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Grazielle Nascimento-Silva, Gabriela B Oliveira, Christiene R.L. Matos, Edouard Metzger, Christian J Sanders, et al. Phosphate buffering in mangrove sediment pore water under eutrophication and deforestation influences. *Marine Pollution Bulletin*, 2024, 201, pp.116130. 10.1016/j.marpolbul.2024.116130 . hal-04469670

**HAL Id: hal-04469670**

**<https://nantes-universite.hal.science/hal-04469670v1>**

Submitted on 6 Jan 2025

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# Phosphate buffering in mangrove sediment pore water under eutrophication and deforestation influences

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## ARTICLE INFO

### Keywords:

Pore water phosphate  
Eutrophication  
Mangroves  
Net consumption rates  
Mangrove deforestation  
Nutrient sinks

## ABSTRACT

Phosphorus (P) behavior was evaluated in mangrove wetlands impacted by urban sewage, including a deforested site. Sediment cores were analyzed for grain size, organic carbon, total nitrogen, stable isotopes ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ), P contents, and pore water  $\text{PO}_4^{3-}$  concentrations and net consumption/production rates. Under stronger eutrophication influence, significantly higher P (1390 vs. <1000  $\mu\text{g/g}$ ),  $\delta^{15}\text{N}$  (8.9 vs. <6.7 ‰) and algal material contents (with lower C/N ratio and heavier  $\delta^{13}\text{C}$ ) occurred. Depth-integrated  $\text{PO}_4^{3-}$  consumption rates in eutrophicated sites were up to two orders of magnitude higher (at the deforested site) than in a moderately preserved mangrove. The whole core of the moderately preserved site presented no saturation of  $\text{PO}_4^{3-}$  buffering capacity, while more eutrophicated sites developed buffering zones saturated at ~18–26 cm depth. Contrasting to nearby subtidal environments, eutrophication did not cause larger pore water  $\text{PO}_4^{3-}$  concentration, evidencing the role of  $\text{PO}_4^{3-}$  buffering on P filtering by mangrove wetlands.

## 1. Introduction

The coastal zones are experiencing anthropogenic pressures that increase nutrient loadings and affect trophic states, including those areas that host ecologically and socioeconomically important coastal vegetated ecosystems, such as mangrove wetlands at low latitudes (Saenger et al., 2008; Southwell et al., 2010; Lacerda et al., 2021). The main nutrients that cause eutrophication are nitrogen (N) and phosphorus (P), which are mostly derived from untreated sewage, fertilizers, and livestock, causing pollution of aquatic environments, the excessive growth of primary producers, and large changes in biogeochemical processes (Richardson and Jørgensen, 1996; Kitsiou and Karydis, 2011; Duarte and Krause-Jensen, 2018).

In mangrove sediments affected by anthropogenic nutrient loading, P accumulation rates can be up to one order of magnitude higher than in pristine sites (Pérez et al., 2021). Because these sediments are efficient P sinks, they are often used to evaluate specific types of historical impacts

over time (Borges et al., 2009; Pérez et al., 2017, 2020). However, this is not the case for N, since mangroves can act as a N sink or source, especially regarding dissolved N forms and denitrification process, as a result of the high availability of sediment organic substrates (Adame and Lovelock, 2011; Reis et al., 2017; Wang et al., 2019). Less is known, however, about the diagenetic nutrient behavior in mangrove sediment pore water as a response to anthropogenic pressures, such as sewage-induced eutrophication, which likely affects the nutrient retention capacity of mangrove sediments. This nutrient retention capacity influences the migration of dissolved nutrients at the sediment-water interface and its potential contribution to determine coastal trophic states, as has been observed in other coastal environments (Rozan et al., 2002; Zilius et al., 2015; Matos et al., 2016).

Indeed, the study of pore water composition can contribute to better understand key mechanisms involved in determining the biogeochemical processes of sedimentary systems, which may not be detected in the sediment solid phase alone. Better knowledges of these mechanisms may

