

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

MOURA, D.S., LIMA NETO, I.E., CLEMENTE, A., OLIVEIRA, S., PESTANA, C.J., APARECIDA DE MELO, M. and CAPELO-NETO, J.

2020



# Journal Pre-proof

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Diana S. Moura, Iran E. Lima Neto, Allan Clemente, Samylla Oliveira, Carlos J. Pestana, Maria Aparecida de Melo, José Capelo-Neto



PII: S0045-6535(19)32926-1

DOI: <https://doi.org/10.1016/j.chemosphere.2019.125686>

Reference: CHEM 125686

To appear in: *ECSN*

Received Date: 2 October 2019

Revised Date: 10 December 2019

Accepted Date: 16 December 2019

Please cite this article as: Moura, D.S., Lima Neto, I.E., Clemente, A., Oliveira, S., Pestana, C.J., Aparecida de Melo, M., Capelo-Neto, José., Modeling phosphorus exchange between bottom sediment and water in tropical semiarid reservoirs, *Chemosphere* (2020), doi: <https://doi.org/10.1016/j.chemosphere.2019.125686>.

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

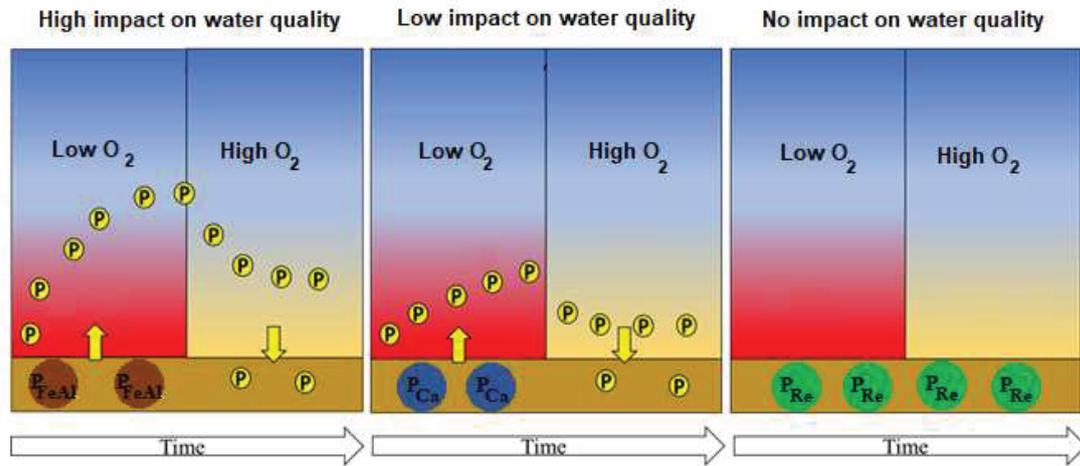
3

4 Diana S. Moura<sup>a,b</sup>, Iran E. Lima Neto<sup>a</sup>, Allan Clemente<sup>a</sup>; Samylla Oliveira<sup>a</sup>, Carlos J.  
5 Pestana<sup>b</sup>, Maria Aparecida de Melo<sup>a</sup>, José Capelo-Neto<sup>a</sup>

6 <sup>a</sup> School of Civil and Environmental Engineering, Department of Hydraulic and  
7 Environmental Engineering, Federal University of Ceará, Fortaleza, Brazil.

8 <sup>b</sup> School of Pharmacy and Life Sciences, Robert Gordon University, Aberdeen, UK

## Graphical abstract:



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

3

4 **Abstract**

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

20

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

23

## 24 1. Introduction

25

26 Phosphorus (P) present in bottom sediment has a major influence on eutrophication and  
27 water quality deterioration (Baker et al., 2014; Jarvie et al., 2017; Kane et al., 2014;  
28 Chen et al., 2018). High P concentration can favor the formation of harmful algal  
29 blooms (HABs), increase biomass, turbidity, and the risks associated with toxic or  
30 noxious secondary metabolites. HABs represent a significant challenge to water  
31 treatment, increasing the economic burden of water utilities as filter run time is  
32 decreased and additional chemicals are needed (He et al., 2016). The problem of P in  
33 sediments is prolonged since it is persistent and P can be released from sediment as  
34 deep as 20 cm (Søndergaard et al., 2003). In order to assess the magnitude of the  
35 problem, the likelihood of P release needs to be evaluated, since various P fractions  
36 have different solubility under different water conditions (Cong et al., 2014). This  
37 assessment can be achieved by sequential chemical fractionation of the inorganic  
38 phosphorus ( $P_I$ ) present in the bottom sediment of a reservoir. According to Rydin  
39 (2000),  $P_I$  can be fractionated into:

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

47 A number of authors (Mortimer, 1971; Chapra and Canale, 1991; Ruley and Rusch,  
48 2004; Beutel et al., 2008; Chen et al., 2018) have discussed the dynamics of P exchange

49 across the sediment-water interface. However, because of the complexities involved, it  
50 has not been found in the recent literature a conceptual model describing P exchange  
51 based on P fractions. Three major challenges are: the proportion and amount of the  
52 aforementioned P fractions can vary considerably among different lakes and reservoirs  
53 sediments; the impact of P fractions on the exchange rates between sediment and water  
54 is still not fully understood, and; environmental factors such as pH, temperature, and  
55 dissolved oxygen affect the exchange rates differently. Therefore, further studies are  
56 needed to elucidate these dynamics.

57 In tropical semiarid regions, like the Brazilian Northeast, a dense network of thousands  
58 of surface water reservoirs has been built to meet increasing water demand (Campos et  
59 al., 2016). However, these reservoirs face a nutrient-enriched sediment deposition  
60 (Braga et al., 2019) associated with high water temperatures, which promote  
61 stratification in the water column (Dantas et al., 2008) and fast organic degradation,  
62 frequently forcing anoxic conditions over the bottom sediment. Therefore, P internal  
63 loading is expected to significantly impact water quality in these reservoirs. Moreover,  
64 reservoirs in the tropical semiarid regions are usually shallow and present high water  
65 level variation because of recurrent droughts and high evaporation rates (Barbosa et al.,  
66 2012). The combination of these factors perpetuates eutrophication and HAB,  
67 significantly overloading water treatment (Pestana et al., 2019) and requiring in-lake  
68 treatment techniques such as artificial aeration (Pacheco and Lima Neto, 2017) or  
69 application of phosphorus binding clay (Oosterhout and Lürling, 2013) to mitigate the  
70 impacts on water quality.

