



Phosphorus chemical speciation in surface sediments from Cananéia – a non-impacted estuary

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ABSTRACT

Phosphorus (P) is found in estuarine sediments, which belong to the biogeochemical cycle of this element in aquatic environments. This study examines the distribution of P in different chemical speciations in surface sediments at 14 stations in the southern region of the Cananéia-Iguape Estuarine-Lagoon Complex. P chemical fractions were determined using a sequential extraction method of fractional extraction that measures five P forms: (i) exchangeable P (P_{exch}), loosely adsorbed or exchangeable; (ii) P-Fe (P-Fe), P-bound Fe oxyhydroxides; (iii) authigenic P (P-CFAP), including carbonate fluorapatite, biogenic apatite (fish debris), and P-bound calcium carbonate; (iv) detrital P (P-FAP), igneous or metamorphic apatites; (v) organic P (P_{org}); and (vi) total P (P_{total}). The P fractions associated with the sedimentary properties of grain size and organic content can be used as a proxy for understanding environmental conditions. The average percentage of each P fraction of the surface sediments in this region follows the sequence: P-Fe (38%) > P_{org} (32%) > P_{exch} (14%) > P-FAP (9%) > P-CFAP (7%). In all stations, P-Fe and P_{org} were the main fractions of P in the sediments. $CaCO_3$ accounted for less than 30% of it, essentially indicating lithoclastic characteristics, whereas organic carbon (C_{org}) showed values below 2%. Finally, P_{total} showed concentrations that are consistent with an unpolluted environment, with values below 16 $\mu\text{mol g}^{-1}$.

Keywords: Phosphorus speciation, Organic phosphorus, Organic carbon, CIELC, Autochthonous and allochthonous origins

INTRODUCTION

Estuaries are coastal environments in which human activities on land meet the natural conditions of the aquatic system, generating interfaces of anthropogenic action whose limits and extensions show dynamics that must be intensively studied (Braga, 1995). In Brazil, of its 25 most important metropolitan regions, 14 lie in estuaries, in which

harbor activities and petrochemical industries are concentrated (Diegues, 1987). Thus, many chemical pollutants are introduced into these environments, with serious consequences for water and sediment quality. Nutrient discharge constitutes a serious global problem affecting estuarine areas in the vicinity of sewage, waste, industrial, agricultural, and harbor activities, leading to eutrophication (Braga et al., 2000; Bricker et al., 2008; Hughes et al., 2011; Rabalais et al., 2014; Berbel et al., 2015; Rao et al., 2021). Thus, eutrophication seriously affects and changes the physicochemical properties of the water column and sediments. Eutrophication in coastal

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areas over the course of many years contributes to hypoxia and benthic light limitation, which are due to high levels of phytoplankton production that increase the amount of organic matter that reaches the sediments (Andersen and Conley, 2009; Lillebo et al., 2011; Rao et al., 2021; Onck et al., 2022). Phosphorus (P) is considered a key nutrient that can limit primary productivity and influence the biogeochemical cycles in marine environments (Tyrrell, 1999; Paytan and McLaughlin, 2007; Yang et al., 2019). Regarding dissolved nutrients, the region of the Cananéia-Iguape Estuarine-Lagoon Complex (CIELC) is considered a pristine area, with low values of dissolved nutrients in its southern sector (nitrate - $\text{NO}_3^- < 5.00 \text{ mmol L}^{-1}$ and phosphate - $\text{HPO}_4^{2-} < 1.00 \text{ mmol L}^{-1}$ – Amaral et al., 2021). According to Fisher et al. (1982), sediments provide approximately 28–35% of the P necessary for primary productivity in non-impacted coastal areas. This sedimentary P influences the mobility and bioavailability of this element between sediment and the water column (Solomons et al., 2020). In Brazil, some studies of P chemical speciation have been carried in coastal areas (Carreira and Wagener, 1998; Pagliosa et al., 2006; Berbel et al., 2015). However, a study about phosphorus speciation in CIELC sediments was reported by Barcellos et al. (2005), including two P forms (P_{org} and P_{inorg}).

