



Modeling phosphorus exchange between bottom sediment and water in tropical semiarid reservoirs

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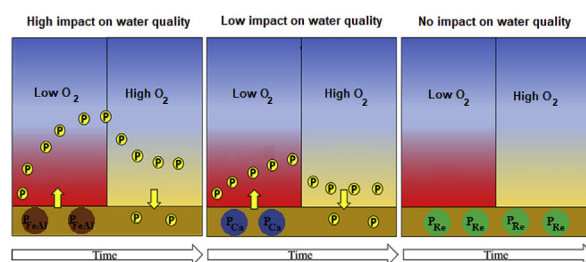
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HIGHLIGHTS

- Phosphorus (P) release potential was directly proportional to reservoir age.
- Sediments rich in iron and aluminium-bound P may have higher impact on water quality.
- P release rates were higher than precipitation rates.
- Not all P released at the anoxic phase was precipitated after oxic condition was reestablished.
- Release and precipitation rates are well described by zero- and first-order models.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigated phosphorus (P) dynamics in the sediment-water interface of three distinct reservoirs located in a tropical semiarid region. Sequential chemical fractionation of the P content in the sediment and controlled experiments of the sediment-water interface were performed to understand and model the effect of the different P fractions on the exchange dynamics under anoxic and oxic scenarios. The results revealed that the older the reservoir, the higher the amount of iron and aluminium-bound P in the sediment, and that this fraction was responsible for a 10-fold increase in P concentration in the water during anoxic conditions. After aeration, P in water decreased but did not return to its initial concentration. The most recently constructed reservoir showed the lowest P concentration in the sediment and dominance of the unavailable P fraction, resulting in no potential impact on water quality. Phosphorus release and precipitation rates were well described by zero- and first-order models, respectively. Reservoirs with high P availability in the sediment, not only released more phosphorus but also presented a lower precipitation rate, resulting in higher potential damage to water quality and making some in-lake treatment techniques potentially ineffective.

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1. Introduction

Phosphorus (P) present in bottom sediment has a major influence on eutrophication and water quality deterioration (Baker et al., 2014; Jarvie et al., 2017; Kane et al., 2014; Chen et al.,

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2018). High P concentration can favor the formation of harmful algal blooms (HABs), increase biomass, turbidity, and the risks associated with toxic or noxious secondary metabolites. HABs represent a significant challenge to water treatment, increasing the economic burden of water utilities as filter run time is decreased and additional chemicals are needed (He et al., 2016). The problem of P in sediments is prolonged since it is persistent and P can be released from sediment as deep as 20 cm (Søndergaard et al., 2003). In order to assess the magnitude of the problem, the likelihood of P release needs to be evaluated, since various P fractions have different solubility under different water conditions (Cong et al., 2014). This assessment can be achieved by sequential chemical fractionation of the inorganic phosphorus (P_i) present in the bottom sediment of a reservoir. According to Rydin (2000), P_i can be fractionated into:

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

A number of authors (Mortimer, 1971; Chapra and Canale, 1991; Raley and Rusch, 2004; Beutel et al., 2008; Chen et al., 2018) have discussed the dynamics of P exchange across the sediment-water interface. However, because of the complexities involved, it has not been found in the recent literature a conceptual model describing P exchange based on P fractions. Three major challenges are: the proportion and amount of the aforementioned P fractions can vary considerably among different lakes and reservoirs sediments; the impact of P fractions on the exchange rates between sediment and water is still not fully understood, and; environmental factors such as pH, temperature, and dissolved oxygen affect the exchange rates differently. Therefore, further studies are needed to elucidate these dynamics.

In tropical semiarid regions, like the Brazilian Northeast, a dense network of thousands of surface water reservoirs has been built to meet increasing water demand (Campos et al., 2016). However, these reservoirs face a nutrient-enriched sediment deposition (Braga et al., 2019) associated with high water temperatures, which promote stratification in the water column (Dantas et al., 2008) and fast organic degradation, frequently forcing anoxic conditions over the bottom sediment. Therefore, P internal loading is expected to significantly impact water quality in these reservoirs. Moreover, reservoirs in the tropical semiarid regions are usually shallow and present high water level variation because of recurrent droughts and high evaporation rates (Barbosa et al., 2012). The combination of these factors perpetuates eutrophication and HAB, significantly overloading water treatment (Pestana et al., 2019) and requiring in-lake treatment techniques such as artificial aeration (Pacheco and Lima Neto, 2017) or application of phosphorus binding clay (Oosterhout and Lürling, 2013) to mitigate the impacts on water quality.

A recent study carried out by Cavalcante et al. (2018) evaluated the potential contribution of P sediment load in reservoirs in the State of Rio Grande do Norte, also located in the Brazilian semiarid region. The results revealed high amounts of soluble and easily bioavailable forms of P in the sediments, thereby enhancing eutrophication and phytoplankton growth. Hence, when the hypolimnion of a reservoir becomes anoxic and depending on the fraction of P present, a significant release of P to the water would be expected. However, how different fractions of P will contribute to P concentration in the water under this scenario is still not fully

understood. To the authors' best knowledge, this is the first study modeling the potential exchange between bottom sediment and water in artificial water reservoirs of different P fractions. The hypothesis raised in this paper is that, by elucidating the distribution of the P fractions in the bottom sediment, it would be possible to assess the P exchange potential in different reservoirs. Therefore, the objective of this work was to mathematically model P exchange dynamics in reservoirs with different characteristics under oxic and anoxic conditions considering the different fractions available.

2. Materials and methods

2.1. Study site and sediment sampling

The semiarid region of northeastern Brazil provides the ideal study ground for drinking water reservoirs that undergo periodical drought-and-refill cycles. The selected study area is located in the central region of the Ceará state, in the experimental watershed of the Forquilha River. This region encompasses a geomorphological diversity representative of the crystalline area of the Brazilian semiarid region. The experimental watershed has an area of 221 km² and an average elevation of 315 m. The vegetation is shrub-like, heavily degraded due to the widespread practice of fires for the preparation of agricultural areas. Preceding this study, the selected area experienced five years of precipitation below the historical average. This situation was confirmed in the field surveys when the selected reservoirs were completely dry. Three reservoirs R#1, R#2 and R#3 with capacities of about one hm³ and different ages were selected (Fig. 1 and Table 1). Sediment sampling was carried out in duplicate in the lacustrine zone of each reservoir until a depth of approximately 5 cm with the aid of a sediment trap. In total, three composite samples were collected.