71 A recent study carried out by Cavalcante et al. (2018) evaluated the potential  
72 contribution of P sediment load in reservoirs in the State of Rio Grande do Norte, also  
73 located in the Brazilian semiarid region. The results revealed high amounts of soluble

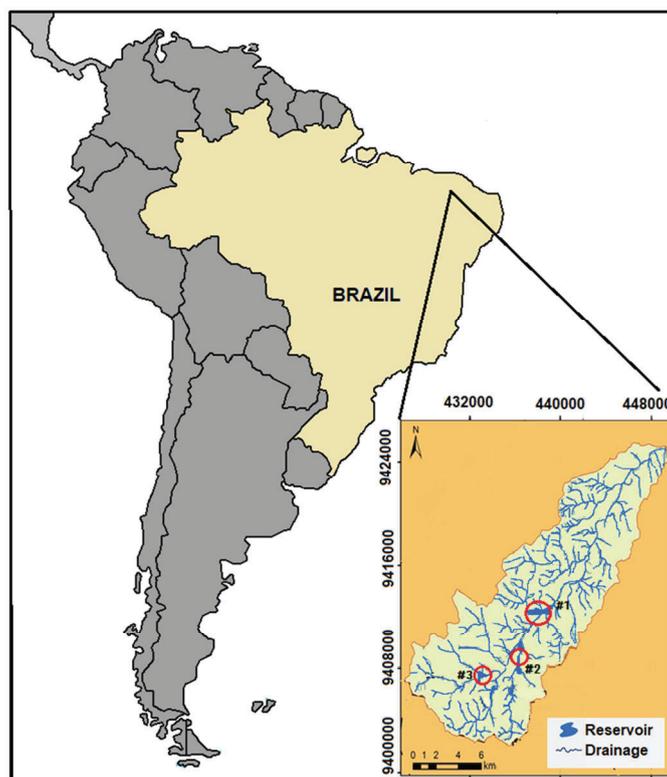
74 and easily bioavailable forms of P in the sediments, thereby enhancing eutrophication  
75 and phytoplankton growth. Hence, when the hypolimnion of a reservoir becomes anoxic  
76 and depending on the fraction of P present, a significant release of P to the water would  
77 be expected. However, how different fractions of P will contribute to P concentration in  
78 the water under this scenario is still not fully understood. To the authors' best  
79 knowledge, this is the first study modeling the potential exchange between bottom  
80 sediment and water in artificial water reservoirs of different P fractions. The hypothesis  
81 raised in this paper is that, by elucidating the distribution of the P fractions in the  
82 bottom sediment, it would be possible to assess the P exchange potential in different  
83 reservoirs. Therefore, the objective of this work was to mathematically model P  
84 exchange dynamics in reservoirs with different characteristics under oxic and anoxic  
85 conditions considering the different fractions available.

## 86 **2. Materials and Methods**

### 87 **2.1 Study site and sediment sampling**

88  
89 The semiarid region of northeastern Brazil provides the ideal study ground for drinking  
90 water reservoirs that undergo periodical drought-and-refill cycles. The selected study  
91 area is located in the central region of the Ceará state, in the experimental watershed of  
92 the Forquilha River. This region encompasses a geomorphological diversity  
93 representative of the crystalline area of the Brazilian semiarid region. The experimental  
94 watershed has an area of 221 km<sup>2</sup> and an average elevation of 315 m. The vegetation is  
95 shrub-like, heavily degraded due to the widespread practice of fires for the preparation  
96 of agricultural areas. Preceding this study, the selected area experienced five years of  
97 precipitation below the historical average. This situation was confirmed in the field  
98 surveys when the selected reservoirs were completely dry. Three reservoirs R#1, R#2

99 and R#3 with capacities of about one hm<sup>3</sup> and different ages were selected (figure 1 and  
 100 table 1). Sediment sampling was carried out in duplicate in the lacustrine zone of each  
 101 reservoir until a depth of approximately 5 cm with the aid of a sediment trap. In total,  
 102 three composite samples were collected.



103  
 104 Figure 1. Selected reservoirs (R#1, R#2 and R#3) in the experimental watershed of Forquilha, in the State  
 105 of Ceará, Brazilian semiarid region.  
 106

107 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

108

## 109 2.2 Phosphorus extraction of from sediment and analysis

110 Analysis of P in the sediment was performed before the water-sediment interface  
 111 simulation in order to characterize the sediment and to assess its interaction with the  
 112 water. Total phosphorus (P<sub>T</sub>) content in the sediments was analyzed as soluble

113 phosphate after extraction by heating the sediment at 500 °C for 1 hour followed by  
 114 high temperature (340 °C) acid hydrolysis, according to the methodology proposed by  
 115 Hedley et al. (1982).  $P_T$ , in turn, can be subdivided into inorganic ( $P_I$ ) and organic  
 116 phosphorus ( $P_O$ ).  $P_O$  was obtained by subtracting  $P_T$  from  $P_I$  concentration (Eq. 1)

$$117 \quad P_O = P_T - (P_M + P_{FeAl} + P_{Ca} + P_{Re}) \quad (1)$$

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

124 Table 2. Methods of P extraction from the sediment by sequential chemical fractionation of the inorganic  
 125 phosphorus

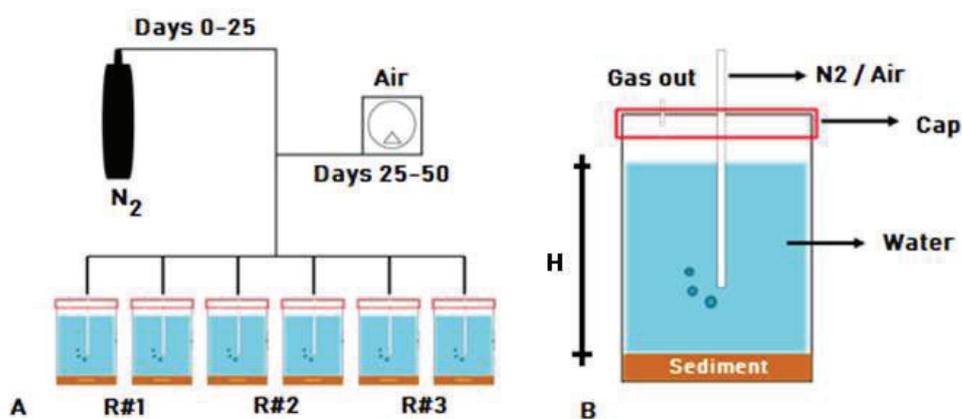
Fractioning sequence	P fraction	Extraction solution (Conc.)	Conditions	Method
1 <sup>st</sup> .	$P_M$	NH <sub>4</sub> Cl (0.5 N)	10 minutes	Adapted from Psenner et al. (1998)
2 <sup>nd</sup>	$P_{FeAl}$	NaOH (0.1 N)	17 hours	
3 <sup>rd</sup>	$P_{Ca}$	HCl (0.1 N)	24 hours	
4 <sup>th</sup>	$P_{Re}$	HCl (0.1 N)	Heating (500 °C) for 1 hour followed by high temperature (340 °C) acid hydrolysis for 10 minutes.	Adapted from Hedley et al. (1982)