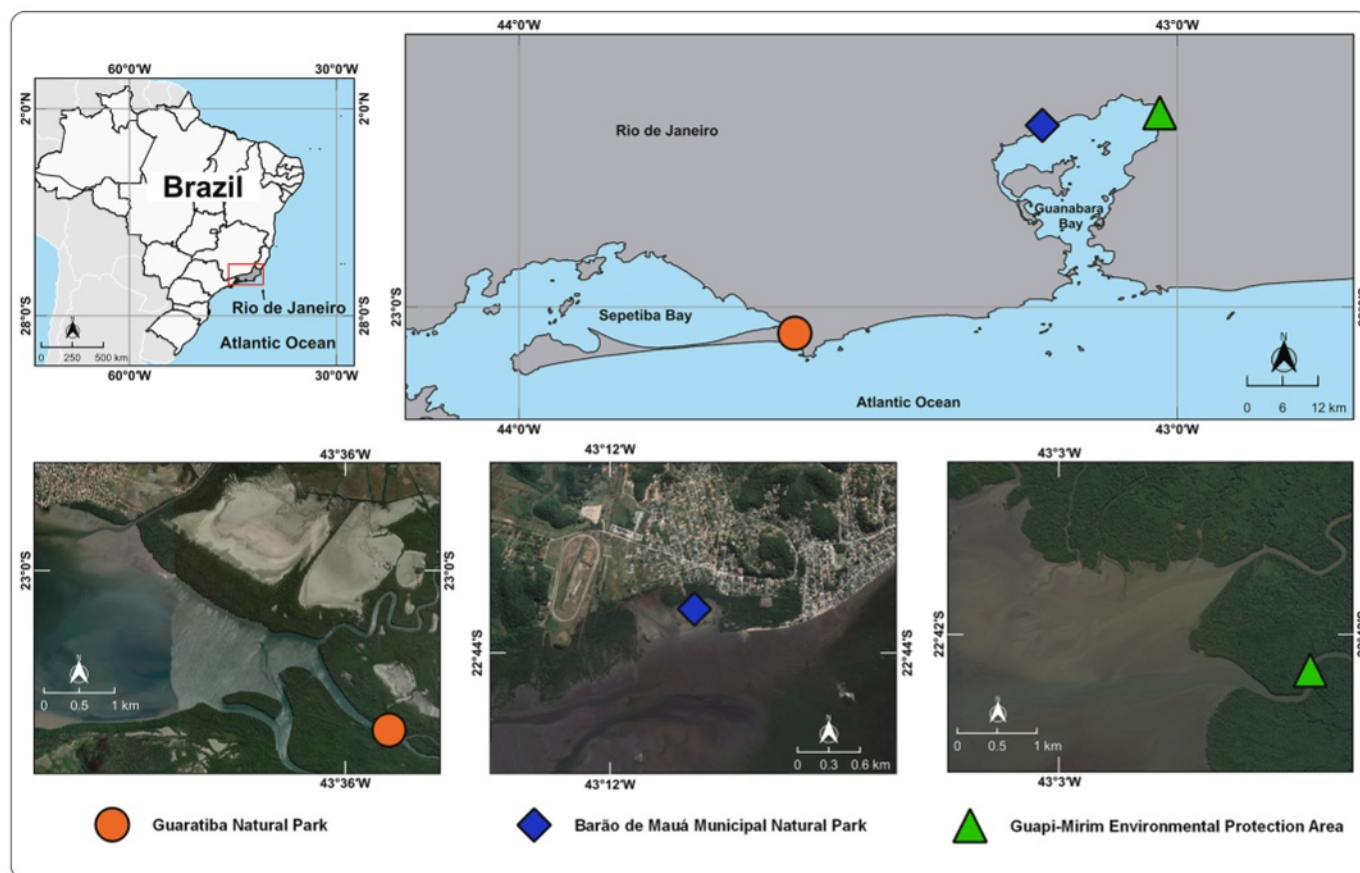


Fig. 1. Location of the mangrove highly eutrophicated (Guaratiba Natural Park, Sepetiba Bay), deforested eutrophicated (Barão de Mauá Municipal Natural Park, Guanabara Bay) and moderately preserved (Guapi-Mirim Environmental Protection Area, Guanabara Bay).

assist in improving our understanding of early diagenesis (Bernier, 1980; Schultz and Zabel, 2006). However, biogeochemical processes are difficult to be assessed in mangrove wetlands, since the concentration of dissolved pore water chemical species can be modified by multiple factors, such as microbial activity, sedimentation/erosion balance, chemical reactions with inorganic and organic matter, plant cover and the presence of a rhizosphere, and bioturbation effects on redox conditions, among other spatial and temporal factors (McKee, 1993; Alongi et al., 2004; Schultz and Zabel, 2006).

Phosphorus from natural or anthropogenic sources can be transported into mangrove environments by tides, in organic and inorganic forms (Jahnke, 1992). In mangroves, this nutrient is typically retained adsorbed on mineral phases of fine-grained sediment or incorporated in the sedimentary organic matter itself (Alongi et al., 1992). To assist in identifying sources of organic matter, carbon and nitrogen isotopic signatures ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) are frequently used (Sanders et al., 2016; Koszelnik et al., 2018). In this sense, the total organic carbon to total nitrogen ratio (C/N) and the stable isotopes signature of organic carbon ( $\delta^{13}\text{C}$ ) can indicate allochthonous and autochthonous sources of organic matter (Meyers, 1994, 1997), while the coastal eutrophication can concurrently affect the sedimentary  $\delta^{15}\text{N}$  signals, which also contributes to evaluate the anthropogenic fertilization effects on organic matter quality and sources in combination with  $\delta^{13}\text{C}$  and C/N ratios (Monteiro et al., 2012; Sanders et al., 2014; Barroso et al., 2022; Chynel et al., 2022).

As an important net effect of these multiple factors associated with eutrophication, the availability of phosphate ( $\text{PO}_4^{3-}$ ) in pore water that may be transported, incorporated by organisms, or even lost to overlying water, will be dependent on the sediment capacity of buffering these  $\text{PO}_4^{3-}$  concentrations (Falcão et al., 2006). This buffering effect of solid

particles on dissolved  $\text{PO}_4^{3-}$  is mainly attributed to sorption processes onto metal (hydr)oxides, of which occurs both in surface waters (Conley et al., 1995) and pore water (Slomp et al., 1996) along coastal systems. Therefore, a pore water  $\text{PO}_4^{3-}$  “buffering zone” may be found in an area of low concentrations at specific depth intervals, controlled by sorption-desorption equilibria and pore water transport (Sundby et al., 1992). The production rate of  $\text{PO}_4^{3-}$ , the buffering capacity of the sediment, and the thickness of the diffusive boundary layer at the sediment-water interface control the shape of the pore-water profile and the  $\text{PO}_4^{3-}$  cycling across this interface (Sundby et al., 1992).

Two main processes are generally responsible for regulating the behavior of dissolved P along the water-sediment interface: sorption/desorption reactions between sediment solid phase and pore water, and diffusive and convective movements of pore water and overlying water (Nichols, 1983; Lai and Lam, 2008). As observed for other coastal environments, it is well known that eutrophication can considerably modify the redox conditions in the first decimeters of the sediments. Indeed, the variability of redox conditions can affect metal (hydr)oxides that retain P in the sediment solid phase, influencing the spatial and temporal variability in the sediment capacity of buffering pore water  $\text{PO}_4^{3-}$  within upper layers and its exchanges across the water-sediment interface (Metzger et al., 2007). Concurrently, a decrease in benthic fauna activity due to anoxia would decrease the production of metal (hydr)oxides by bioturbation, also limiting the buffering effect on dissolved P (Zilius et al., 2015).

