{tsr}) developed by Cunha et al. (2013) and already successfully applied at the Castanhão reservoir to study changes in trophic of the system by Santos et al. (2016). Equations that accounted for the concentrations of chlorophyll-*a* (Chl_a; µg L⁻¹) and total phosphorus (TP; µg L⁻¹) and the defined limits for the trophic state classes used are the same as in Santos et al. (2016).

Sediments were collected with a Van Veen grabber, placed in plastic bags, and kept refrigerated until arrival at the laboratory. In the laboratory, each sample was dry in an oven at controlled temperature of 60 °C, homogenized, and preserved in glass vials until analysis. The extraction of total P (TP) and inorganic P (TIP) were done following Berner and Rao (1994), whereas total organic P (TOP) was obtained by difference between TP and TIP. The organic matter was obtained following the Loring and Rantala (1992).

The average data for each parameter were submitted to ANOVA and Tukey HSD test analysis with *p* ≤ 0.05. Pearson correlation analysis was used to describe the relationships between variables and a cluster analysis to evaluate the longitudinal patterns in the reservoir and explore the similarities among sampling stations and define groups of associated ones. The analyses were performed using the STATISTICA 8.0 software package (StatSoft, Inc., Tulsa), assuming a

Fig. 2 Water volume fluctuation in the Castanhão reservoir, NE Brazil, between 2011 and 2014 (DNOCS 2014)



significance level of $\alpha = 0.05$. For the cluster analysis data were standardized in Z and the Ward amalgamation and squared Euclidean distance methods were used.

Results

Hydrochemistry

Physical and chemical parameters in the Castanhão reservoir are presented in Tables 1 and 2. The surface of the reservoir remained well oxygenated throughout the monitoring period, with oxygen concentrations $>5 \text{ mg L}^{-1}$, the threshold established by the Brazilian legislation (National Council for the Environment, CONAMA no. 357/05) (Brasil 2005). Events of suboxia in bottom waters of the reservoir occurred in January 2013, in sampling stations P3 (0.46 mg L^{-1}) and P4 (2.49 mg L^{-1}); in August 2013, in sampling station P3 (0.20 mg L^{-1}); and in May 2014, in sampling stations P4 (0.11 mg L^{-1}) and P5 (0.07 mg L^{-1}) (Table 1). When the oxygen concentration reaches low levels ($\sim 4 \text{ mg L}^{-1}$), biological processes produce large amount of reducing compounds which also consume oxygen in their oxidation processes (Edwards 2011). In the fish farming (Table 2), oxygen concentrations below 5 mg L^{-1} were observed in October 2012 and January 2013 in surface and bottom waters.

There was a significant increase in pH during the monitoring period with highest values (8.8) observed in May 2014 when the reservoir volume reached its minimum and total suspended matter concentration was maximum. This results

from smaller dilution of salts due to decreasing reservoir volume.

In the fish farm area, pH and TSS varied throughout the monitoring period, probably reflecting the inputs from the farming processes, such as aquafeed addition, fish excreta discharge, as well as physical stirring of the water column by boats and cages transport, which may result in random changes in water chemistry.

During the monitored period, the depth of sampling stations ranged from 6 to 35 m, stations P3 (23 m) and P4 (35 m) were deeper, and thermal stratification was observed in station P4 in August 2013 and May 2014 (Fig. 3).

During the sampling period, following the decrease in the reservoir volume, there was an increase in TP, SRP and chlorophyll-*a* in the water column. When the reservoir reached its minimum volume, bottom waters TP and SRP concentrations were particularly high. In May 2014, the largest concentrations of TP and of chlorophyll-*a* in the water column were accompanied by the change of the trophic state of the reservoir. The trophic state index ranked the reservoir as mesotrophic in January 2013 and August 2013 and eutrophic in May 2014.

A comparison of all TP concentrations in the water column is presented in Fig. 4. In general, bottom waters presented higher TP concentrations compared with surface waters, in most stations and sampling campaigns. Interesting to note is that TP concentrations in waters under the influence of the fish farm (Psi) are not the highest, as expected, when compared to the deeper stations P3 and P4, where stratification was observed. However, Psi concentrations are higher than those from other stations (P1, P2, P5).