126

### 127 2.3 Water-sediment interface simulation

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

135 microcosms were protected from light to avoid oxygen generation by photosynthetic  
 136 organisms.



137  
 138 Figure 2. Experimental setup for the sediment-water column interaction: (a) microcosms sparged initially  
 139 with nitrogen and then with air; and (b) single microcosm containing sediment, natural water and gas  
 140 input/output details.

141  
 142 Natural water quality was determined prior (Table 3) and during the experiment  
 143 including Total phosphorus – TP (APHA, 2017 - Method 4500-P), orthophosphate - OP  
 144 (APHA, 2017 - Method 4500-P), dissolved oxygen - DO (YSI 55, USA), 254 nm  
 145 absorbance (Spectrophotometer GENESYS 10S UV – VIS, USA), and pH (AN 2000,  
 146 China). Absorbance at 254 nm was determined as an estimation of dissolved organic  
 147 material in the water. All reagents used were of analytical grade.

148 Table 3. Water quality parameters for the natural water used in the sediment-water interface studies.

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

149  
 150 The microcosms were submitted to anoxic followed by oxic condition. In the anoxic  
 151 phase, nitrogen (N<sub>2</sub>) was sparged gently in order to maintain DO below 0.5 mg L<sup>-1</sup> for  
 152 25 days or until phosphorus concentrations in water stabilized. This value is consistently  
 153 lower than the limit of 1.0 mg L<sup>-1</sup> proposed by Mortimer (1971) for triggering anaerobic

154 release. Note that other authors such as Chapra and Canale (1991) and Ruley and Rusch  
155 (2004) assumed higher limits of 1.5 and 3.0 mg L<sup>-1</sup>, respectively, in order to compensate  
156 for the fact that the hypolimnion of real lakes is actually not well mixed, differently  
157 from our lab conditions. The next stage consisted of gently sparging air in order to reach  
158 DO of approximately 4.5 mg L<sup>-1</sup>, a condition normally found in the reservoirs,  
159 maintained for 25 days or until phosphorus concentrations in the water stabilized.  
160 Observe that this upper limit (4.5 mg L<sup>-1</sup>) is also higher than the above-mentioned  
161 thresholds suggested by Chapra and Canale (1991) and Ruley and Rusch (2004). It is  
162 also important to stress that no visible resuspension of sediment occurred during  
163 sparging. Change in phosphorus concentration was calculated based on the initial water  
164 concentration, considering the volume of the aliquot subtracted for analysis.

#### 165 **2.4 Phosphorus exchange model**

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

$$168 \quad V \frac{dC}{dt} = k_r A - k_s AC \quad (2)$$

169 where C (mg m<sup>-3</sup>) is the concentration of TP or OP, A (m<sup>2</sup>) and V (m<sup>3</sup>) are the cross-  
170 sectional area and water volume of the experimental chambers (figure 2), respectively,  
171 k<sub>r</sub> (mg m<sup>-2</sup> day<sup>-1</sup>) and k<sub>s</sub> (m day<sup>-1</sup>) are the reaction coefficients to account for release and  
172 precipitation of P, respectively, while t is the elapsed time. Note that the above equation  
173 is equivalent to that proposed by Larsen et al. (1979). A one-compartment model was  
174 used here instead of the two-compartment model of Chapra and Canale (1991), as P  
175 burial was neglected under the present experimental conditions.

176 Thus, in order to model the behavior of TP and OP in the microcosm water, it was  
177 assumed that P net-release occurred during the anoxic stage, while P net-precipitation  
178 occurred in the oxic stage, resulting in the following analytical solutions from Eq. (2):

179 Release (anoxic stage):  $C = C_0 + 1/H(k_r t)$  (3)

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

181 where  $C_0$  ( $\text{mg m}^{-3}$ ) is the initial concentration of TP or OP, and  $H$  ( $=V/A$ ) is the water  
182 depth in the chambers (figure 2).

### 183 2.5 Statistical analysis

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

- 193 • Normally distributed dependent variable ( $p < 0.05$ ) at the significance level of
- 194 5%;
- 195 • Independent variable coefficients significant ( $p < 0.05$ ) by t-test;
- 196 • Obtained model shows significant F-statistics ( $p < 0.05$ );
- 197 • Homoscedasticity of the residues ( $p > 0.05$ ) by F-statistic;
- 198 • Normally distributed residues ( $p > 0.05$ );
- 199 • Graphic analysis of residues.

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

204

205

### 206 3. Results and Discussion

#### 207 3.1 Sediment phosphorus analysis

208 Sediment pH increased slightly while  $P_T$  content decreased to a greater extent from R#1  
209 to R#3 (Table 4). Wu et al. (2014) evaluated the effects of pH on P release from  
210 sediments under laboratory conditions and demonstrated that more P was released under  
211 alkaline than acidic conditions. According to Boström et al. (1988), low pH increases  
212 the phosphorus binding capacity of iron in lakes, decreasing the phosphorus flux from  
213 sediment to the water column.