Therefore, it is expected that the variability in the degree of coastal eutrophication can affect the importance of this buffering effect as a factor in determining the P cycling near the water-sediment interface. However, despite the known role of mangrove sediments as nutrient sinks, the dimensioning of pore water  $\text{PO}_4^{3-}$  buffering capacity (i.e.,



buffering zone development and  $\text{PO}_4^{3-}$  consumption rates within these zones) have not been previously estimated for mangroves impacted by differing degrees of eutrophication and other major anthropogenic impacts. For example, mangrove deforestation is known as a factor that allows stronger susceptibility to erosion and loss of sediment constituents, affecting the sediment capacity to retain inorganic and organic matter and associated elements (Pérez et al., 2017). This is increasingly relevant considering the estimates that at about 0.7–3.0 % of the mangrove areas lost per year at a worldwide scale (Pendleton et al., 2012), despite their ecological and socioeconomic roles (Alongi, 2002; Ferreira and Lacerda, 2016).

This study combines an evaluation of sedimentary characteristics along a gradient of anthropogenic impacts in three contrasting mangrove areas (i.e., highly eutrophicated, deforested eutrophicated and moderately preserved) within two tropical bays in south-eastern Brazil, contributing to better understanding the processes controlling the role of mangrove ecosystems as P sinks. Our aim was to test the effects of different degrees of coastal eutrophication and mangrove deforestation on net rates of  $\text{PO}_4^{3-}$  production and consumption in mangrove sediment pore waters along short vertical profiles (~30 cm depth), and their relationships with total organic carbon (TOC), total nitrogen (TN), total sediment phosphorus (TP), and carbon and nitrogen isotopes ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ).

## 2. Materials and methods

### 2.1. Study sites

The Guanabara and Sepetiba Bays (Rio de Janeiro State, SE Brazil; Fig. 1) and their fringing mangroves have shown a well-documented degradation history during the past few decades (Kjerfve et al., 1997; Molisani et al., 2004; Soares-Gomes et al., 2016), including the losses of mangrove plant cover combined with the pollution of remaining mangrove areas (Borges et al., 2009; Araújo et al., 2017; Pérez et al., 2018), considering that both drainage basins are among the most industrialized and urbanized coastal regions in Brazil. These degradation effects occur despite this region present several Marine Protected Areas (MPAs) that aims to preserve the remaining mangroves, such as those sampled in this study, which possibly imply in losses of mangrove ecosystems functions and environmental services, particularly in the cases of mangrove forest removal (Nascimento-Silva et al., 2021). For these two bays, previous studies on pore water  $\text{PO}_4^{3-}$  were dedicated only to subtidal environments, indicating  $\text{PO}_4^{3-}$  mobilization to pore water under eutrophicated conditions associated to a more intense sulfate reduction respiration pathway (i.e.,  $\text{PO}_4^{3-}$  release from the organic matter decomposition, besides the desorption from metal (hydr)oxides; Matos et al., 2016). However, substantial differences can be expected to occur for the intertidal mangrove sediments along the bays.

Encompassing different degrees of anthropogenic fertilization impacts, we compared here a highly impacted mangrove in Sepetiba Bay (located at the Guaratiba Natural Park) and two mangroves in Guanabara Bay, located at the Barão de Mauá Municipal Natural Park (impacted deforested mangrove) and Guapi-Mirim Environmental Protection Area (moderately preserved mangrove), as indicated in the Fig. 1. These contrasting conditions between sites were previously characterized for surface sediments. As demonstrated by fatty acid markers (Chynel et al., 2022), isotopic ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) signatures (Barroso et al., 2022; Chynel et al., 2022), sterol markers and even increased  $\text{CO}_2$  emissions to the atmosphere (Barroso et al., 2022), there is greater sewage and algal material input to Guaratiba site compared to Guapi-Mirim site, which is consistent with the urbanization differences in the drainage basins and the associated urban sewage loadings to these sites (Barroso et al., 2022).

Organic P contents have been used as proxy for eutrophication effects in the three sites, with the Guaratiba mangrove presenting significantly higher values than the Guapi-Mirim mangrove (Barroso et al.,

2022), while the deforested site at Barão de Mauá mangrove is affected by a heavily urbanized drainage basin (Borges et al., 2009) and reached organic P values in surface sediments (Pérez et al., 2018) close to those found in Guapi-Mirim. In addition to the impacts of untreated effluents that caused increased P concentrations and accumulation rates in Barão de Mauá site, it experienced mangrove deforestation for urban expansion nearly three decades before sampling (Borges et al., 2009; Pérez et al., 2018).

These contrasting coastal regions, therefore, offer opportunity to improve the understanding on the biogeochemistry of coastal sediments under different levels of anthropogenic pollution influence. These previous studies observed contrasts in relation to the composition of top sediment layers in mangrove wetlands from the two bays considered in the present study, however, they were performed without testing the vertical variability responses to the identified eutrophication gradient in relation to sediment solid phase and pore water compositions.

### 2.2. Sediment and pore water sampling and analyses

The three study areas were sampled during low tide in May (Barão de Mauá), October (Guapi-Mirim) and December (Guaratiba), 2018. At each one, two sediment cores were collected by using acrylic tubes (50 cm in length,  $\varnothing = 8$  cm). After collection, the cores were transported to a field laboratory next to the collection area for further treatment and analysis. For pore water extraction at different depths, one of the cores from each site was kept vertical and pore water samples were extracted and filtered using a Rhyzon® system (Seeberg-Elverfeldt et al., 2005) attached to a 20 mL syringe. To avoid oxidation, the syringes were removed, closed, and placed inside the glove bag under an  $\text{N}_2$  atmosphere, for further porewater sub-sampling. For solid-phase analysis, the second core sampled from each site was sectioned at 1-cm depth resolution. A fraction of the sediment was stored in polyethylene tubes for analysis of grain size, TOC, NT, P,  $\delta^{13}\text{C}$ , and  $\delta^{15}\text{N}$ . Sediment samples were stored frozen and freeze dried before analysis.