Table 1 Mean values and standard deviation of the variables monitored in surface and bottom waters in the Castanhão reservoir, NE Brazil

Variables	Depth	January 2013	August 2013	May 2014
Temperature ($^{\circ}\text{C}$)	Surface	$29.4 \pm 0.8^{\text{a}}$	$29.2 \pm 0.5^{\text{a}}$	$31.2 \pm 1.2^{\text{b}}$
	Bottom	$28.3 \pm 0.4^{\text{a}}$	$28.3 \pm 0.2^{\text{a}}$	$29.5 \pm 0.6^{\text{b}}$
DO (mg L^{-1})	Surface	$6.7 \pm 0.4^{\text{a}}$	$6.6 \pm 0.4^{\text{a}}$	$7.9 \pm 2.2^{\text{a}}$
	Bottom	$4.1 \pm 2.6^{\text{a}}$	$4.9 \pm 2.7^{\text{a}}$	$3.6 \pm 3.9^{\text{a}}$
pH	Surface	$7.4 \pm 0.2^{\text{a}}$	$8.3 \pm 0.5^{\text{b}}$	$8.8 \pm 0.7^{\text{b}}$
	Bottom	$7.2 \pm 0.7^{\text{a}}$	$8.3 \pm 0.5^{\text{b}}$	$8.6 \pm 0.6^{\text{b}}$
Chlorophyll- <i>a</i> ($\mu\text{g L}^{-1}$)	Surface	$4.2 \pm 1.6^{\text{a}}$	$4.7 \pm 2.8^{\text{a}}$	$15.1 \pm 13.7^{\text{b}}$
	Bottom	$1.6 \pm 1.5^{\text{a}}$	$3.5 \pm 1.1^{\text{a}}$	$18.3 \pm 14.7^{\text{b}}$
TP ($\mu\text{g L}^{-1}$)	Surface	$32.0 \pm 10.7^{\text{ab}}$	$22.4 \pm 8.0^{\text{a}}$	$45.7 \pm 9.7^{\text{b}}$
	Bottom	$46.8 \pm 21.8^{\text{ab}}$	$17.6 \pm 6.4^{\text{a}}$	$64.8 \pm 33.0^{\text{b}}$
SRP ($\mu\text{g L}^{-1}$)	Surface	$3.4 \pm 3.0^{\text{a}}$	$6.6 \pm 2.8^{\text{ab}}$	$16.0 \pm 6.6^{\text{b}}$
	Bottom	$17.9 \pm 19.2^{\text{a}}$	$8.5 \pm 5.7^{\text{a}}$	$33.9 \pm 41.2^{\text{a}}$
Secchi (m)	–	$2.7 \pm 0.5^{\text{a}}$	$2.5 \pm 0.6^{\text{a}}$	$2.1 \pm 0.9^{\text{a}}$
TSS (mg L^{-1})	Surface	$1.7 \pm 0.6^{\text{a}}$	$2.0 \pm 0.4^{\text{a}}$	$3.7 \pm 3.5^{\text{a}}$
	Bottom	–	–	–
Volume (m^3)	–	3.6×10^9	3.2×10^9	2.6×10^9
TSI_{sr}	–	53.6	53.2	56.2
Trophic state category	–	Mesotrophic	Mesotrophic	Eutrophic

Different letters are significant different mean values ($p \leq 0.05$)

DO dissolved oxygen, TP total phosphorus, SRP soluble reactive phosphorus, TSS total suspended solids, TSI_{sr} trophic state index

Table 2 Mean values and standard deviation of the variables monitored in surface and bottom waters under the influence of the tilapia cages in the aquaculture area of the Castanhão reservoir, NE Brazil