214 Reservoir R#1 presented the highest  $P_T$  ( $998.72 \text{ mg kg}^{-1}$ ) and  $P_{FeAl}$  ( $567.43 \text{ mg kg}^{-1}$ ,  
215 57% of  $P_T$ ) (table 4), indicating a high potential of P-recharge to water, as Fe-bond are  
216 mostly responsible for the release of P from sediments (Chen et al., 2018). In R#2,  $P_T$   
217 was  $671.31 \text{ mg kg}^{-1}$  with  $P_{Ca}$  predominating ( $421.90 \text{ mg kg}^{-1}$ ) and representing 61% of  
218  $P_T$ . As  $P_{Ca}$  can be considered hardly available (Rydin, 2000), this sediment should have  
219 a moderate impact on this reservoir's trophic level. The lowest concentration of  $P_T$   
220 ( $302.91 \text{ mg kg}^{-1}$ ) was observed in R#3, with the unavailable fraction ( $P_{Re}$ ) representing  
221 68%, indicating that this sediment should have little or no influence on water quality in  
222 the reservoir.

223 Calcium-bond P found in lake sediments are normally associated with the adsorption of  
224 calcium carbonate and the formation of calcium phosphates (Brown, 1980;  
225 Golterman,1998). Huang et al. (2005) observed that the quantity of Ca-P fraction  
226 retained in the sediments, after a release experiment, increased with the increase of the  
227 pH values in solutions indicating that that calcium-bound P release to water mainly  
228 occurred at lower pH, while the amounts of Ca-P released would reach bottom at pH 8

229 to 10. The high amount of Ca-P fraction in the sediment of reservoir R#2 could be  
 230 explained if its water were normally alkaline. However, it was not possible to verify that  
 231 hypothesis since the reservoir was completely dry during the sampling campaign.  
 232 It is also interesting to stress that as  $P_I$  increased with reservoir age,  $P_O$  decreased (Table  
 233 4). This trend is supported by the study of Shinohara et al. (2017), in which the  
 234 concentration of inorganic P in the sediment of a shallow eutrophic lake in Japan  
 235 increased over time whereas the concentration of organic P decreased. Such a result  
 236 suggests that organic P is converted into inorganic P, as bacteria in the sediment can  
 237 decompose the organic matter, consuming oxygen and releasing inorganic P.  
 238 Additionally, we can observe that the fraction of  $P_{FeAl}$  is the only one shown in Table 4  
 239 that clearly increases with reservoir age.

240

241 Table 4. Concentration of phosphorus in the sediment, phosphorus forms,  $P_I$  fractions and percentage in  
 242 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 <sup>-1</sup> )	998.72	100	694.2	100	368.17	100
$P_M$ (mg kg <sup>-1</sup> )	58.17	6	11.96	2	11.96	3
$P_{FeAl}$ (mg kg <sup>-1</sup> )	567.43	57	177.74	26	28.18	8
$P_{Ca}$ (mg kg <sup>-1</sup> )	329.47	33	421.9	61	13.76	4
$P_{Re}$ (mg kg <sup>-1</sup> )	191.57	19	59.71	9	249.01	68
$P_I$ (mg kg <sup>-1</sup> )	998.72	100	671.31	97	302.91	82
$P_O$ (mg kg <sup>-1</sup> )	0	0	20.83	3	65.26	18

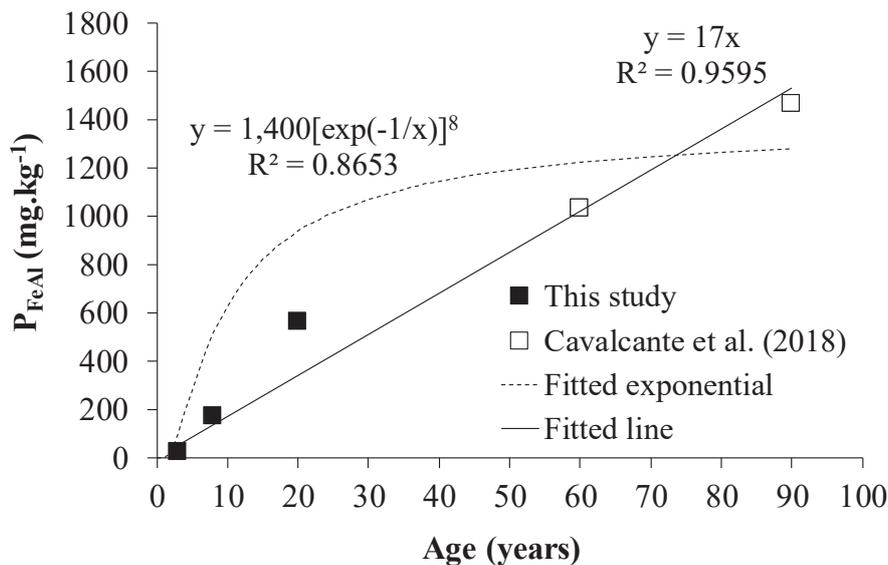
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244 Overall, the P concentrations measured were lower in comparison to those reported by  
 245 Cavalcante et al. (2018) in other tropical semiarid reservoir sediments, but within the  
 246 values obtained in other climatic regions (Rydin, 2000; Wang et al., 2006; Roy et al.,  
 247 2017). Sediment R#1 presented the highest concentrations of  $P_{FeAl}$ , followed by R#2  
 248 and R#3, at a significance level of 5%. Considering the reservoirs in this study, it is

249 observed that as the age increased, the concentration of P in the sediment also increased,  
 250 as well as the dominant fraction  $P_{FeAl}$ , and consequently, the potential P-release. This  
 251 trend is consistent with the results of Cavalcante et al. (2018) who reported higher  $P_{FeAl}$   
 252 concentrations in older reservoirs (60 and 90 years). Combining our results with those  
 253 of Cavalcante et al. (2018), we were able to fit the following linear relationship to  
 254 describe the effect of reservoir age on the concentration of  $P_{FeAl}$  (figure 3):

$$255 \quad P_{FeAl} = 17(\text{age}) \quad (5)$$

256 where  $P_{FeAl}$  and age are given in  $\text{mg kg}^{-1}$  and years, respectively. Note that this linear  
 257 relationship better fitted the data than the exponential curve also shown in figure 3,  
 258 which implies that, for the range of ages evaluated here, no clear  $P_{FeAl}$  saturation is  
 259 observed.