2.2. Phosphorus extraction from sediment and analysis

Analysis of P in the sediment was performed before the water-sediment interface simulation in order to characterize the sediment and to assess its interaction with the water. Total phosphorus (P_T) content in the sediments was analyzed as soluble phosphate after extraction by heating the sediment at 500 °C for 1 h followed by high temperature (340 °C) acid hydrolysis, according to the methodology proposed by Hedley et al. (1982). P_T , in turn, can be subdivided into inorganic (P_i) and organic phosphorus (P_O). P_O was obtained by subtracting P_T from P_i concentration (Eq. (1))

$$P_O = P_T - (P_M + P_{FeAl} + P_{Ca} + P_{Re}) \quad (1)$$

Extracting P_i from the sediment was carried out by sequential chemical fractionation until that fraction became soluble phosphate. This method consists of sequentially fractionating P_i into mobile phosphorus (P_M), iron and aluminum-bound phosphorus (P_{FeAl}), calcium-bound phosphorus (P_{Ca}) and residual phosphorus (P_{Re}). The methods used for each P-fractioning are listed in Table 2. For the analysis of soluble phosphate, the method 4500-P from APHA (2017) was used.

2.3. Water-sediment interface simulation

To simulate sediment-water interaction in a controlled environment, 25 g of bottom sediment from the top 5-cm layer from each reservoir was ground with a pestle and mortar and placed into sealed glass vessels (microcosms), in duplicate (Fig. 2). The sediment was slowly and gently covered in order to prevent resuspension until a height of $H = 15$ cm with 1600 mL (size of the microcosms used) of natural water. Since all three reservoirs were

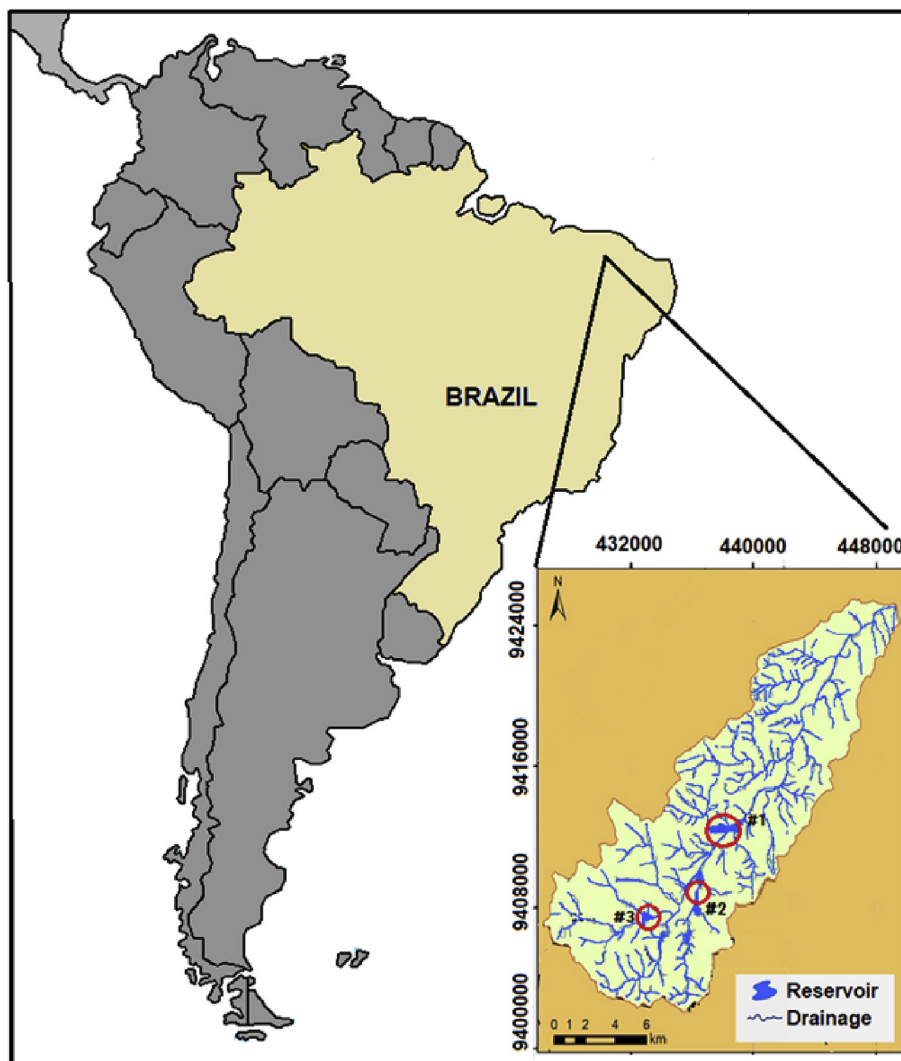


Fig. 1. Selected reservoirs (R#1, R#2 and R#3) in the experimental watershed of Forquilha, in the State of Ceará, Brazilian semi-arid region.

Table 1

Coordinates of the sediment sampling points, maximum depth and ages of the studied reservoirs.

Reservoir	Age (years)	Maximum depth (m)	Geo-coordinates
R#1	20	5.5	5°18'57" S 39°33'25" W
R#2	8	4.0	5°21'27" S 39°36'29" W
R#3	3	4.6	5°21'35" S 39°36'14" W

completely dry, natural water from another reservoir was used to approximate the experiments to the natural conditions found in the sediment. The microcosms were protected from light to avoid oxygen generation by photosynthetic organisms.