Variables	Depth	November 2011	October 2012	January 2013
Temperature (°C)	Surface	30.0 ± 1.6 ^a	28.9 ± 0.1 ^a	31.7 ± 1.6 ^a
	Bottom	28.8 ± 0.7 ^a	28.4 ± 0.1 ^a	29.5 ± 0.9 ^a
DO (mg L ⁻¹)	Surface	7.5 ± 0.4 ^a	6.5 ± 0.7 ^a	3.6 ± 0.5 ^b
	Bottom	6.1 ± 0.8 ^a	4.1 ± 0.9 ^a	4.1 ± 0.7 ^a
pH	Surface	8.1 ± 0.1 ^a	6.2 ± 0.2 ^b	8.0 ± 0.3 ^a
	Bottom	7.4 ± 0.4 ^a	6.4 ± 0.4 ^a	6.0 ± 1.6 ^a
Chlorophyll- <i>a</i> (µg L ⁻¹)	Surface	2.5 ± 0.4 ^a	4.0 ± 0.3 ^b	5.8 ± 0.0 ^c
	Bottom	–	–	–
TP (µg L ⁻¹)	Surface	17.2 ± 1.8 ^a	25.4 ± 2.4 ^a	31.2 ± 10.7 ^a
	Bottom	49.3 ± 7.8 ^a	38.2 ± 6.3 ^a	37.0 ± 5.4 ^a
SRP (µg L ⁻¹)	Surface	3.5 ± 0.4 ^a	7.7 ± 2.0 ^b	8.0 ± 3.0 ^b
	Bottom	27.1 ± 1.6 ^a	14.6 ± 7.1 ^a	14.7 ± 8.7 ^a
Secchi (m)	–	2.6 ± 0.3 ^a	3.7 ± 0.1 ^a	2.5 ± 0.5 ^a
TSS (mg L ⁻¹)	Surface	2.1 ± 1.4 ^a	1.8 ± 0.2 ^a	1.9 ± 0.2 ^a
	Bottom	–	–	–
Volume (m ³)		5.0 × 10 ⁹	4.0 × 10 ⁹	3.6 × 10 ⁹

Different superscript letters are significant different mean values ($p \leq 0.05$)

DO dissolved oxygen, TP total phosphorus, SRP soluble reactive phosphorus, TSS total suspended solids

Relevant to highlight is the strong negative correlation between soluble reactive phosphorus in surface waters with the reservoir volume (−0.914), suggesting that indeed the decrease of the volume is diminishing the dilution capacity of the incoming P load. On the contrary, bottom water showed a positive but nonsignificant correlation with volume (0.380), which may imply in remobilization of bottom water SRP to surface layers contribution with the increase in SRP in the superficial waters in the reservoir. Increasing TSS in the water column during the study period (Table 1) also showed a significant negative correlation with volume (−0.655). Although rather than reflecting less dilution, TSS is significantly correlated with chlorophyll-*a* concentrations (0.982), suggesting change in primary productivity following SRP enrichment of surface waters and living cells dominating the TSS when the

reservoir volume decreases and the trophic state index point to become eutrophic.

The waters of the reservoir were grouped as to the similarity of the monitored variables. The analysis resulted in three different groups (Fig. 5). Group 1, formed by only one sampling station (P1), is near the entrance of the Jaguaribe River, and is therefore mostly influenced by the upstream watershed, as noted in previous studies (Molisani et al. 2010, 2013). Group 2 includes stations P2, P5, and Psi. Although stations P2 and P5 are the most distant stations from fish farms, both may receive runoff from irrigated agriculture areas; therefore, they present some similarity with the aquaculture influenced Psi station. Group 3, formed by stations P3 and P4, is located near the area of irrigated agriculture and fish farms, but is much deeper and presented thermal stratification during most of the monitoring period.

Fig. 3 Thermal structure of the water column in sampling station P4 in the Castanhão reservoir, NE Brazil, in August 2013 and May 2014