260

261 Figure 3. Effect of reservoir age on the concentration of phosphorus linked to iron and aluminum in  
 262 tropical semiarid reservoirs, which is responsible for phosphorus release from anoxic sediments.  
 263

### 264 3.2 Water-sediment interface simulation

#### 265 3.2.1 Phosphorus in water

266 The experiment was run for approximately 50 days under identical conditions. The water  
 267 temperature was maintained at  $27 \pm 2^\circ\text{C}$  and the pH varied according to table 5. As stated

268 in the materials and methods section, the DO in the anoxic phase was maintained at  
 269 approximately  $0.5 \text{ mg L}^{-1}$ , while, in the aerated phase, DO was approximately  $4.5 \text{ mg L}^{-1}$ .  
 270

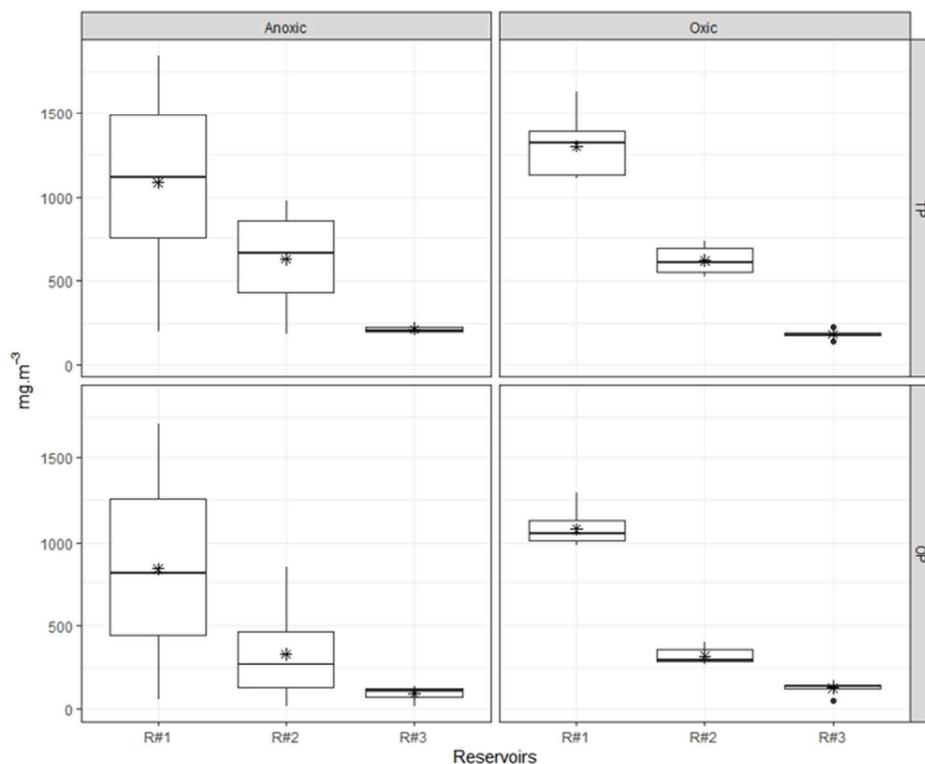
271 Except for microcosms containing R#1 sediment, where pH average and standard  
 272 deviation (SD) in water did not remarkably change in both phases, both values increased  
 273 during the oxic phase (Table 5). Jiang et al. (2006) performed P release experiments  
 274 using bottom sediments and also observed a pH increase from 8.6 to 9.5 in the water at  
 275 the anoxic condition but no obvious changes in the aerobic condition. Sediment pH did  
 276 not appear to influence the pH of the supernatant water. Likewise, Herlihy and Mills  
 277 (1986) observed that the pH values of sediments (between 6.0 and 7.0) did not reflect  
 278 the pH values (as low as 3.5) of the underlying water in Lake Anna, Virginia.

279 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

280

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



285

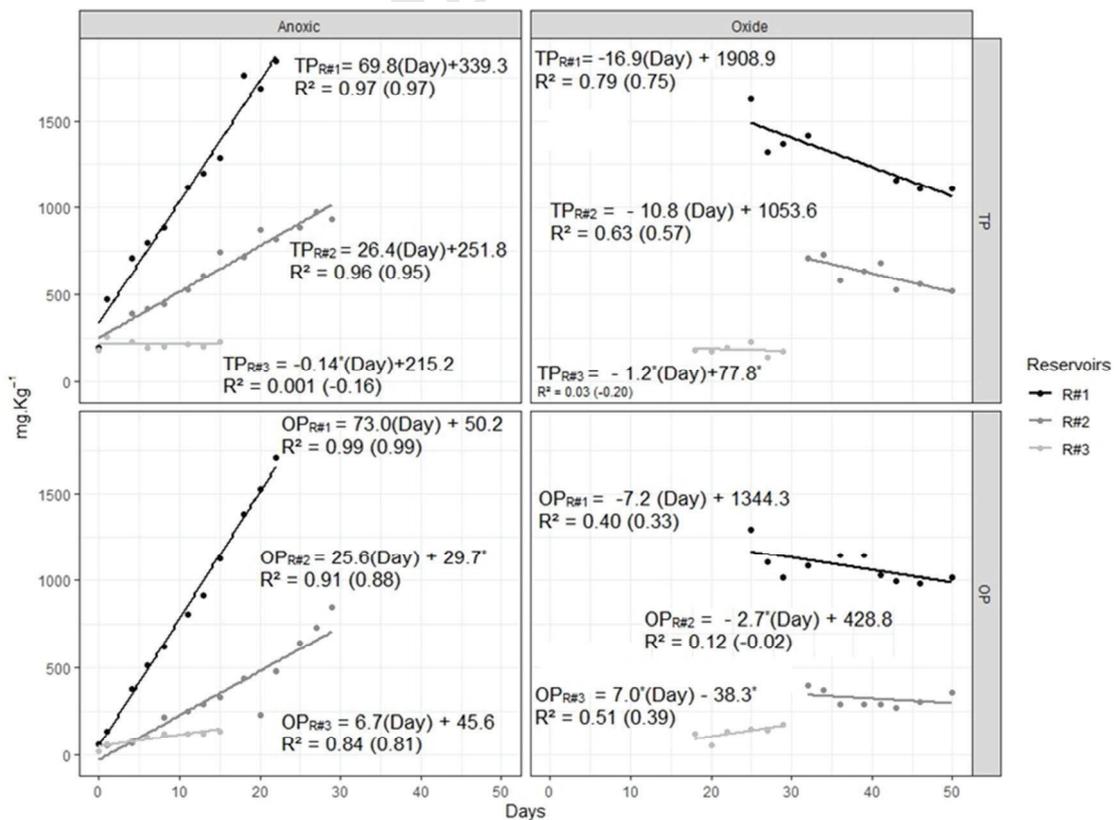
286 Figure 4. OP and TP concentration variation in microcosms containing sediments R# 1, R# 2, and R# 3 in  
 287 the anoxic and oxic phases.