Table 2

Methods of P extraction from the sediment by sequential chemical fractionation of the inorganic phosphorus.

Fractioning sequence	P fraction	Extraction solution (Conc.)	Conditions	Method
1st.	P _M	NH ₄ Cl (0.5 N)	10 min	Adapted from Psenner et al. (1998)
2nd	P _{FeAL}	NaOH (0.1 N)	17 h	
3rd	P _{Ca}	HCl (0.1 N)	24 h	
4th	P _{Re}	HCl (0.1 N)	High temperature (340 °C) acid hydrolysis for 10 min.	Adapted from Hedley et al. (1982)

Natural water quality was determined prior (Table 3) and during the experiment including Total phosphorus – TP (APHA (2017) - Method 4500-P), orthophosphate - OP (APHA (2017) - Method 4500-P), dissolved oxygen - DO (YSI 55, USA), 254 nm absorbance (Spectrophotometer GENESYS 10S UV–VIS, USA), and pH (AN2000; China). Absorbance at 254 nm was determined as an estimation of dissolved organic material in the water. All reagents used were of analytical grade.

The microcosms were submitted to anoxic followed by oxic condition. In the anoxic phase, nitrogen (N₂) was sparged gently in order to maintain DO below 0.5 mg L⁻¹ for 25 days or until phosphorus concentrations in water stabilized. This value is consistently lower than the limit of 1.0 mg L⁻¹ proposed by Mortimer (1971) for triggering anaerobic release. Note that other authors such as Chapra

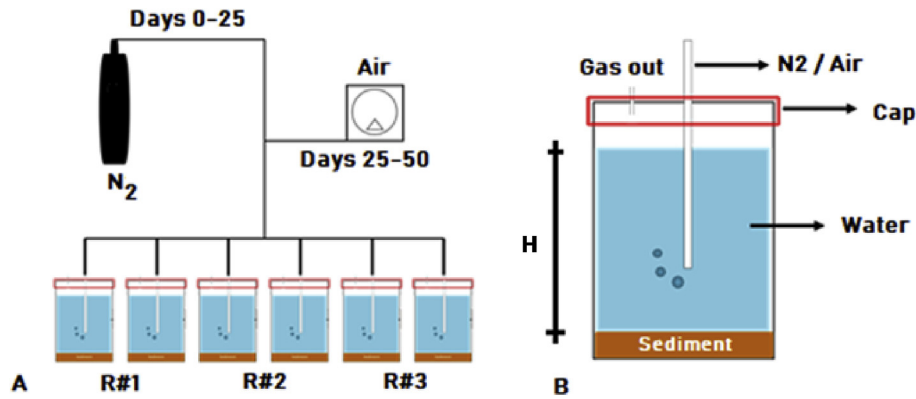


Fig. 2. Experimental setup for the sediment-water column interaction: (a) microcosms sparged initially with nitrogen and then with air; and (b) single microcosm containing sediment, natural water and gas input/output details.

and Canale (1991) and Ruley and Rusch (2004) assumed higher limits of 1.5 and 3.0 mg L⁻¹, respectively, in order to compensate for the fact that the hypolimnion of real lakes is actually not well mixed, differently from our lab conditions. The next stage consisted of gently sparging air in order to reach DO of approximately 4.5 mg L⁻¹, a condition normally found in the reservoirs, maintained for 25 days or until phosphorus concentrations in the water stabilized. Observe that this upper limit (4.5 mg L⁻¹) is also higher than the above-mentioned thresholds suggested by Chapra and Canale (1991) and Ruley and Rusch (2004). It is also important to stress that no visible resuspension of sediment occurred during sparging. Change in phosphorus concentration was calculated based on the initial water concentration, considering the volume of the aliquot subtracted for analysis.

2.4. Phosphorus exchange model

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

$$V \frac{dC}{dt} = k_r A - k_s A C \quad (2)$$

where C (mg m⁻³) is the concentration of TP or OP, A (m²) and V (m³) are the cross-sectional area and water volume of the experimental chambers (Fig. 2), respectively, k_r (mg m⁻² day⁻¹) and k_s (m day⁻¹) are the reaction coefficients to account for release and precipitation of P, respectively, while t is the elapsed time. Note that the above equation is equivalent to that proposed by Larsen et al. (1979). A one-compartment model was used here instead of the two-compartment model of Chapra and Canale (1991), as P burial was neglected under the present experimental conditions.

Thus, in order to model the behavior of TP and OP in the microcosm water, it was assumed that P net-release occurred during the anoxic stage, while P net-precipitation occurred in the

oxic stage, resulting in the following analytical solutions from Eq. (2):

$$\text{Release (anoxic stage)} : C = C_0 + 1/H(k_r t) \quad (3)$$

$$\text{Precipitation (oxic stage)} : C = C_0 \exp[1/H(-k_s t)] \quad (4)$$

where C₀ (mg m⁻³) is the initial concentration of TP or OP, and H (=V/A) is the water depth in the chambers (Fig. 2).

2.5. Statistical analysis

Shapiro-Wilk normality test was performed on the TP and OP data for the three sediments (R # 1, R # 2 and R # 3) under anoxic and oxic conditions. Normality was observed in all tests at a significance level of 5%. Pearson's correlation coefficient was calculated considering three association intensities: Strong: above 80%; Medium: between 60 and 80% and; Weak: below 60%. The same significance level was considered (5%). To confirm the causality between the number of days of the experiment and the concentrations of TP and OP in the microcosms, a linear regression analysis was performed and R² and adjusted R² were calculated. For such, it was assumed:

- Normally distributed dependent variable (p > 0.05) at the significance level of 5%;
- Independent variable coefficients significant (p < 0.05) by t-test;
- Obtained model shows significant F-statistics (p < 0.05);
- Homoscedasticity of the residues (p > 0.05) by F-statistic;
- Normally distributed residues (p > 0.05);
- Graphic analysis of residues.

We used nonparametric one-tailed pairwise Wilcoxon rank-sum tests with Bonferroni correction with a level of significance of 5% to verify a significant reduction in TP and OP between microcosms. Details of the statistical analyses mentioned above are available in the supplementary materials.