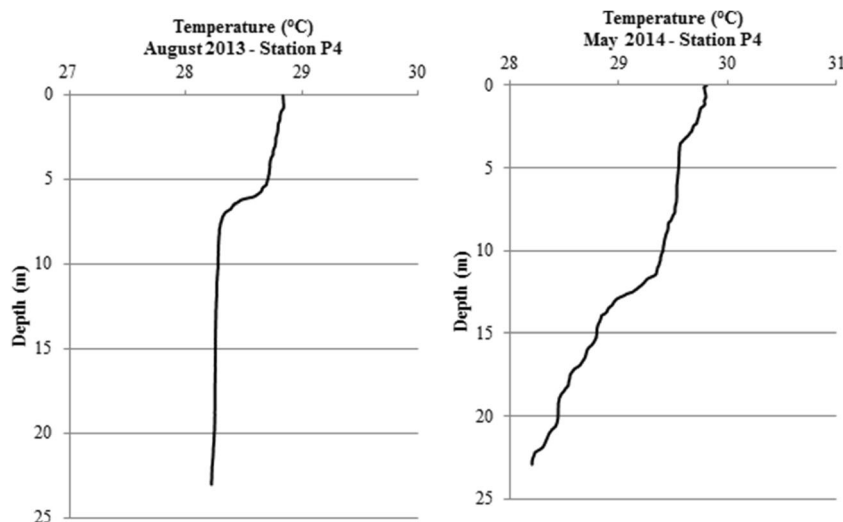
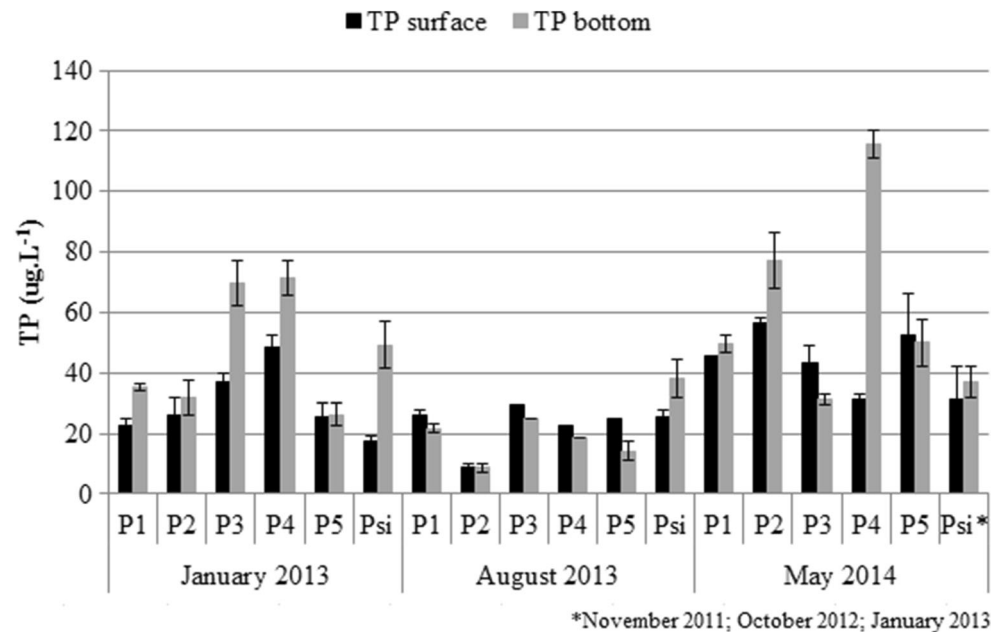


Fig. 4 TP concentrations in surface and bottom waters of the Castanhão reservoir and in the fish farming area (Psi)



Geochemistry of P in sediments

Total phosphorus distribution in sediments of the reservoir and the fish farm influenced area is presented in Fig. 6. Concentrations were higher in stations P1 and P5 and lowest in fish farm sediments. Concentrations increased from January 2013 to May 2014 in the deeper stations P3 and P4, but remained constant or even decreased in the other stations including in the fish farm area, although this stations showed very high variability in P concentrations with a coefficient of variation of nearly 100 % and again suggesting abrupt and random P inputs from fish farming activities.

The geochemical partitioning of phosphorus in the Castanhão sediments is presented in Fig. 7. TIP is the dominant P form in the Castanhão sediments, including in sediments under the influence of fish farming activities, whereas TOP represented from 10 to 70 % of the TIP content depending on station and sampling campaign. Different from TP distribution, both TIP and TOP showed variability within the reservoir in the different sampling periods. TOP decreased significantly from station P1 to station P4 in January 2013, suggesting stronger influence from the upstream watershed, in agreement with the nutrient mass balance proposed by Molisani et al. (2010, 2013). However, as the reservoir volume decreases, TOP and TIP concentrations increased in the stations downstream from station P1, suggesting the augmenting importance of local phosphorus sources. TIP concentrations varied spatially from 60 $\mu\text{g g}^{-1}$ (station Psi in August 2013) to 240 $\mu\text{g g}^{-1}$ (station P1, in August 2013), whereas TOP variability was larger temporally and varied from 10 $\mu\text{g g}^{-1}$ (station Psi, in August 2013 and January 2014) to 100 $\mu\text{g g}^{-1}$ (in station P1 in January 2013).