288

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

298 According to Cong et al. (2014),  $P_{FeAl}$  is easily desorbed from the sediments and  
 299 released into the supernatant water. In R#1, sediment showed the greatest potential to

300 impact the water quality due to the P release significantly higher than in the other  
 301 reservoirs presenting after 22 days, 1842 mg m<sup>-3</sup> of TP and 1704 mg m<sup>-3</sup> of OP.  
 302 Iron oxides and hydroxides are involved in phosphorus sorption/desorption and  
 303 precipitation/dissolution on water and sediment in lakes (Boström et al., 1988; Holtan et  
 304 al., 1988; Ruttenberg, 2003). Iron oxides and hydroxides in water and in sediments  
 305 come ultimately from the catchment soil (Dillon and Molot, 2005) and are connected to  
 306 site geology and climate conditions and can influence TP concentration in water  
 307 columns and in the sediment (Buol et al., 2011). Bottom sediments of two small shallow  
 308 reservoirs in Poland were investigated by Smal et al. (2013). The researchers established  
 309 a strong linear relationship between TP content and Fe and Al concentrations in the  
 310 sediments, implying that the high levels of Fe and Al in sediments contributed to the TP  
 311 accumulation.  
 312



313  
 314 Figure 5. Linear regression fit of TP and OP versus time for both anoxic and oxic conditions using three

315 sediments (R#1, R#2, R#3). The symbol (\*) indicates that the fit was not significant ( $p > 0.05$ ). The values  
316 in parentheses after  $R^2$  represent the adjusted  $R^2$ .  
317

318 Figure 5 also shows the equations of the straight lines obtained by linear regression for  
319 the experimental data. Under anoxic conditions, the sediment from R#1 presented the  
320 highest solubilization rate of TP ( $69.8 \text{ mg m}^{-3} \text{ day}^{-1}$ ) to the microcosmos water, while  
321 the sediment R#2 presented a rate of  $26.4 \text{ mg m}^{-3} \text{ day}^{-1}$ , and R # 3 showed no significant  
322 solubilization ( $p > 0.05$ ). Similarly, OP solubilization was also higher in R#1 ( $73.0 \text{ mg}$   
323  $\text{m}^{-3} \text{ day}^{-1}$ ) followed by R#2 ( $25.6 \text{ mg m}^{-3} \text{ day}^{-1}$ ) and than R#3 ( $6.7 \text{ mg m}^{-3} \text{ day}^{-1}$ ). In the  
324 case of microcosms containing R # 1 and R # 2 sediments, the solubilization rate of TP  
325 and OP were statistically the same ( $p > 0.05$ ) indicating that P release occurred in  
326 soluble format.

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

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

340 In R#1, the OP released was  $2449 \text{ mg m}^{-3}$  and the precipitated was  $937 \text{ mg m}^{-3}$ ,  
341 representing a 38% reduction of P in the water column. Beutel et al. (2008) experiments  
342 presented approximately  $300 \text{ mg m}^{-3}$  at the end of the anoxic phase but only  $50 \text{ mg.m}^{-3}$   
343 at the end of the oxic phase. However, in Beutel et al. (2008) dissolved oxygen went up  
344 to  $9 \text{ mg L}^{-1}$ , whereas the conditions found in the Ceará state reservoirs and in the  
345 microcosms were about half of that ( $4.5 \text{ mg L}^{-1}$ ). Although several environmental  
346 variables influence the P release from bottom sediment (Kleeberg & Kozerski, 1998),  
347 DO in the overlying water is probably the most important one (Wang et al.,2008). The  
348 mechanism of the effects of DO on the P-release from sediments is related basically to  
349 the redox and pH variations (Baudo, 1990).

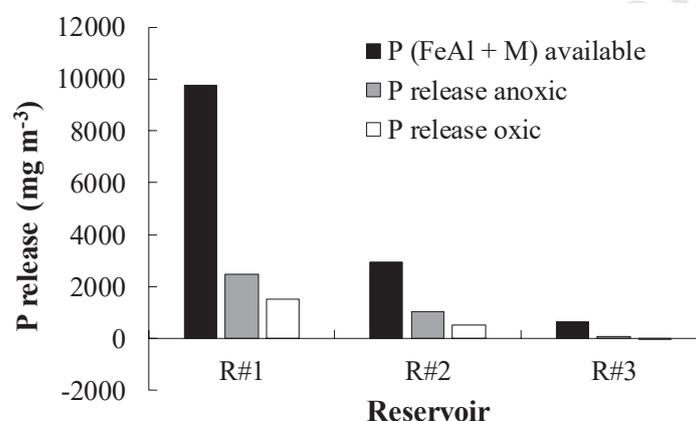
350 In microcosms R#2, the concentrations of TP and OP in the water increased during the  
351 anoxic phase, reaching 931 and  $842 \text{ mg m}^{-3}$  after 29 days, respectively, similar to what  
352 happened in microcosms R#1 but with a lower final concentration. This behavior may  
353 be explained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

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

361 According to Singleton and Little (2006), the aeration of the reservoir's hypolimnion  
362 can be used as a recovery measure. In addition to preventing the release of P to the  
363 water column, this technique helps precipitate it, thus improving water quality.

364 However, the present study showed that this measure alone may not be able to revert the  
 365 release of P during anoxic conditions.

366 Knowing the concentration of each easily available fraction ( $P_{FeAl}$  and  $P_M$ ) at the  
 367 sediment (25g), the amount of P that could potentially be released to the water was  
 368 calculated. Although R#1 sediment released a higher amount of P, it represented only  
 369 25% of the potentially available P to water, while at R#2, P released was 35% of the  
 370 potentially available P in the sediment (Figure 6).