3. Results and discussion

3.1. Sediment phosphorus analysis

Sediment pH increased slightly while P_T content decreased to a greater extent from R#1 to R#3 (Table 4). Wu et al. (2013) evaluated the effects of pH on P release from sediments under laboratory conditions and demonstrated that more P was released under

Table 3

Water quality parameters for the natural water used in the sediment-water interface studies.

Parameter	Result
Dissolved oxygen - DO (mg L ⁻¹)	4.7
254 nm absorbance	0.369
pH	7.1
Total phosphorus - TP (µg L ⁻¹)	197.5
Orthophosphate - OP (µg L ⁻¹)	56.4

alkaline than acidic conditions. According to Boström et al. (1988), low pH increases the phosphorus binding capacity of iron in lakes, decreasing the phosphorus flux from sediment to the water column.

Reservoir R#1 presented the highest P_T (998.72 mg kg⁻¹) and P_{FeAl} (567.43 mg kg⁻¹, 57% of P_T) (Table 4), indicating a high potential of P-recharge to water, as Fe-bond are mostly responsible for the release of P from sediments (Chen et al., 2018). In R#2, P_T was 671.31 mg kg⁻¹ with P_{Ca} predominating (421.90 mg kg⁻¹) and representing 61% of P_T . As P_{Ca} can be considered hardly available (Rydin, 2000), this sediment should have a moderate impact on this reservoir's trophic level. The lowest concentration of P_T (302.91 mg kg⁻¹) was observed in R#3, with the unavailable fraction (P_{Re}) representing 68%, indicating that this sediment should have little or no influence on water quality in the reservoir.

Calcium-bond P found in lake sediments are normally associated with the adsorption of calcium carbonate and the formation of calcium phosphates (Brown, 1980; Golterman et al., 1998). Huang et al. (2005) observed that the quantity of Ca-P fraction retained in the sediments, after a release experiment, increased with the increase of the pH values in solutions indicating that calcium-bound P release to water mainly occurred at lower pH, while the amounts of Ca-P released would reach bottom at pH 8 to 10. The high amount of Ca-P fraction in the sediment of reservoir R#2 could be explained if its water were normally alkaline. However, it was not possible to verify that hypothesis since the reservoir was completely dry during the sampling campaign.

It is also interesting to stress that as P_i increased with reservoir age, P_o decreased (Table 4). This trend is supported by the study of Shinohara et al. (2017), in which the concentration of inorganic P in the sediment of a shallow eutrophic lake in Japan increased over time whereas the concentration of organic P decreased. Such a result suggests that organic P is converted into inorganic P, as bacteria in the sediment can decompose the organic matter, consuming oxygen and releasing inorganic P. Additionally, we can observe that the fraction of P_{FeAl} is the only one shown in Table 4 that clearly increases with reservoir age.

Overall, the P concentrations measured were lower in comparison to those reported by Cavalcante et al. (2018) in other tropical semiarid reservoir sediments, but within the values obtained in other climatic regions (Rydin, 2000; Wang et al., 2006; Roy et al., 2017). Sediment R#1 presented the highest concentrations of P_{FeAl} , followed by R#2 and R#3, at a significance level of 5%. Considering the reservoirs in this study, it is observed that as the age increased, the concentration of P in the sediment also increased, as well as the dominant fraction P_{FeAl} , and consequently, the potential P-release. This trend is consistent with the results of Cavalcante et al. (2018) who reported higher P_{FeAl} concentrations in older reservoirs (60 and 90 years). Combining our results with those of Cavalcante et al. (2018), we were able to fit the following linear relationship to describe the effect of reservoir age on the

concentration of P_{FeAl} (Fig. 3):

$$P_{FeAl} = 17(\text{age}) \quad (5)$$

where P_{FeAl} and age are given in mg kg⁻¹ and years, respectively. Note that this linear relationship better fitted the data than the exponential curve also shown in Fig. 3, which implies that, for the range of ages evaluated here, no clear P_{FeAl} saturation is observed.

3.2. Water-sediment interface simulation

3.2.1. Phosphorus in water

The experiment was run for approximately 50 days under identical conditions. The water temperature was maintained at 27 ± 2 °C and the pH varied according to Table 5. As stated in the materials and methods section, the DO in the anoxic phase was maintained at approximately 0.5 mg L⁻¹, while, in the aerated phase, DO was approximately 4.5 mg L⁻¹.

Except for microcosms containing R#1 sediment, where pH average and standard deviation (SD) in water did not remarkably change in both phases, both values increased during the oxic phase (Table 5). Jiang et al. (2006) performed P release experiments using bottom sediments and also observed a pH increase from 8.6 to 9.5 in the water at the anoxic condition but no obvious changes in the aerobic condition. Sediment pH did not appear to influence the pH of the supernatant water. Likewise, Herlihy and Mills (1986) observed that the pH values of sediments (between 6.0 and 7.0) did not reflect the pH values (as low as 3.5) of the underlying water in Lake Anna, Virginia.

Water-sediment P fluxes varied between anoxic to oxic phases and between the three different sediments tested (Fig. 4). For both TP and OP, at a significance level of 5%, the water concentration in R # 1 was greater than in R # 2 ($p_{TP} = 0.046$ and $p_{OP} = 0.002$) which in turn was greater than in R # 3 ($p_{TP} = 0.002$ and $p_{OP} = 0.004$).

In the anoxic phase, the TP concentration in the water of the microcosms containing the sediment of reservoirs R#1 and R#2 showed significant ($p < 0.05$) positive correlations with the number of days of the experiment (Fig. 5) while in the oxic phase, there were significant negative correlations for both ($p < 0.05$). For R#3 the correlations were not significant ($p > 0.05$) in both phases (Fig. 5). A significant ($p < 0.05$), strong and positive correlations in R # 1, R # 2 and R # 3 was observed between OP and the number of days of the experiment in anoxic phase, while in the oxic phase, only R # 1 showed a significant ($p > 0.05$), but moderate, negative correlation. Thus, the behavior of the OP differed slightly from that observed for the TP.