In this study, a sequential extraction method (SEDEX) (Ruttenberg, 1992) was employed to operationally discriminate five forms of sedimentary P: (i) exchangeable P (P_{exch}), an important fraction that can be easily released into the overlying water (Zhou et al., 2016); (ii) bound Fe-P (P-Fe), which releases P under reducing conditions (Ruttenberg, 1992; Coelho, 2004; Marz et al., 2014; Berbel et al., 2015); (iii) authigenic apatite (P-CFAP), a fraction that includes fish skeletons and teeth, which is composed of hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$), whereas the fluorapatite carbonate mineral ($\text{Ca}_5(\text{PO}_4)_{2.6}(\text{CO}_3)_{0.4}$ F) is precipitated from the interstitial solution as a consequence of the oxidation of organic matter and/or the reduction of Fe oxyhydroxide; (iv) detrital P (P-FAP), a sedimentary P of igneous and metamorphic origin that is incorporated into sediments; and (v) organic P (P_{org}), a sedimentary

form from organic matter that undergoes oxidation, releasing inorganic P.

These forms of P in the sediment show the potential bioavailability of this nutrient to primary production, its capacity to be removed to organic forms, and its potential to be retained in inorganic particulate forms – that is, more refractory forms – in the sediment reservoir. Knowledge of P partition in the sediment is important in estuarine and coastal studies as it helps researchers to evaluate estuarine and marine environments and the risk of eutrophication.

METHODS

STUDY AREA

The study area lies on the southwest coast of the state of São Paulo, between latitudes $24^{\circ} 54.0$ and $25^{\circ} 04.5$ S and longitudes $47^{\circ} 50.5$ and $47^{\circ} 59.0$ W, and comprises the municipalities of Iguape, Ilha Comprida and Cananéia, in which the CIELC is located. The area is recognized by UNESCO as being part of the biosphere reserve due to its importance as a natural environment and its traditional cultures (CETESB, 2007). This protected wetland area is included on the Ramsar list (<https://rsis.ramsar.org/ris/2310>).

Cananéia Island is one of three islands in the southern region of the CIELC, in which 14 surface sediments were sampled (Figure 1) in three interconnected water bodies: Mar de Cubatão, stations (10 to 13); Mar de Cananéia, stations (1 to 6); and Trapandé Bay, stations (7 to 9).

The climate of the region is characterized as humid subtropical, with annual average temperatures above 21°C and annual rainfall above 2,000 mm, with the highest values for rainfall occurring in February/March and August being the driest month (DAEE, 2006). The vegetation is well preserved and is characterized by extensive areas of well-structured mangroves covering around 200 km^2 (SUDELPA, 1987).

Cananéia Island is influenced by two important sources of fresh water. Its northern sector receives the discharge from the Ribeira de Iguape River and its southwest is drained by a small hydrographic basin composed of the Taquari/Carapara, Minas/ Mandira, Itapitanguí, and Iririáia rivers. The Ribeira

de Iguape River contributes freshwater inputs, with a flow rate of 1741 m³/s in March and 101 m³/s in August (Bérgamo, 2000; Barcellos, 2005). The Ribeira de Iguape River is an important source of P from the continent (Aidar, 1980; Braga, 1995; Barreira-Alba et al., 2007). The region under study is classified as eutrophic; this was even the case when the Valo Grande was closed, according to Braga (1995). The tidal regime is semidiurnal with amplitudes from 0.2 to 1.5 m.