371

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

374

### 375 3.2.2 P exchange rates

376

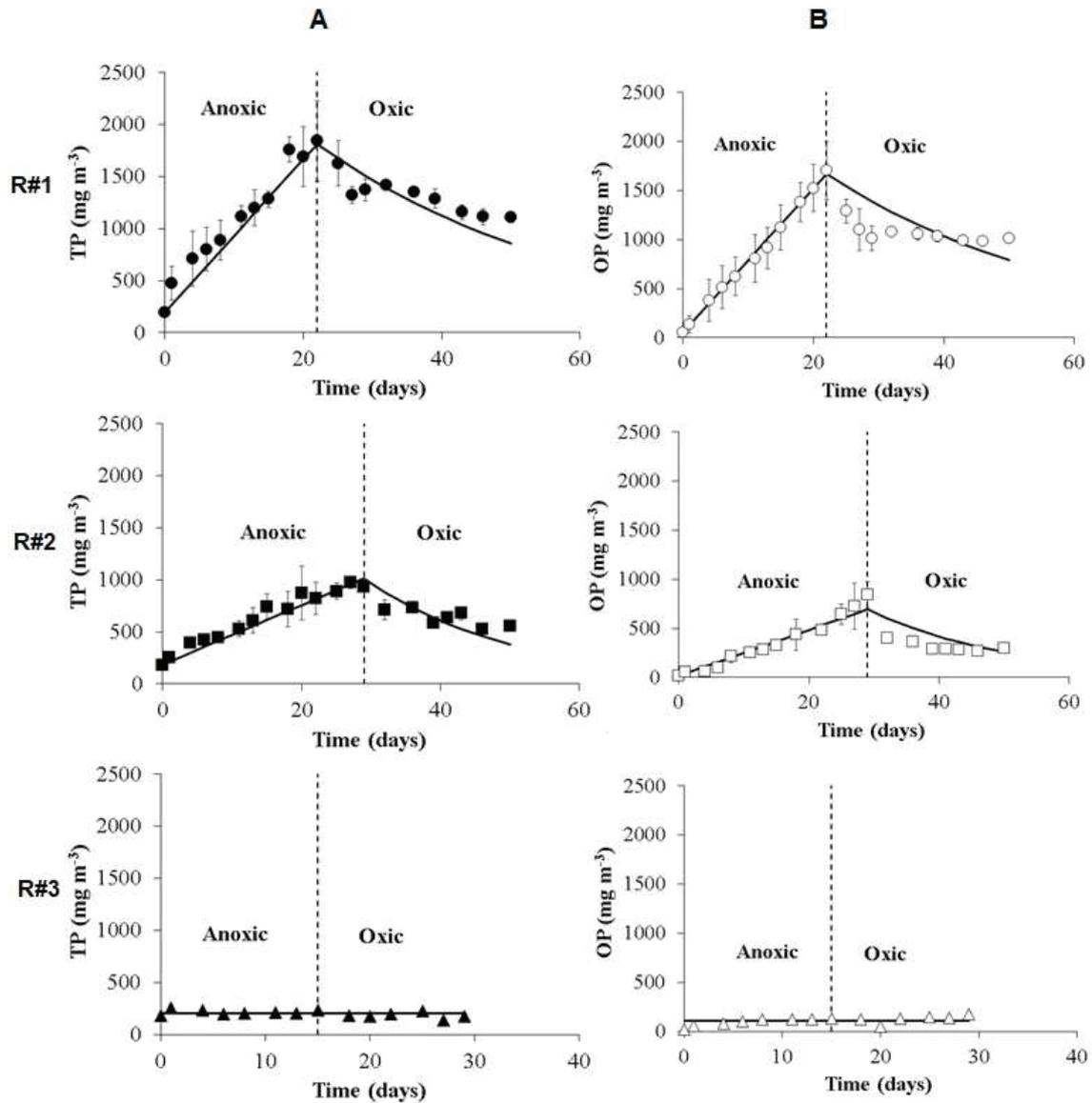
377 The model fit (Eqs. 3 and 4 presented at the Materials and Methods section) to the TP  
 378 and OP experimental data resulted in the release coefficients  $k_r$  of 11.0 and 4.0 mg m<sup>-2</sup>  
 379 day<sup>-1</sup> and in the precipitation coefficients  $k_s$  of 0.004 and 0.07 m day<sup>-1</sup> for microcosms  
 380 R#1 and R#2, respectively (table 6 and figure 7). Note that the same  $k_r$  and  $k_s$  values  
 381 were used for adjusting the data of TP and OP for each microcosm, resulting in  
 382 coefficients of determination ( $R^2$ ) ranging from 0.770 to 0.973 for TP and from 0.540 to  
 383 0.995 for OP. This may indicate that the exchange rates between sediment and water  
 384 were well represented by zero- and first-order models, respectively, as proposed by

385 Larsen et al. (1979) and Ruley and Rusch (2004). Furthermore, it suggests that the  
 386 models can be used to simulate the release and precipitation of P in tropical semiarid  
 387 reservoirs. It is also important to note that the adjusted values of P exchange rates  
 388 obtained for microcosms R#1 and R#2 were lower than those summarized by Ruley and  
 389 Rusch (2004). This probably occurred because, here, we avoided sediment resuspension  
 390 and growth of photosynthetic organisms in the experimental chambers, potentially  
 391 reducing the  $k_r$  and  $k_s$  values, respectively. Contrastingly to the above-mentioned trends  
 392 for the anoxic and oxic stages in R#1 and R#2, the microcosm R#3 did not present any  
 393 clear trend over time, and the  $k_r$  and  $k_s$  values were considered zero (table 6 and figure  
 394 7). Observe that the  $k_r$ -values decreased from R#1 to R#3, as the available P fractions in  
 395 the sediment also decrease accordingly (figure 5). On the other hand, the  $k_s$ -values were  
 396 higher for R#2, which suggests that reservoirs with high available P fractions, such as  
 397 R#1, not only release more P but also present a lower precipitation rate of P, resulting in  
 398 higher potential impacts on water quality than R#2 and R#3.

399 Table 6. Fitted phosphorus release and precipitation rates obtained in the present study compared with the  
 400 ranges reported in the literature.