Solid phase P and dissolved  $\text{PO}_4^{3-}$  concentrations were determined spectrophotometrically, according to Grasshoff et al. (1999). Solid phase analysis of lyophilized and homogenized sediment subsamples followed the extraction procedures from Aspila et al. (1976). The extractions were performed by agitation in 1 M hydrochloric acid solution to obtain the inorganic P (IP) fraction. Total phosphorus (TP) extractions were performed by the same procedure but preceded by sample ignition in a muffle at 450 °C for 4 h. Organic phosphorus (OP) was calculated by the difference between TP and IP. The analysis was performed using a wavelength of 880 nm in a Thermo Scientific Genesys UV-vis spectrophotometer. The PACS-3 certified reference material was also used to assess the accuracy of the analytical method and applicability of the calibration curves.

For the analysis of the elemental and isotopic composition of organic matter, subsamples of lyophilized sediments were macerated and decarbonated (through acidification with 1 M hydrochloric acid) and encapsulated to determine concentrations and isotope ratios of TOC. For TN, non-decarbonated subsamples were used. Concentrations and isotope ratios were determined in an elemental analyzer coupled to an isotope ratio mass spectrometer (IRMS), at Southern Cross University, Australia.

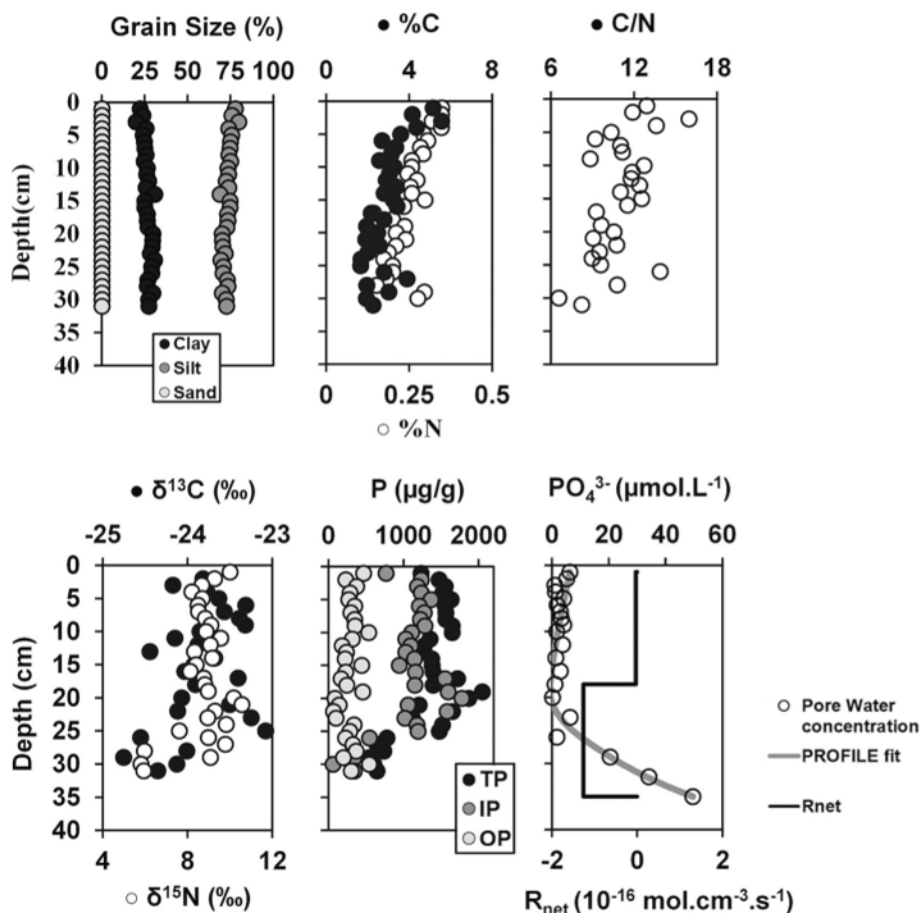
The grain size analysis was performed after removing the carbonate and organic matter from the samples. A particle size meter CILAS model 1064 was used, after sample disaggregation by agitation in a  $\text{Na}_4\text{P}_2\text{O}_7$  solution. Grain size parameters were calculated using the GRADISTAT software.

The diffusion-based computer code PROFILE (Berg et al., 1998) was applied for modeling the  $\text{PO}_4^{3-}$  concentrations. The diffusion coefficient used was obtained from the study of Li and Gregory (1974). The interpretation of the data is through the zero-order rates of production or consumption of interstitial water concentration (Rnet) that can vary from negative values (consumption) to positive values (production)

**Table 1**

Median, minimum, and maximum values of compared mangrove sites. Medians showing different superscript letters correspond to statistically significant differences (Kruskal-Wallis test,  $p < 0.05$ ).

Site		Clay (%)	Silt (%)	Sand (%)	TN (%)	TOC (%)	C/N	$\delta^{15}\text{N}$ (‰)	$\delta^{13}\text{C}$ (‰)	TP ( $\mu\text{g/g}$ )	IP ( $\mu\text{g/g}$ )	OP ( $\mu\text{g/g}$ )	$\text{PO}_4^{3-}$ ( $\mu\text{M}$ )
Guaratiba	<b>Median</b>	26.5 <sup>a</sup>	73.5 <sup>a</sup>	0	0.26 <sup>a</sup>	2.80 <sup>a</sup>	11.0 <sup>a</sup>	8.9 <sup>a</sup>	-23.9 <sup>a</sup>	1393 <sup>a</sup>	1149 <sup>a</sup>	289 <sup>a</sup>	3.1 <sup>a</sup>
	Min.	20.1	69.1	0	0.14	1.67	6.58	5.8	-25.1	540	60.9	65.3	0.1
	Max.	30.9	80.0	0	0.40	5.55	20.1	10.6	-22.7	2046	1780	544	49.6
Barão de Mauá	<b>Median</b>	11.5 <sup>b</sup>	88.4 <sup>b</sup>	0	0.35 <sup>b</sup>	5.61 <sup>b</sup>	16.0 <sup>a,b</sup>	6.6 <sup>b</sup>	-24.5 <sup>a,b</sup>	996 <sup>b</sup>	427 <sup>b</sup>	535 <sup>b</sup>	5.4 <sup>a,b</sup>
	Min.	8.6	85.7	0	0.33	4.91	6.42	6.3	-25.0	302	157	85.9	0.1
	Max.	14.3	91.4	0.2	0.46	6.49	18.8	8.2	-24.3	1466	683	783	235
Guapi-Mirim	<b>Median</b>	17.6 <sup>c</sup>	82.2 <sup>c</sup>	0	0.42 <sup>b</sup>	7.07 <sup>c</sup>	16.8 <sup>b</sup>	6.1 <sup>b</sup>	-26.4 <sup>b</sup>	815 <sup>b</sup>	702 <sup>c</sup>	94 <sup>c</sup>	10.7 <sup>b</sup>
	Min.	12.5	77.4	0	0.20	6.31	12.7	4.5	-27.1	584	521	27.6	0.3
	Max.	22.6	85.8	4.2	0.50	7.82	34.6	10.2	-26.0	1339	1243	464	26.2