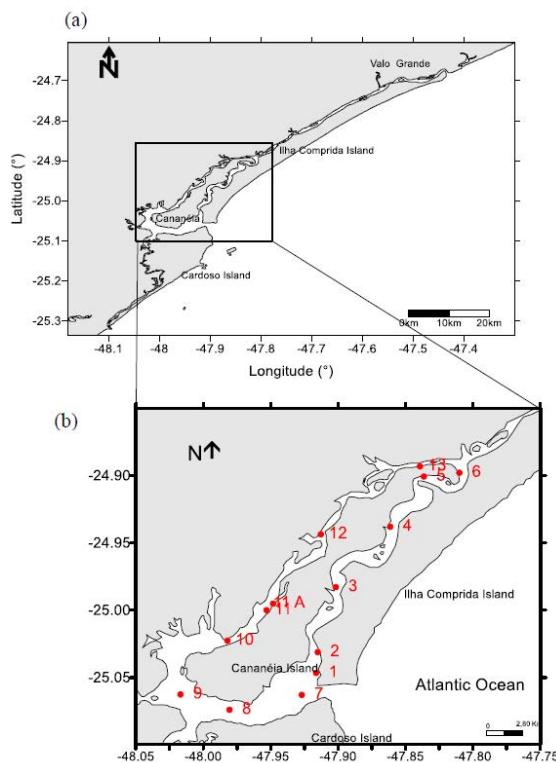


Figure 1. (a) CIELC region - Iguape (in which Valo Grande is located), Ilha Comprida Island, and Cananéia Island (study area). (b) Sampling stations around Cananéia Island: Mar de Cubatão (stations 10 to 13), Mar de Cananéia (stations 1 to 6), and Trapandé Bay (stations 7 to 9).

Some authors have observed that the sediment in the CIELC shows a mosaic distribution composed of different grain size fractions with fine sand, silt, and clay. According to Tramonte et al. (2016), the dominant textural classes are fine sands in Cananéia. Its northern region suffers the influence of Valo Grande, an artificial channel in the northern part of the CIELC that enables the river water from the Ribeira de Iguape River to input

directly into the complex. This channel has been opened and closed many times. It has remained open since 1995; contributing suspended material to the CIELC. This dynamic is also reflected in the surface distribution of the P fraction.

Regarding the seasonal periods, during the summer, input from the Ribeira de Iguape River increases via Valo Grande, which intensifies the transportation of suspended material from the northern region to the southern portion of the CIELC in which the Cananéia region is located.

The CIELC is a region that is considered pristine regarding water and sediment quality, living conditions, and the absence of toxicological responses to its ichthyofauna, which has been confirmed by various studies (Azevedo et al., 2009; Amaral et al., 2021).

SURFACE SEDIMENTS

In total, 14 surface sediment samples (0–5 cm) were obtained using an inox steel van Veen grab in February 2006 (summer). The sediments were frozen at -20 °C and freeze-dried for 72 h. After drying, the sediment was ground to a powder with a mortar and pestle prior to chemical analyses of P speciation, organic carbon (C_{org}), and total Fe being conducted. Grain size analysis was performed using the method in Suguio (1973). Carbonate content was performed according to Ingram's (1971) method.

P SPECIATION ANALYSES

Samples were determined in duplicates, as described by Ruttenberg (1992). SEDEX consists of five steps (Table 1) that are followed to separate the major reservoirs of sedimentary P into five pools: (i) loosely sorbed or exchangeable (P_{exch}); (ii) Fe bound to oxyhydroxides (P–Fe); (iii) authigenic P (P–CFAP), including carbonate fluorapatite (CFA), biogenic apatite (fish debris) and P-bound calcium carbonate (CaCO₃); (iv) P–FAP, an igneous or metamorphic apatite; and (v) P_{org}. The phosphate concentrations in all steps, except for the P–Fe step, were determined by the colorimetric method (Grasshoff et al., 1983) using a Genesys 2 spectrophotometer. Sedimentary P–Fe in citrate-dithionitebicarbonate (CDB) was determined

using a combined CDB–MAGIC (magnesium-induced coprecipitation) method (Huerta-Díaz et al., 2005). The quantitative P removal from CDB solutions was accomplished by the alkaline precipitation of $Mg(OH)_2$ with 10 mol L⁻¹ of an NaOH solution. After separation by centrifugation and two washings with 10% NH_4OH solution, the precipitate was redissolved in 10% HCl solution. The P concentration in the HCl extract was measured by the conventional colorimetric method, as described above. The relative standard deviations of the replicates lie below 6, 9, 6, 7, and 5% for P-Fe, P_{exch} , P-CFAP, P-FAP, and P_{org} , respectively, and the quantification limits are 0.22, 0.87, 0.16, 0.04, and 0.10 $\mu\text{mol g}^{-1}$, respectively. P_{total} was calculated as the sum of the five P forms.