Table 4

Concentration of phosphorus in the sediment, phosphorus forms, P_i fractions and percentage in relation to the P_T for each reservoir.

Parameter	R#1	% of P_T	R#2	% of P_T	R#3	% of P_T
Depth (cm)	0–5	–	0–7	–	0–5	–
pH	5.88	–	6.03	–	6.47	–
P_T (mg kg ⁻¹)	998.72	100	694.2	100	368.17	100
P_M (mg kg ⁻¹)	58.17	6	11.96	2	11.96	3
P_{FeAl} (mg kg ⁻¹)	567.43	57	177.74	26	28.18	8
P_{Ca} (mg kg ⁻¹)	329.47	33	421.9	61	13.76	4
P_{Re} (mg kg ⁻¹)	191.57	19	59.71	9	249.01	68
P_i (mg kg ⁻¹)	998.72	100	671.31	97	302.91	82
P_o (mg kg ⁻¹)	0	0	20.83	3	65.26	18

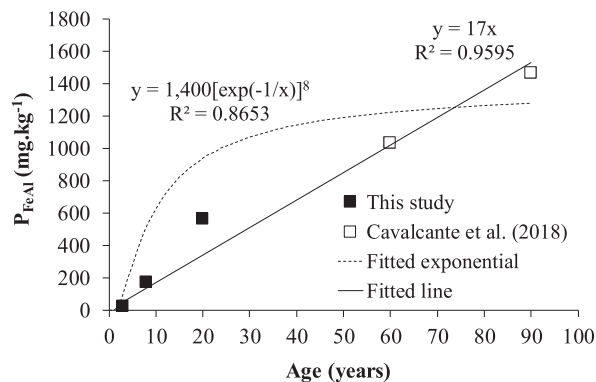


Fig. 3. Effect of reservoir age on the concentration of phosphorus linked to iron and aluminum in tropical semiarid reservoirs, which is responsible for phosphorus release from anoxic sediments.

Table 5
pH average and standard deviation (SD) during the experiment's anoxic and oxic phases.

Sediment	Anoxic		Oxic	
	average	SD	average	SD
#1	7.15	0.15	7.12	0.13
#2	7.13	0.34	7.55	1.45
#3	7.03	0.16	7.41	0.37

According to Cong et al. (2014), P_{FeAl} is easily desorbed from the sediments and released into the supernatant water. In R#1, sediment showed the greatest potential to impact the water quality due to the P release significantly higher than in the other reservoirs presenting after 22 days, 1842 $mg\ m^{-3}$ of TP and 1704 $mg\ m^{-3}$ of OP.

Iron oxides and hydroxides are involved in phosphorus sorption/desorption and precipitation/dissolution on water and sediment in lakes (Boström et al., 1988; Holtan et al., 1988; Ruttenberg, 2003). Iron oxides and hydroxides in water and in sediments come ultimately from the catchment soil (Dillon and Molot, 2005) and are connected to site geology and climate conditions and can influence TP concentration in water columns and in the sediment (Buol et al., 2011). Bottom sediments of two small shallow reservoirs in Poland were investigated by Smal et al. (2013). The researchers established a strong linear relationship between TP content and Fe and Al concentrations in the sediments, implying that the high levels of Fe and Al in sediments contributed to the TP accumulation.

Fig. 5 also shows the equations of the straight lines obtained by linear regression for the experimental data. Under anoxic conditions, the sediment from R#1 presented the highest solubilization rate of TP ($69.8\ mg\ m^{-3}\ day^{-1}$) to the microcosmos water, while the sediment R#2 presented a rate of $26.4\ mg\ m^{-3}\ day^{-1}$, and R # 3

showed no significant solubilization ($p > 0.05$). Similarly, OP solubilization was also higher in R#1 ($73.0\ mg\ m^{-3}\ day^{-1}$) followed by R#2 ($25.6\ mg\ m^{-3}\ day^{-1}$) and than R#3 ($6.7\ mg\ m^{-3}\ day^{-1}$). In the case of microcosms containing R # 1 and R # 2 sediments, the solubilization rate of TP and OP were statistically the same ($p > 0.05$) indicating that P release occurred in soluble format.

In the oxide phase, the microcosm water containing R#1 sediment also presented the highest precipitation rate, reducing the TP concentration by approximately $17\ mg\ m^{-3}\ day^{-1}$, while in the R# 2 the precipitation rate observed was $10.8\ mg\ m^{-3}\ day^{-1}$. R # 3 also showed no significant precipitation ($p > 0.05$). Regarding OP, the R # 1 sediment microcosm presented a precipitation rate of $7.3\ mg\ m^{-3}\ day^{-1}$ while the other microcosm showed no significant reductions.

After 10 days into the oxic phase in microcosms R#1, TP and OP were 1108 and 1013 $mg\ m^{-3}$, respectively, representing total precipitation of only around 40% of TP and OP. Contrary to what was observed in our experiment, Beutel et al. (2008) found that the concentrations of Soluble Reactive Phosphorus (SRP), referred to in our study as orthophosphate (OP), practically returned to the initial conditions after aeration. In their anoxic phase, the amount of SRP released was approximately $250\ mg\ m^{-3}$, practically the same amount returned to the sediment after aeration.