The reservoir sediments were grouped as to the similarity of the sedimentary variables monitored (TP, TIP, and TOP). It is observed that three groups have been defined. Group 1, including stations P1, P2 and P3, is characterized by stations more influenced by the upstream inputs from the Jaguaribe River basin. Group 2, including stations P4 and P5, which, with the exception of the sediments from station 1 in particular in January 2013, showed the highest concentrations of TP and TIP but not of TOP. This group includes the deepest stations located in the open lake area. Group 3, defined by the fish farm station (Psi), showed lowest concentrations of all P forms relative to all other reservoir stations (Fig. 8). It is observed that the variables monitored in water and those monitored in the sediment grouped the sampling stations differently.

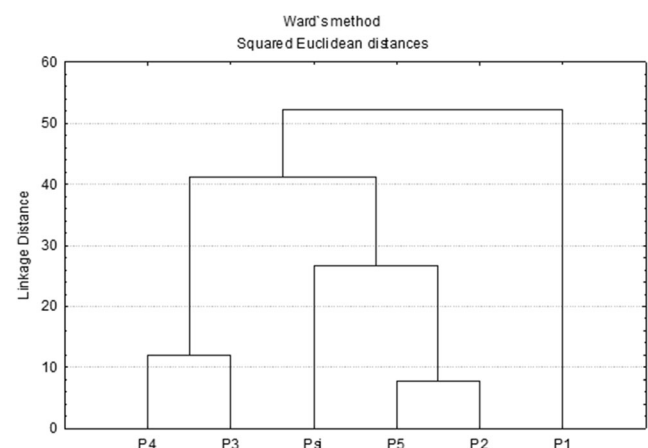
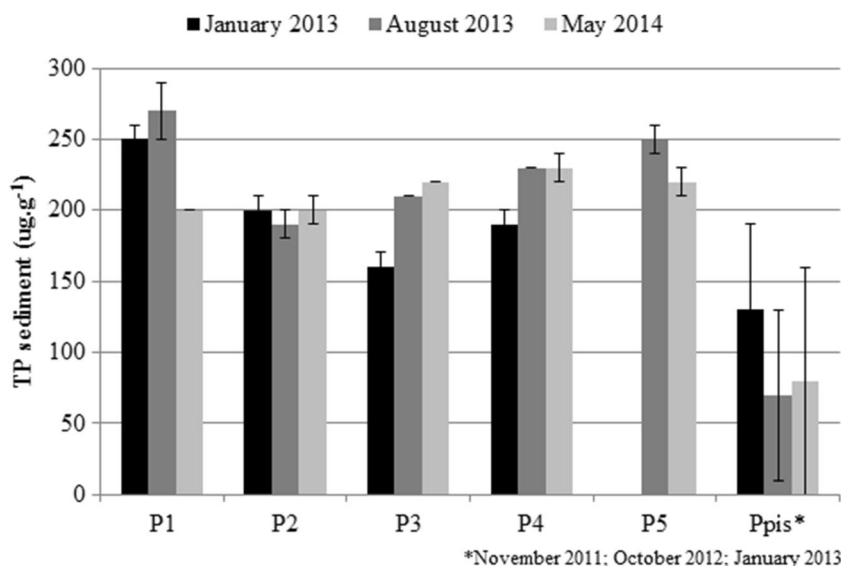


Fig. 5 Cluster analysis of the sampling stations in the Castanhão reservoir in NE Brazil based on all limnological variables measured

Fig. 6 Total phosphorus concentrations in lake and fish farming sediments in the Castanhão Reservoir, NE Brazil. Sediment samples from the station P5 in January 2013 was lost during transport



Discussion

Sediments of the Jaguaribe River downstream from the dam showed increasing TP concentrations during the past decade (Marins et al. 2007). In sediments from the Castanhão reservoir, notwithstanding higher TP concentrations than those, no significant increase of PT levels in the sediment along the reservoir was found. PIT is the major fraction of phosphorus in the Castanhão sediments, always higher than POT. According to Fonseca et al. (2011), the high contribution of PIT in tropical reservoirs supports the importance of lithology, as apatite or Fe and Al oxides/hydroxides, as the source of P to

reservoir, and this seems to be supported by the higher TP and TIP concentrations in station P1 relative to all others in January 2013 and August 2013, before a significant decrease in the reservoir volume occurred. However, the potential release of P to the water column will depend on TIP speciation in sediments and redox conditions which may affect phosphorus-iron complexes (Boström et al. 1988; Mhamdi et al. 1994; Pettersson 1998; Chalar and Tundisi 2001; Søndergaard et al. 2003; Fonseca et al. 2011; Lukawska-Matuszewska et al. 2013).