**Fig. 2.** Sediment grain size, geochemical properties and pore water modeling of Guaratiba (highly eutrophicated).

(Berg et al., 1998). This modeling allows the separation of results into vertical zones, dimensioning the diagenetic process per zone, generating Rnet estimates integrated by depth.

### 2.3. Statistical analysis

The physical and geochemical parameters in each sampling site did not show normal distribution, according to the Shapiro-Wilk normality test ( $p > 0.05$ ) even after transformations. Accordingly, significant differences between the three sites GNP, BM and GM were assessed using the non-parametric Kruskal-Wallis test at a significance level  $p < 0.05$ . All statistical tests were performed using the Statistica® software, version 12, while graphs were produced using the software Microsoft Excel®.

### 3. Results and discussion

A statistical comparison of median sediment characteristics of the different areas is presented in Table 1, while depth profiles are presented in Figs. 2–4. The sediments were essentially composed of silt, with comparatively low clay and negligible sand contents. The highly impacted site (Guaratiba) had significantly higher clay and lower silt contents. These fine-grained sediments also presented larger median TP compared to others, consistent with a higher sewage input expected for this site (Barroso et al., 2022). In turn, a large predominance of IP fractions was found in Guaratiba and Guapi-Mirim (Figs. 2 and 4), although IP and OP have shown similar concentrations in the site Barão de Mauá (Fig. 3). Nevertheless, deforestation can also affect the geochemical partitioning of P, considering that the input of organic matter is affected by plant cover removal (Pérez et al., 2018). An



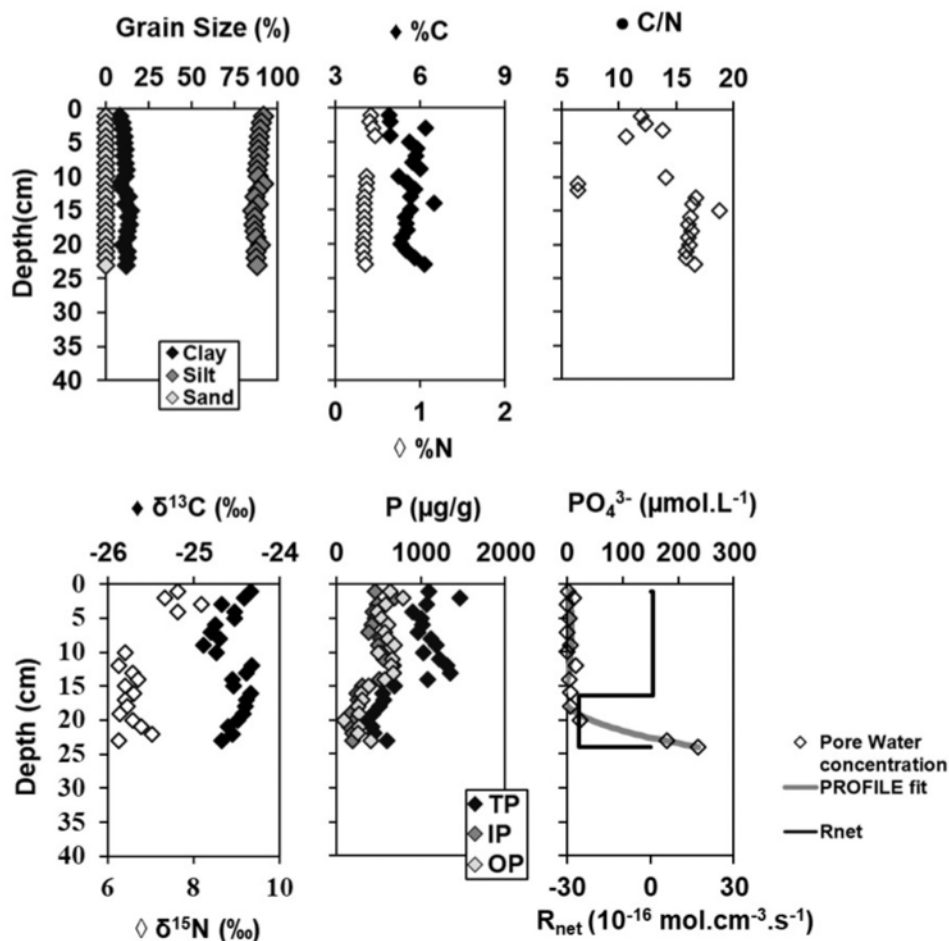


Fig. 3. Sediment grain size, geochemical properties and pore water modeling of Barão de Mauá (deforested eutrophicated).

expected initial consequence is the increased relative contribution of fallen mangrove tree materials in comparison with algal organic matter input, whereas new local production of mangrove organic matter is interrupted, favoring a subsequent higher algal relative contribution. However, these changes are probably combined with a large OP deposition fueled by eutrophication, which may affect both algal and mangrove organic matter depositions (Sanders et al., 2014) and may contribute to explain the significantly larger OP concentrations observed in this deforested site (Fig. 3).