In R#1, the OP released was $2449\ mg\ m^{-3}$ and the precipitated was $937\ mg\ m^{-3}$, representing a 38% reduction of P in the water column. Beutel et al. (2008) experiments presented approximately $300\ mg\ m^{-3}$ at the end of the anoxic phase but only $50\ mg\ m^{-3}$ at the end of the oxic phase. However, in Beutel et al. (2008) dissolved oxygen went up to $9\ mg\ L^{-1}$, whereas the conditions found in the Ceará state reservoirs and in the microcosms were about half of that ($4.5\ mg\ L^{-1}$). Although several environmental variables influence the P release from bottom sediment (Kleeberg and Kozerski, 1998), DO in the overlying water is probably the most important one (Wang et al., 2008). The mechanism of the effects of DO on the

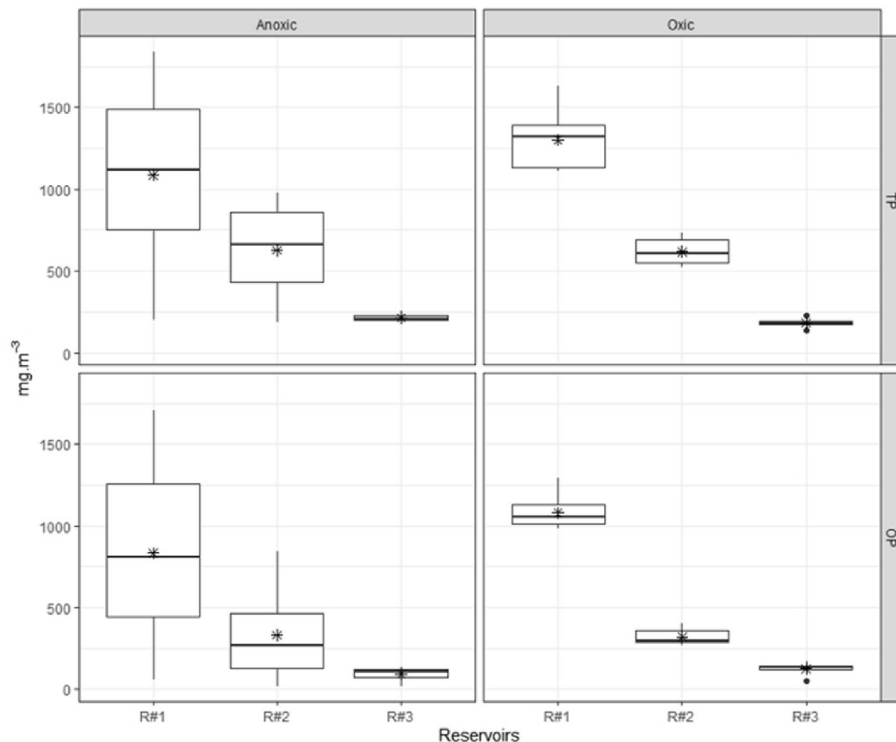


Fig. 4. OP and TP concentration variation in microcosms containing sediments R# 1, R# 2, and R# 3 in the anoxic and oxic phases.

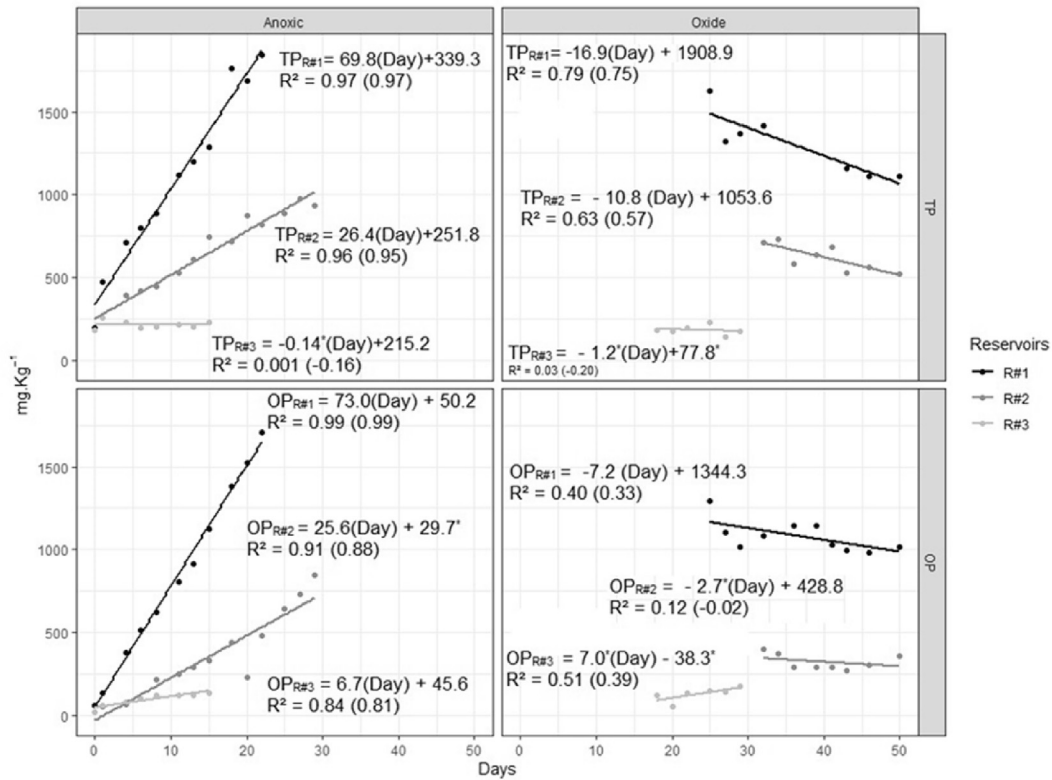


Fig. 5. Linear regression fit of TP and OP versus time for both anoxic and oxic conditions using three sediments (R#1, R#2, R#3). The symbol (*) indicates that the fit was not significant ($p > 0.05$). The values in parentheses after R^2 represent the adjusted R^2 .

P-release from sediments is related basically to the redox and pH variations (Baudo et al., 1990).

In microcosms R#2, the concentrations of TP and OP in the water increased during the anoxic phase, reaching 931 and 842 mg m^{-3} after 29 days, respectively, similar to what happened in microcosms R#1 but with a lower final concentration. This behavior may be explained by the dominant P_i fractions found in the sediments of R#2, the not readily available P_{Ca} (421.9 mg kg^{-1} , 61% of P_T). After 21 days of aeration, the concentration of TP and OP in the water was reduced to 520 mg m^{-3} and 357 mg m^{-3} , respectively.