In the Jaguaribe River sediments, iron phosphates are the major TIP species. This TIP fraction associated with iron will

Fig. 7 Geochemical partitioning of phosphorus in sediments from the lake and farm area in the Castanhão Reservoir, NE Brazil

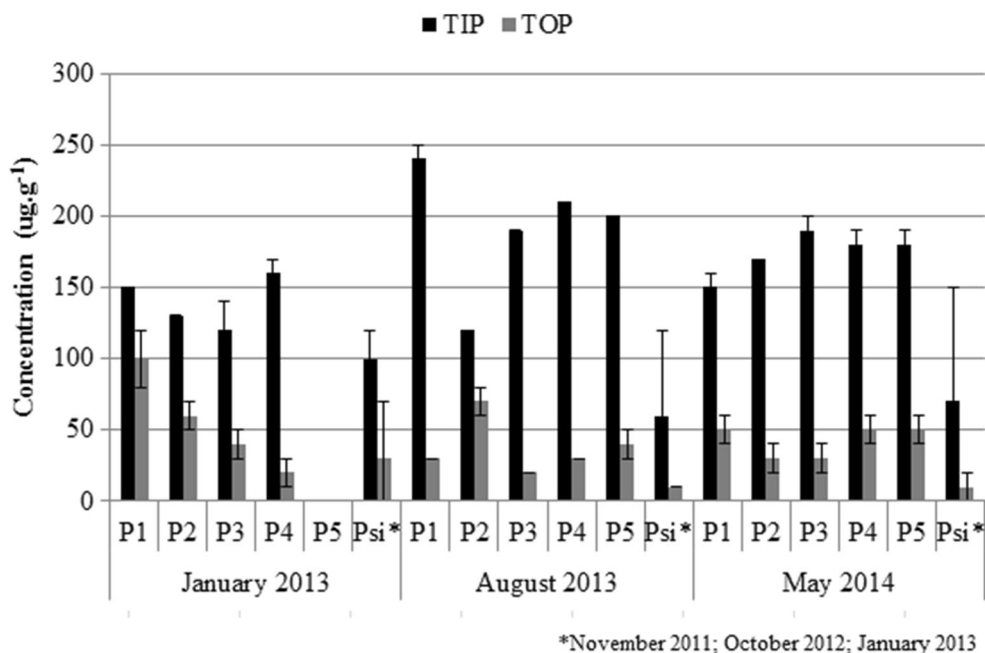
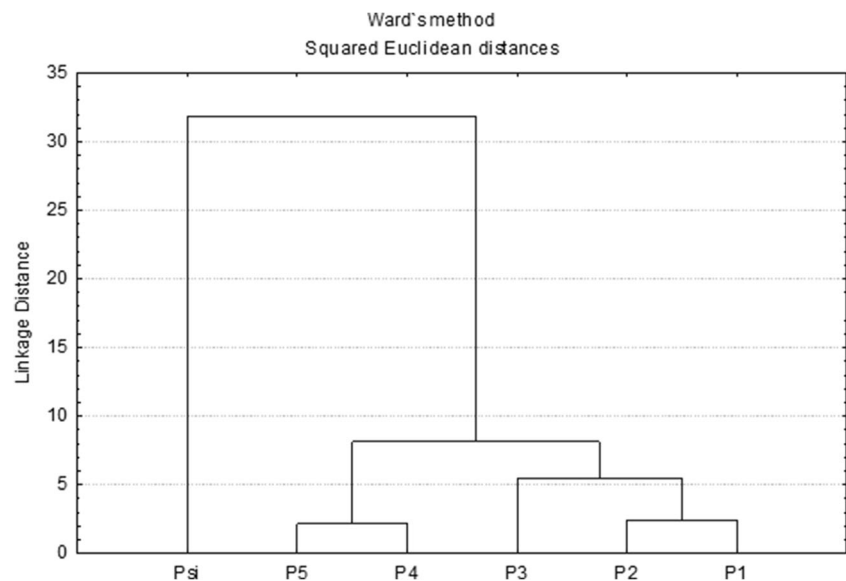