A significantly heavier median  $\delta^{15}\text{N}$  value was also found in the most eutrophicated site in comparison with less eutrophicated conditions (Table 1). These observations confirm the previous conclusions that the Guaratiba mangrove is strongly impacted by eutrophication due to a connection to a densely urban watershed, associated with large discharges of untreated wastewaters (Barroso et al., 2022; Chynel et al., 2022). The TOC and TN concentrations were significantly lower in this area, due to a greater input of suspended mineral materials derived from anthropogenically enhanced land erosion (Borges and Nittrouer, 2016), as can be observed in the Fig. 5. This comparison suggests that only the Guapi-Mirim site is relatively preserved from anthropogenic sources, which affected most of the parameters within the sediments from the mangrove highly impacted. In turn, the deforested site apparently suffers from an intermediate anthropogenic influence, generally presenting results closer to those of site highly impacted, with a higher algal contribution indicated by a significantly lower C/N and slightly heavier  $\delta^{13}\text{C}$  (Meyers, 1994, 1997).

Aquatic sediments can play an important role as P sinks. However, these ecosystems may also become a source of P to the aquatic environments depending on the physical-chemical properties of sediments

and overlying water (Richardson, 1985; Deborde et al., 2008). In this way, mangrove sediments may be a sink for solid phase P related to the high sorption capacity of the typical fine-grained texture, while their pore water  $\text{PO}_4^{3-}$  buffering efficiency can limit the P export by pore water exchanges with overlying and surrounding waters. Our findings indicate the presence of large  $\text{PO}_4^{3-}$  buffering zones with very low concentrations in porewaters (~18–26 cm depth; Figs. 2 and 3) at the two more eutrophicated sites in comparison with smaller buffering zones found for subtidal coastal sedimentary environments elsewhere (i.e., of only few centimeters; e.g., Sundby et al., 1992; Slomp et al., 1996), and even in sediments of the same two tropical bays studied (Wagener et al., 1988; Matos et al., 2016). These differences may also be affected by the temporal variability in the physicochemical and geochemical conditions of the sediments (e.g., controlling the production and preservation of metal (hydr)oxides that retain P and the oxidation of organic matter that releases P), which can affect the pore water  $\text{PO}_4^{3-}$  variability with depth and between sites (Metzger et al., 2007; Matos et al., 2022).

On the other hand, the buffering zone of the Guapi-Mirim moderately preserved site occurred along the whole core, only presenting relatively low  $\text{PO}_4^{3-}$  concentrations oscillations with depth (Fig. 4). The  $\text{PO}_4^{3-}$  concentrations ranged from 0.11 and 6.4  $\mu\text{M}$  in the Guaratiba buffering zone (highly impacted), 0.11 and 23.8  $\mu\text{M}$  in the buffering zone of Barão de Mauá (impacted deforested) and 0.31 and 26.2  $\mu\text{M}$  in along the entire Guapi-Mirim (moderately preserved) depth profile. The  $\text{PO}_4^{3-}$  concentrations trends suggest that the sediment solid phase buffering capacity was not saturated in Guapi-Mirim (Fig. 4), whereas variable buffering saturation depths were found for the other sites, resulting in deepest layers that concentrate dissolved  $\text{PO}_4^{3-}$  in porewater (Figs. 2 and 3).

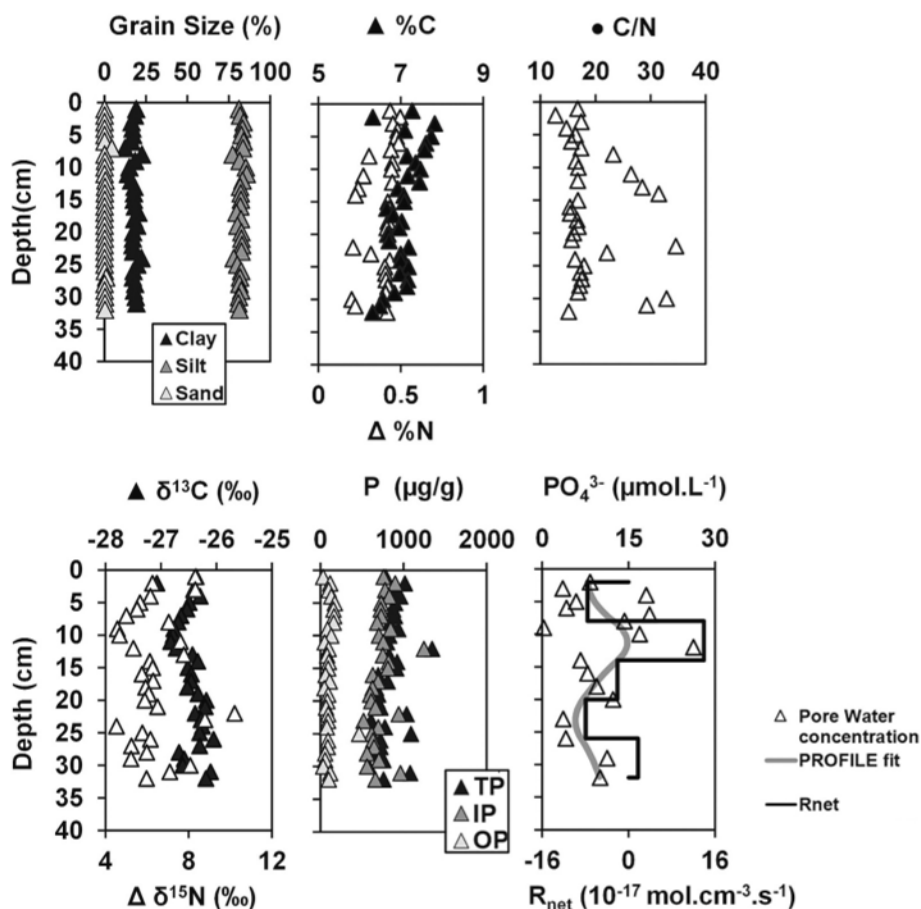


Fig. 4. Sediment grain size, geochemical properties and pore water modeling of Guapi-Mirim (moderately preserved).