In R#3, a high concentration of P_{Re} ($249.01 \text{ mg kg}^{-1}$, 68% of P_T), which is considered unavailable, was present in the sediment. In contrast to the other reservoirs, the easily available fractions in the sediment represented only 11% of P_T and therefore, the concentrations of TP in the water showed very little variation in the anoxic phase and no significant ($p > 0.05$) variation in the oxic stages (Fig. 5).

According to Singleton and Little (2006), the aeration of the reservoir's hypolimnion can be used as a recovery measure. In addition to preventing the release of P to the water column, this technique helps precipitate it, thus improving water quality. However, the present study showed that this measure alone may not be able to revert the release of P during anoxic conditions.

Knowing the concentration of each easily available fraction (P_{FeAl} and P_M) at the sediment (25 g), the amount of P that could potentially be released to the water was calculated. Although R#1 sediment released a higher amount of P, it represented only 25% of the potentially available P to water, while at R#2, P released was 35% of the potentially available P in the sediment (Fig. 6).

3.2.2. P exchange rates

The model fit (Eqs. (3) and (4)) presented at the Materials and

Methods section) to the TP and OP experimental data resulted in the release coefficients k_r of 11.0 and $4.0 \text{ mg m}^{-2} \text{ day}^{-1}$ and in the precipitation coefficients k_s of 0.004 and 0.07 m day^{-1} for microcosms R#1 and R#2, respectively (Table 6 and Fig. 7). Note that the same k_r and k_s values were used for adjusting the data of TP and OP for each microcosm, resulting in coefficients of determination (R^2) ranging from 0.770 to 0.973 for TP and from 0.540 to 0.995 for OP. This may indicate that the exchange rates between sediment and water were well represented by zero- and first-order models, respectively, as proposed by Larsen et al. (1979) and Rulley and Rusch (2004). Furthermore, it suggests that the models can be used to simulate the release and precipitation of P in tropical semiarid reservoirs. It is also important to note that the adjusted values of P exchange rates obtained for microcosms R#1 and R#2

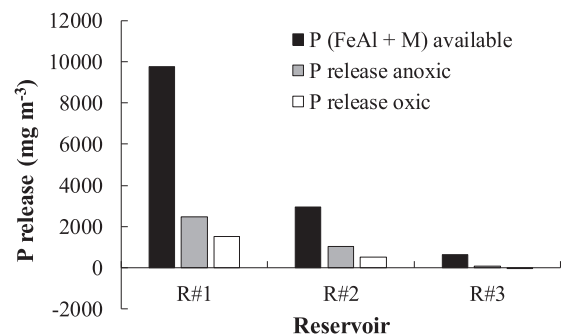


Fig. 6. Available phosphorus ($P_{FeAl} + P_M$) present in 25 g of sediment in 1600 mL compared to the concentration of total phosphorus released at the end of the anoxic and oxic phases for each reservoir.

Table 6

Fitted phosphorus release and precipitation rates obtained in the present study compared with the ranges reported in the literature.

Parameter	R#1	R#2	R#3	Ruley and Rusch (2004)
k_r ($\text{mg m}^{-2} \text{ day}^{-1}$)	11.0	4.0	0.0	19.0–46.0
k_s (m day^{-1})	0.004	0.007	0.0	0.009–0.120

were lower than those summarized by Ruley and Rusch (2004). This probably occurred because, here, we avoided sediment resuspension and growth of photosynthetic organisms in the experimental chambers, potentially reducing the k_r and k_s values, respectively. Contrastingly to the above-mentioned trends for the anoxic and oxic stages in R#1 and R#2, the microcosm R#3 did not present any clear trend over time, and the k_r and k_s values were considered zero (Table 6 and Fig. 7). Observe that the k_r -values decreased from R#1 to R#3, as the available P fractions in the sediment also decrease accordingly (Fig. 5). On the other hand, the k_s -values were higher for R#2, which suggests that reservoirs with high available P fractions, such as R#1, not only release more P but also present a lower precipitation rate of P, resulting in higher potential impacts on water quality than R#2 and R#3.

Fig. 8 shows the fitting of the adjusted values of k_r (Table 6) to

the concentration of P_{FeAl} for each microcosm (R#1, R#2 and R#3). It is clearly seen that k_r can be linearly related to P_{FeAl} :

$$k_r = 0.0196 (P_{\text{FeAl}}) \quad (6)$$

where k_r and P_{FeAl} are given in $\text{mg m}^{-2} \text{ day}^{-1}$ and mg kg^{-1} , respectively.

As already discussed, the dominant fraction for P release from sediments (P_{FeAl}) is also linearly related to reservoir age by equation (5) (Fig. 3). Thus, as the reservoirs studied here (R#1, R#2 and R#3) had a relatively small age (<20 years), we expect, as a consequence, lower values of k_r as compared to the older reservoirs studied by Cavalcante et al. (2018). Hence, applying equation (6) to these reservoirs, with ages of 60 and 90 years, we obtain values of k_r of 19.4 and 29.1 $\text{mg m}^{-2} \text{ day}^{-1}$, respectively, which are within the typical range reported by Ruley and Rusch (2004) in Table 5. On the other hand, as already mentioned, one possible cause of lower k_s -values (Table 6) is the absence of algae in the experimental chambers, which would also contribute to dissolved P removal from the water column (Chapra and Canale, 1991). The explanation for the lower precipitation rates found here remains to be explored in future experiments.