Fig. 8 Cluster analysis of the sediment sampling stations, based on sedimentary characteristics, in the Castanhão reservoir, NE Brazil



render higher mobility to phosphorus depending on the redox potential of waters (Marins et al. 2007). Ding et al. (2016) provide in situ evidence for the coupling of Fe to P mobilization in sediments based on the use of ZrO-Chelex DGT, which was demonstrated by a simultaneous release of Fe(II) and P to pore water together with a coincident resupply of pore water Fe(II) and P from sediment solids. Teles et al. (2015) showed that reduced iron Fe^{2+} is the dominant fraction in the reservoir sediments, suggestion that reduction of ferric species due to low redox potential is already occurring in the sediments. Our results on dissolved oxygen in bottom waters support this conclusion and allow the release of phosphorus to the water column from the sediment environment.

In sediments, where the ability to retain P depends on the iron, the pH is also particularly important because the binding capacity of P in the sediment decreases with increasing pH, since the hydroxyl ions compete with P ions, thereby decreasing the absorption of phosphate to iron hydro-oxides (Søndergaard 1988). The impact of pH on P in the sediment dynamics was discussed by Koski-Vahala and Hartikainen (2001), showing that high pH can increase the contribution of internal load when associated with resuspension.

Water and sediment variables measured during the monitoring period classified the sampling stations differently. However, station P4, belong to the group with the highest TP and lower dissolved oxygen concentrations in the water column and with the highest concentrations of TP and TIP in the sediment. On the other hand, the sediments under the influence of the fish farm presented lower TP concentrations than most of the other stations in all sampling campaigns. Molisani et al. (2015) observed a significant loss of aquafeed particles in the local aquaculture process; they estimated relatively long residence time of such particles in water, allowing

their export from fish farming areas to the open lake area. Oliveira et al. (2015) described the surface and bottom water currents in the studied farm area (station Psi). Surface currents move from the open lake to the farm area due to wind forcing, but bottom currents flow from the farm area to the open lake. This hydrodynamics is very efficient in transporting particles from the fish farming areas to the deeper parts of the reservoir, where they are accumulated, at least when stratification is present avoiding mixing with surface waters. This totally agrees with our results and explains the somewhat paradoxical lower TP concentrations in sediments under the fish cages.

In a Rio Grande do Norte reservoir, also in NE Brazil, Moura et al. (2014) found a strong influence of a fish farming in the rates of PT sedimentation, values 100 times higher inside the fish cage area (up to $129.9 \mu\text{g cm}^{-2} \text{day}^{-1}$) than in areas further away from cages (up to $1.1 \mu\text{g cm}^{-2} \text{day}^{-1}$). However, some studies showed no significant differences between areas with and without fish farming (Bezerra et al. 2014; Montanhini et al. 2015). Moura et al. (2016) by analyzing the sustainability of Nile tilapia farming in reservoirs of Brazil's semiarid region noted that the average annual amount of P released into the sediment was $\sim 20.6 \text{ kg}$ representing a small accumulation of P in the sediment relative to fish production (0.9 kg t^{-1} of fish). However, the authors pointed out that the continuous entry of solid wastes in the production environment progressively increases the concentrations of total N and P in the sediment over time, since about 90 % of the waste generated is organic material.

The accumulation of solids in suspension over time due to the excess of aquafeed and fish excreta in reservoirs may eventually alter the chemical composition and physical-chemical properties of bottom sediments, as observed in fish

farms and adjacent areas (Guo and Li 2003). The solid residue generated by fish cage farming is rich in organic matter, nitrogen, and phosphorus and tends to sediment and deposit in the reservoir bed close to the fish farming structures, where it can cause significant environmental changes (Grey et al. 2004). Gondwe et al. (2011) observed that sediments were dispersed in locations with current speeds higher than 9.3 cm s^{-1} , thus minimizing environmental effects on fish farming area. According to Wu et al. (2016), the accumulations of biologically derived P near the dam may also be related to the pattern of sedimentation of the fine particles.