In relation to PROFILE modeling of  $\text{PO}_4^{3-}$  production and consumption rates (i.e., net rates involving biologically, physically and chemically mediated processes governing the modeled concentration gradients), Figs. 2–4 demonstrate that only  $\text{PO}_4^{3-}$  consumption was found at Guaratiba and Barão de Mauá eutrophicated sites. The moderately preserved Guapi-Mirim mangrove presented alternation between consumption (dominating the 0–8 cm depth interval and below 14 cm depth) and production (within the 8–14 cm depth interval), with a net predominant consumption. We found net consumption rates (expressed in  $\text{mol cm}^{-2} \text{s}^{-1}$ ) following the following order: Barão de Mauá, deforested ( $-1.81 \times 10^{-14}$ ) > Guaratiba, highly eutrophicated ( $-1.76 \times 10^{-15}$ ) > Guapi-Mirim, moderately preserved ( $-1.11 \times 10^{-16}$ ), for the integration of whole depth profiles. The different  $\text{PO}_4^{3-}$  buffering capacity of mangrove sediments from more eutrophicated sites resulted in Rnet values one or two orders of magnitude above that estimated for Guapi-Mirim, evidencing that mangrove sediments under eutrophicated conditions buffered efficiently pore water  $\text{PO}_4^{3-}$ , which is dependent on the depth of buffering capacity saturation and the intensity of the buffering effect within the non-saturated buffering zone.

Dissolved  $\text{PO}_4^{3-}$  is released into the interstitial water mainly due to the process of degradation of organic matter and/or during the reduction of iron oxides (Ruttenberg and Berner, 1993; Sun et al., 2021). In the Guaratiba and Barão de Mauá eutrophicated sites, the pore water  $\text{PO}_4^{3-}$  enrichment zones in deeper layers are nearly concurrent with the zones of P impoverishment in the solid phase (Figs. 2 and 3). This can be possibly explained by the degradation of organic matter and metal (hydr)oxides in deeper sediment layers, releasing the P previously retained by the solid phase (e.g., Slomp et al., 1996; Rozan et al., 2002), thus contributing to define the limits of the buffering zones compared in the Figs. 2–4.

Eutrophication was not found to be a factor resulting in larger accumulation of pore water  $\text{PO}_4^{3-}$  within the studied mangrove sediments, differently from nearby subtidal environments (Matos et al., 2016). For example, a more eutrophicated subtidal site in Guanabara Bay (Jurujuba Sound) promoted more pore water  $\text{PO}_4^{3-}$  remobilization, small buffering zone and larger diffusion to overlying water than a less eutrophicated subtidal site in Sepetiba Bay (Coroa Grande Sound), which was associated with more reducing redox conditions, consuming solid phase oxides and more labile algal organic matter that retain P (Matos et al., 2016).

The results here suggest that mangrove sediments under eutrophicated conditions can efficiently buffer pore water  $\text{PO}_4^{3-}$  in the top ~20 cm depth, contributing to trapping anthropogenic P loadings, even when eutrophication is combined with deforestation. This buffering effect is likely affected by redox oscillations typical of intertidal environments, differing from the permanently flooded sediments previously evaluated in these study areas (Wagener et al., 1988; Matos et al., 2016). The water table vertical excursion along tidal cycles is a factor affecting not only the oxygen penetration into the sediments, but also the pore water drainage, while the present study reflects low-tide conditions. Moreover, all studied mangroves are in estuarine areas within the bays, with diagenetic processes susceptible to freshwater input in combination with the redox conditions (e.g., influencing the intensity of microbial oxidation of organic matter; Berner, 1980; Schultz and Zabel, 2006). The combination of these processes may contribute for the observed differences in the P behavior between sites and for the depth variability within each site. Further evaluations of relative contributions of these factors, analyses of Fe (hydr)oxides and the potential role of  $\text{PO}_4^{3-}$  uptake by mangrove plants are recommended for future studies focused on the predominating mechanisms controlling pore water  $\text{PO}_4^{3-}$  trends.



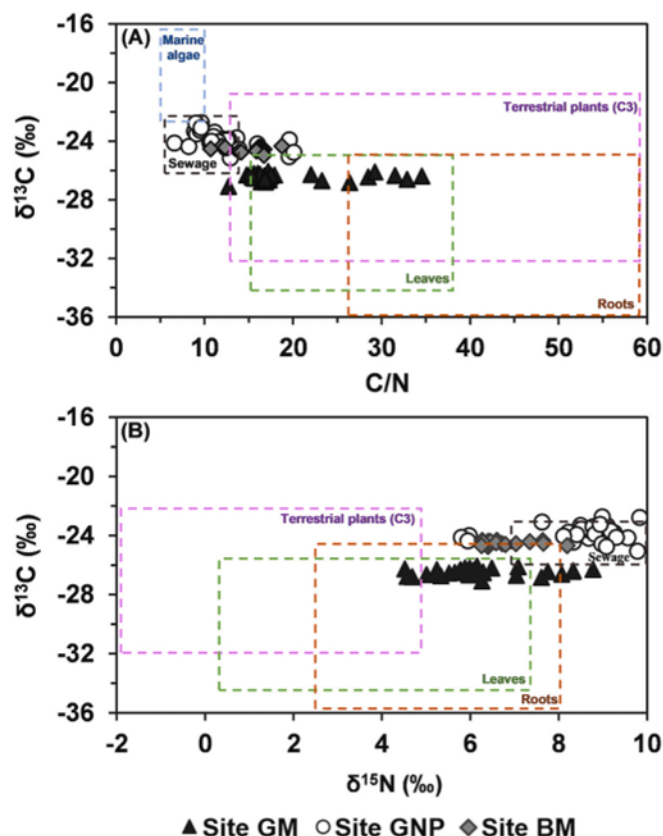


Fig. 5. (A) Relation between  $\delta^{13}\text{C}$  and C/N of study areas; (B) relation between  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  of study areas. The ranges of terrestrial plants, marine algae and freshwater algae are reported in Lamb et al. (2006). Sewage range data is that reported in Barros et al. (2010). Mangrove leaves and roots data are obtained from Barroso et al. (2022). GM, site Guapi-Mirim (moderately preserved); GNP, site Guaratiba National Park (highly eutrophicated); and BM, site Barão de Mauá (deforested eutrophicated).