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

401



402  
403 Figure 7. Model Fit to the experimental data of TP (A) and OP (B) during the anoxic and oxic phases for  
404 each reservoir sediment.  
405

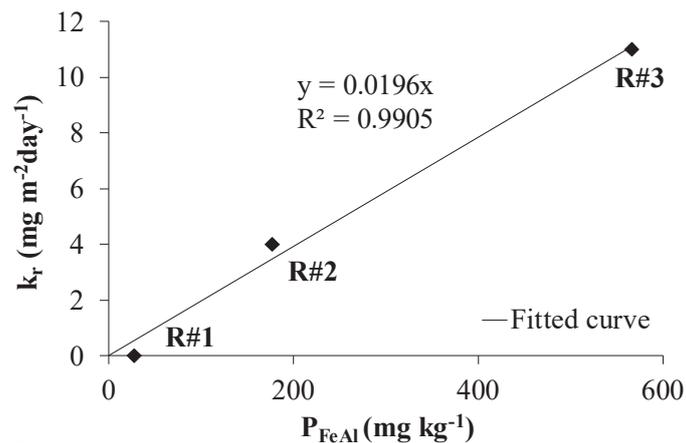
406 Figure 8 shows the fitting of the adjusted values of  $k_r$  (table 6) to the  
407 concentration of  $P_{FeAl}$  for each microcosm (R#1, R#2 and R#3). It is clearly seen that  $k_r$   
408 can be linearly related to  $P_{FeAl}$ :

$$409 \quad k_r = 0.0196 (P_{FeAl}) \quad (6)$$

410  
411 where  $k_r$  and  $P_{FeAl}$  are given in  $\text{mg m}^{-2} \text{day}^{-1}$  and  $\text{mg kg}^{-1}$ , respectively.

412 As already discussed, the dominant fraction for P release from sediments ( $P_{FeAl}$ )  
413 is also linearly related to reservoir age by equation 5 (figure 3). Thus, as the reservoirs

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



424  
 425  
 426  
 427

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

#### 428 4. Conclusions

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

#### 450 5. Acknowledgments

451 This research was funded by Financier of Studies and Projects - FINEP [01.14.0130.00-  
452 1107/13 MCTI/FINEP/CT- HIDRO-01/2013], by the Coordination for the Improvement

453 of Higher Education Personnel - CAPES [Research Grant PROEX 20/2016], by Ceará  
454 State Research Foundation - FUNCAP [PNE-0112-00042.01.00/16], and by Brazilian  
455 National Research Council – CNPq [403116/2016-3].

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**Highlights:**

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

## **1. 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.

**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Journal Pre-proof

Meeting the prerequisites  
Do not meet prerequisites

# TP

	Model	Anoxic										Oxic									
		Shapiro - Wilk	r	Variables	Est. [IC(95%)]	t test	R <sup>2</sup>	Adj R <sup>2</sup>	Model Diagnostics			Shapiro - Wilk	r	Est. [IC(95%)]	t test	R <sup>2</sup>	Adj R <sup>2</sup>	Model Diagnostics			
									F-statistic		NR							F-statistic		NR	
								Model	Var. residues	NR							Model	Var. residues	NR		
R#1	Model	p = 0.771	0.98 (p < 0.001)	Intercept Day	339.3 [226.1 - 452.5] 69.8 [61.0 - 78.5]	p < 0.001 p < 0.001	0.97	0.97	p < 0.001	p = 0.849	p = 0.992	p = 0.309	-0.89 (p = 0.006)	1908.9 [1547.3 - 2270.7] -16.9 [-26.6 - 7.1]	p < 0.001 p < 0.001	0.8	0.76	p = 0.001	p = 0.193	p = 0.920	
	Graphical Analysis																				
R#2	Model	p = 0.437	0.98 (p < 0.001)	Intercept Day	251.8 [195.9 - 307.7] 26.4 [23.1 - 29.7]	p < 0.001 p < 0.001	0.96	0.95	p < 0.001	p = 0.140	p = 0.302	p = -0.416 (p = 0.017)	-0.8 (p = 0.017)	1053.6 [723.6 - 1383.5] -10.8 [-19.0 - (-2.7)]	p < 0.001 p = 0.017	0.64	0.58	p = 0.017	p = 0.947	p = 0.407	
	Graphical Analysis																				
R#3	Model	p = 0.727	-0.03 p = 0.939	Intercept Day	215.1 [177.1 - 253.1] -0.1 [-4.4 - 4.1]	p < 0.001 p = 0.94	0.001	-0.16	p = 0.939	p = 0.191	0.788	p = 0.746 (p = 0.7327)	-0.18 (p = 0.7327)	209.7 [-6.1 - 425.6] -1.2 [-10.3 - 7.9]	p = 0.054 p = 0.733	0.03	-0.2	p = 0.733	p = 0.173	p = 0.780	
	Graphical Analysis																				

Meeting the prerequisites  
Do not meet prerequisites

# OP

	Model	Anoxic										Oxic									
		Shapiro - Wilk	r	Variables	Est. [IC(95%)]	t test	R <sup>2</sup>	Adj R <sup>2</sup>	F-statistic		NR	Shapiro - Wilk	r	Est. [IC(95%)]	t test	R <sup>2</sup>	Adj R <sup>2</sup>	F-statistic		NR	
									Model	Var. residues								Model	Var. residues		
R#1	Graphical Analysis																				
	Model	p = 0.776	0.99 (p < 0.001)	Intercept Day	50.2 [0.8 - 99.7] 73.0 [69.2 - 76.8]	p = 0.047 p < 0.001	0.99	0.99	p < 0.001	p = 0.074	p = 0.302	p = 0.119	-0.63 (p = 0.047)	1344.3 [1077.5 - 1611.1] -7.1 [14.3 - (-0.1)]	p < 0.001 p = 0.047	0.4	0.33	p = .047	p = 0.194	p = 0.758	
R#2	Graphical Analysis																				
	Model	p = 0.255	0.94 (p < 0.001)	Intercept Day	<b>-29.6 [-126.8 - 67.4]</b> 25.5 [ 19.8 - 31.2]	<b>p = -0.520</b> p < 0.001	0.88	0.87	p < 0.001	<b>p = 0.006</b>	<b>p = 0.001</b>	p = 0.129	<b>-0.349</b> (p = 0.396)	428.8 [133.5 - 724.1] <b>-2.72 [-10.0 - 4.5]</b>	p = 0.012 <b>p = 0.396</b>	0.12	-0.02	<b>p = 0.396</b>	p = 0.997	p = 0.086	
R#3	Graphical Analysis																				
	Model	p = 0.168	0.92 p = 0.001	Intercept Day	45.6 [19.9 - 71.2] 6.7 [3.8 - 9.6]	p < 0.001 p < 0.001	0.84	0.82	p < 0.001	p = 0.733	p = 0.82	p = 0.284	<b>0.72</b> (p = 0.107)	<b>-38.3 [-263.2 - 186.5]</b> <b>7.0 [-2.4 - 16.5]</b>	<b>p = 0.661</b> <b>p = 0.107</b>	0.51	0.4	<b>p = 0.122</b>	p = 0.82	p = 0.826	