Troell and Berg (1997) compared carbon, nitrogen, and phosphorus concentrations in the bottom sediment of Lake Kariba, Zimbabwe, before and after the establishment of small ($<10 \text{ t fish ha}^{-1} \text{ year}^{-1}$) and large ($>20 \text{ t fish ha}^{-1} \text{ year}^{-1}$) fish farms dedicated to cage farming Nile tilapia and only observed significant changes for large farms. Tlustý et al. (2000) observed that factors linked to cultivation practices, such as feeding and stocking density, as well as the hydrodynamic characteristics of the site where the fish farms were established, were more relevant than the biomass of produced fish.

In Brazil, the use of reservoirs for fish cage farming has significantly grown in recent years (Dias et al. 2011) because of the regularization of the multiple-use reservoirs, including aquaculture. According to Garcia et al. (2014) and Li et al. (2014), this activity can have a significant impact on aquatic environments and minimizing these risks requires planning, legislating compliance, and managing and monitoring the environmental quality of the fish farms (Nyanti et al. 2012; Ling et al. 2013).

Nutrient loads that reach the reservoir from the watershed maybe either retained within or exported from the reservoir depending on the basin hydrological regime and operation characteristics of a given reservoir (Jossette et al. 1999; Friedl et al. 2004; Teodoru and Wehrli 2005; Cook et al. 2010). In reservoirs located in the semiarid region of northeastern Brazil, water is preferably used for human consumption and irrigation. So, in these reservoirs, there is a strong regulation of water, which implies the reduction of the discharge downstream and releasing controlled flows, defined operationally to supply the estimated water downstream demand. The tight water regulation of the Castanhão reservoir induces high retention of the incoming materials. Molisani et al. (2013) estimated based on inflow-outflow balance of SRP, TP, and TSS that the Castanhão reservoir has a retention capacity of 98 % for SRP and TP and 97 % for TSS. Molisani et al. (2010) observed a positive correlation between TP and TSS ($p < 0.05$), suggesting that the nutrients and particulate matter in suspension are retained within the reservoir by deposition from the water column to the bottom. During their study, the Castanhão reservoir displayed nearly 70 % of its full water storage capacity and was considered oligotrophic, aquaculture was still incipient as a source of nutrients and thermocline was established throughout the

reservoir. Even during our study, when the reservoir reached about 40 % of its capacity, thermocline was still easily recognized in deeper stations.

The reduction in the reservoir volume and the increasing P load due to augmenting the intensity of aquaculture triggered different hydrophysical processes, such as the increasing wind forcing effect on deeper waters, export of aquaculture effluents by bottom currents, and breaking of the thermocline that resulted in the mixing of the water column and increasing TIP concentration, which led to chlorophyll bloom and changing the trophic state of the reservoir to eutrophic.

Unfortunately, a detailed fractionation scheme for inorganic P species was not available hampering a better discussion of the mechanisms involved in trophic state changes of the reservoir. Also, quantifying the sediment-water P flux through incubation would properly quantify the importance of the remobilization processes. These steps will be necessary to properly describe by which property volume reduction affects P remobilization and eventually triggering eutrophication.

Some of these mechanisms have been observed in other reservoirs in the semiarid NE of Brazil (Souza Filho et al. 2006). In the much smaller Pacajus reservoir, Freire et al. (2009) observed that while fluvial inputs during strong rain events respond to the major portion of the nutrient loads to the reservoir during the rainy season, during the dry season, remobilization of bottom accumulated nutrients is the major source to the water column. Nikolai and Dzialowski (2014) observed that even when external sources of phosphorus are decreased, remobilization of bottom waters TP maintains the trophic state of tropical reservoirs. At the Castanhão reservoir, with the extra load of nutrients from the aquaculture, which accumulates in bottom waters when the thermocline is established, upon releasing to the upper layers not only keeps productivity, but indeed trigger eutrophication. Actually in July 2015, the first massive mortality of tilapia, reaching 3000 t in a single week, was an expected result of those processes.

Under the present scenario of climate changes, decreasing annual rainfall, changing their spatial distribution, and the consequent decrease in river inflow will make reservoirs more sensitive to the typical drought of semiarid regions (Dawadi and Ahmad 2013; Umaña 2014). Since under the semiarid climate of NE Brazil drastic reduction of reservoir volume are expected during extreme drought periods, and that reduction in rainfall and increasing the frequency and extension of drought have been observed in the past four decades, the multiuse character of the Castanhão reservoir should be evaluated.

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