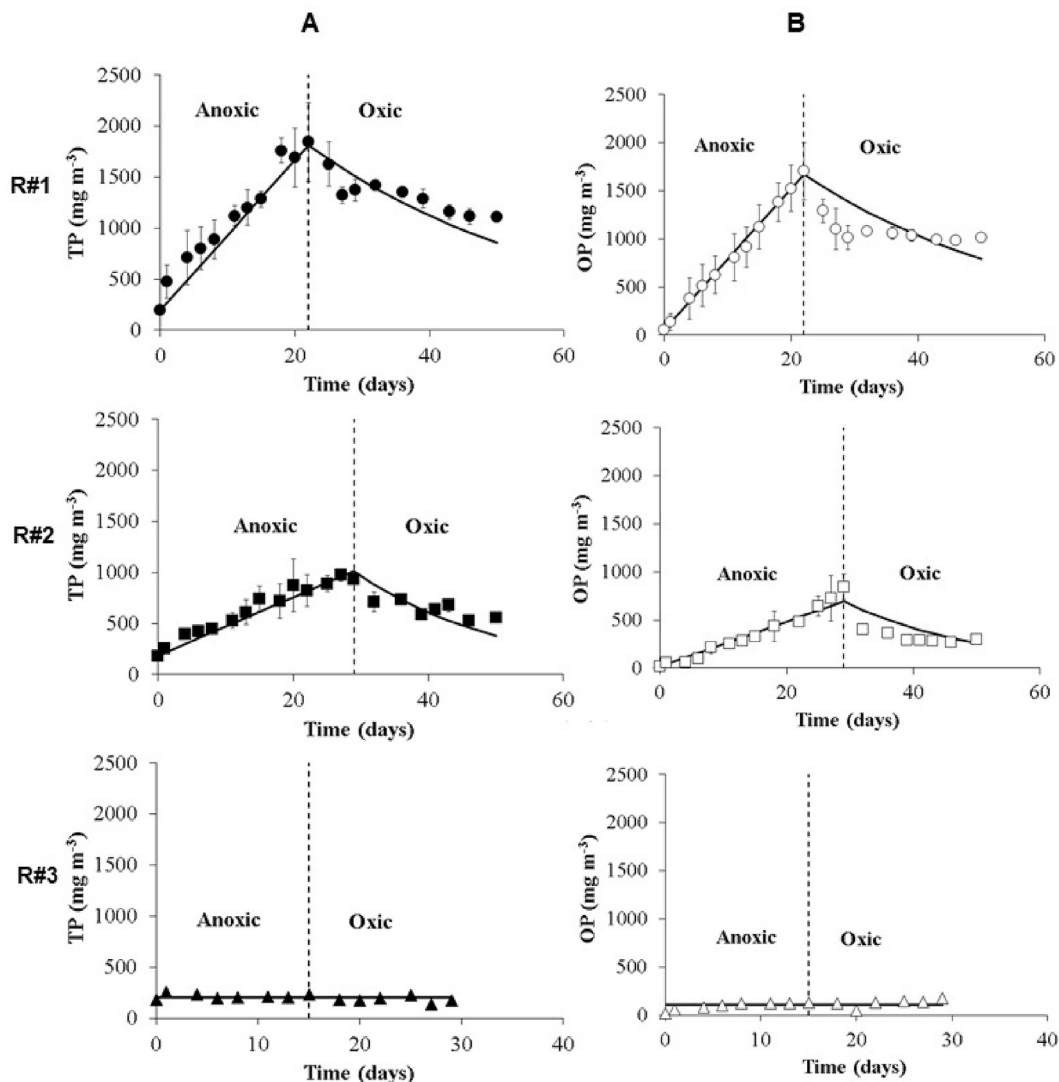


Fig. 7. Model Fit to the experimental data of TP (A) and OP (B) during the anoxic and oxic phases for each reservoir sediment.

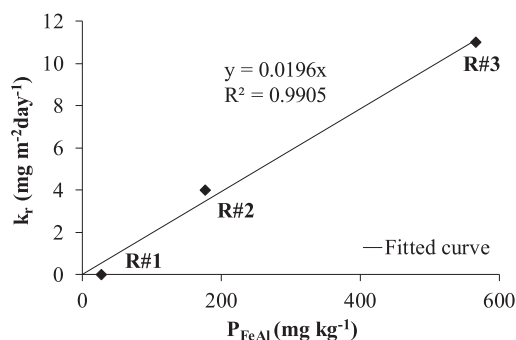


Fig. 8. Fitting of phosphorus release rate as a function of the concentration of phosphorus linked to iron and aluminum for each reservoir.

4. Conclusions

The sediments of three reservoirs of different ages located in the semiarid Northeast of Brazil were investigated regarding P content and chemical fraction distribution. Special attention was given to the potential of P release and precipitation at the sediment-water interface in experimental chambers (microcosms) under anoxic followed by oxic conditions. The older the reservoir, the higher the concentration of P and of iron and aluminum linked-P in the sediment. The concentration of P in the water column during the anoxic experiment using R#1 sediment showed a 10-fold increase due to the amount and fraction of P present (P_{FeAl}). After oxic condition was reached, the P concentration in the water column decreased but did not return to pre-anoxic phase values. The results also indicated that the contribution of P from the sediment occurred mainly in the form of orthophosphate (OP), which increases the primary productivity and the chances of harmful algal blooms in water. Contrastingly, the most recently constructed reservoir showed the lowest concentration of P in the sediment with the dominance of unavailable P fraction (P_{Re}), resulting in low potential impact on water quality. The release and precipitation rates of P between sediment and water were well represented by zero- and first-order models, respectively. Reservoirs with high available P fractions not only released more phosphorus but also proportionally presented lower precipitation rate, increasing the potential impacts on water quality. This study provided new findings regarding phosphorus dynamics at the sediment-water interface and new models and parameters that can be used to simulate the exchange rates of P in tropical semiarid reservoirs.

Author contributions

Diana S. Moura and Samylla Oliveira conducted the field and laboratory studies, literature review, designed the figures and drafted the manuscript. Maria Aparecida de Melo helped to conduct laboratory studies and processed the experimental data. Carlos J. Pestana reviewed the article and provided critical feedback. Iran E. Lima Neto performed the mathematical modeling, analyzed the data, and contributed to the manuscript. José Capelo-Neto helped to draft the field and laboratory planning, helped to conduct the field and laboratory studies, analyzed the data, and contributed to the manuscript. Allan Clemente improved the statistics analysis, analyzed the data, and contributed to the manuscript. All authors have approved the final article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.125686>.

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