Mangrove deforestation is also a concern for these processes. Alongi et al. (1998) showed that, in a comparison of deforested areas in Malaysia, a larger production of pore water  $\text{PO}_4^{3-}$  occurred in a site of recent plant cover removal (2 years) in comparison with two other sites that had plant cover for 15 and 60 years. Since the authors indicated that deforestation caused more oxidizing conditions, a larger oxidation of organic matter may have affected these higher pore water  $\text{PO}_4^{3-}$  concentrations (up to nearly 160  $\mu\text{M}$ ). The deforested area evaluated here, however, differently from those studied by Alongi et al. (1998), is under the influence of eutrophication that can limit oxidizing conditions, even considering that the deforested site does not suffer the strongest nutrient loads, as reflected in the sediment elementary and isotopic signatures (Figs. 2–5). The presence or absence of plant cover may furthermore influence the  $\text{PO}_4^{3-}$  due to living plants uptake to attend nutritional demands (e.g., Duarte et al., 1998), while the development of oxidizing rhizospheres by aquatic plants may also possibly affect pore water nutrient availability, due to atmospheric  $\text{O}_2$  transport to the rhizospheres through aerenchyma root tissues (Deborde et al., 2008; Alongi, 2010).

In any of these cases, it is expected that the tidal cycles affect the redox changes and the net P flux associated with recirculated seawater. Considering these tidal-driven processes, Pan et al. (2019) suggested that sediment porewater tends to be a P source in the subtidal zone and a P sink in the intertidal zone for the overlying seawater, potentially affecting the eutrophication of an adjacent bay in China. An analogous contrast is suggested for intertidal mangrove sediments and subtidal sediments from the Rio de Janeiro bays, considering the larger buffering

capacity suggested by the results here. Moreover, the pore water composition may also be modified by its seepage during low and ebbing tides, affecting the exchanges with tidal channels, in addition to the discussed role of absorption and precipitation processes (Rozan et al., 2002; Matos et al., 2022). The influence of redox oscillations in determining the stocks of Fe (hydr)oxides controlling the P burial efficiency of coastal sediments (e.g., Anschutz et al., 1998), in association with the pore water  $\text{PO}_4^{3-}$  buffering capacity of sediments, remains to be investigated under contrasting environmental conditions experienced by mangrove systems, to allow better comprehension on the processes involved in their role as P sinks.

#### 4. Conclusions

The findings reported here evidenced that P cycling near the water-sediment interface is likely affected by a variable pore water  $\text{PO}_4^{3-}$  buffering capacity by mangrove sediments along a eutrophication gradient in the highly urbanized Rio de Janeiro coast. The development of pore water  $\text{PO}_4^{3-}$  buffering zones (with  $\leq 26 \mu\text{M PO}_4^{3-}$ ) were clearly observed in the two more eutrophicated sites within the upper ~18–26 cm depth, while in the moderately preserved site the buffering zone occurred along the whole core, suggesting no saturation of the sediment solid phase buffering capacity at any depth interval. A pore water  $\text{PO}_4^{3-}$  net consumption trend was found (deforested eutrophicated > highly eutrophicated > moderately preserved), corresponding to differences of one or two orders of magnitude between sites. Eutrophication was therefore not evidenced as a factor resulting in large accumulation of pore water  $\text{PO}_4^{3-}$  in mangrove sediment pore water, in contrast to what was previously observed for nearby subtidal environments, even at a site under the impact of deforestation. Rather, the results here suggest that mangrove sediments under eutrophic conditions can buffer efficiently pore water  $\text{PO}_4^{3-}$  near the sediment-water interface, contributing to the assertion of these environments as sinks for anthropogenic P. These findings provide evidence that the conservation of mangrove systems in areas threatened by eutrophication is strategical to avoid enhanced P input to adjacent coastal waters.

#### CRediT authorship contribution statement

**Grazielle Nascimento-Silva:** Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Conceptualization. **Gabriela B. Oliveira:** Writing – review & editing, Formal analysis. **Christiene R.L. Matos:** Writing – review & editing, Investigation. **Edouard Metzger:** Writing – review & editing, Investigation. **Christian J. Sanders:** Writing – review & editing, Resources, Investigation, Formal analysis. **Humberto Marotta:** Writing – review & editing, Investigation. **Rut Díaz:** Writing – review & editing, Investigation, Formal analysis. **Gwenaél Abril:** Writing – review & editing, Supervision, Methodology, Investigation, Formal analysis, Conceptualization. **Wilson Machado:** Writing – review & editing, Supervision, Investigation, Funding acquisition, Formal analysis, Conceptualization.

#### Declaration of competing interest

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.

#### Data availability

Data will be made available on request.

#### Acknowledgments

We thank the Graduation Program in Geosciences (Geochemistry) from UFF, and the financial support from CAPES. GNS thanks the PhD



scholarship (E-26/200.383/2020(255451)) received from the Research Foundation of Rio de Janeiro State (FAPERJ). W. Machado thanks a Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq-Brazil) research grant. This study is part of the Project FEEDBACKS supported by CAPES-PRINT-UFF program (88881.310184/2018-01) and the France-Brazil International Project VELITROP “Vulnerability of tropical coastal ecosystems against eutrophication” (CNRS/INEE).

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