SEDEX (Ruttenberg, 1992) was chosen in this study due to some advantages according to Loh et al. (2020): (1) differentiating fluorapatite carbonate (P-CFAP), which is of marine origin from fluorapatite (P-FAP), which is metamorphic origin, i.e., of terrigenous origin. The SMT method (standards, measurements, and testing – Ruban et al., 1999 and 2001) extracts both apatite: P-Ca, which include P-FAP + P-CFAP; being unable to differentiate between marine and terrigenous origins, mainly for marine and estuarine sediments. Also, (2) these authors have used a NaOH solution as solvent to extract both exchangeable – P (P_{exch}) and P bound iron (P-Fe). The CIELC sediments are intermediate between riverine and marine environment so this study decided to use SEDEX instead of SMT.

Table 1. SEDEX (Ruthenberg, 1992) – P species, reagents, and sources of sediment phosphorus in each extraction.

| Phosphorus species in this study | Reagents | Sources |
|----------------------------------|--|---|
| P_{exch} | $MgCl_2$ 1 mol L ⁻¹ – each 2 hours/ rising with H_2O | Loosely sorbed or exchangeable |
| P-Fe | Citrate-dithionite – bicarbonate 8h | Iron bound to oxy-hydroxides |
| P-CFAP | Buffer acetic acid / sodium acetate 1 mol L ⁻¹ pH 4.0 for 6h and rinsing of $MgCl_2$ and H_2O | Including carbonate fluorapatite (CFA), biogenic apatite (fish debris), and phosphorus-bound $CaCO_3$ |
| P-FAP | HCl 16 h - 1 mol L ⁻¹ | Apatite of igneous or metamorphic origin |
| P_{org} | Ashing sediment and after extracting HCl for 16 h - mol L ⁻¹ | Organic phosphorus |

To verify the analyte recovery of this method, we analyzed the certified reference material “Estuarine Sediment” (NIST 1646). The result for P_{total} , obtained from the sum of the fractions, totaled 90% when compared to the certified value. More details are in Berbel and Braga (2014).

Corg was determined using a LECO CNS 2000 analyzer after adding 10% HCl to remove carbonates. The quantification limit for C_{org} totaled 0.003%.

STATISTICAL TREATMENT

The Shapiro-Wilk test was used for normality test. Spearman's correlation was used because of the non-normality of the data. Also, this correlation was used to verify the relation between grain size and our geochemical parameters, as was principal component analysis.

RESULTS

TEXTURAL CHARACTERISTICS OF SEDIMENTS

The silt contents in the Cananéia sediments in the summer ranged from 0.02 to 32.54 % (Figure 2a) and that of clay, from 0.00 to 27.11%, with high percentages at stations 3, 8, 9, and 11A (Figure 2b). The sand content in Cananéia were very high (40.4–99.9% – Figure 2c), which corroborates the predominance of sandy sediments in the area, as in Barcellos (2005), Tramonte et al. (2016), and Millo et al. (2021). The content of $CaCO_3$ in marine sediments is considered a product of the depositional environment, and $CaCO_3$ is viewed as being an autochthonous material, whereas the non-carbonate sedimentary fractions are, in

general, considered terrigenous. The CaCO_3 contents in Cananéia ranged from 0.44 to 4.17% (Figure 2d) during the summer and

referred to lithoclastic sediments (below 30% CaCO_3), according to the classification by Larssoner et al. (1982).

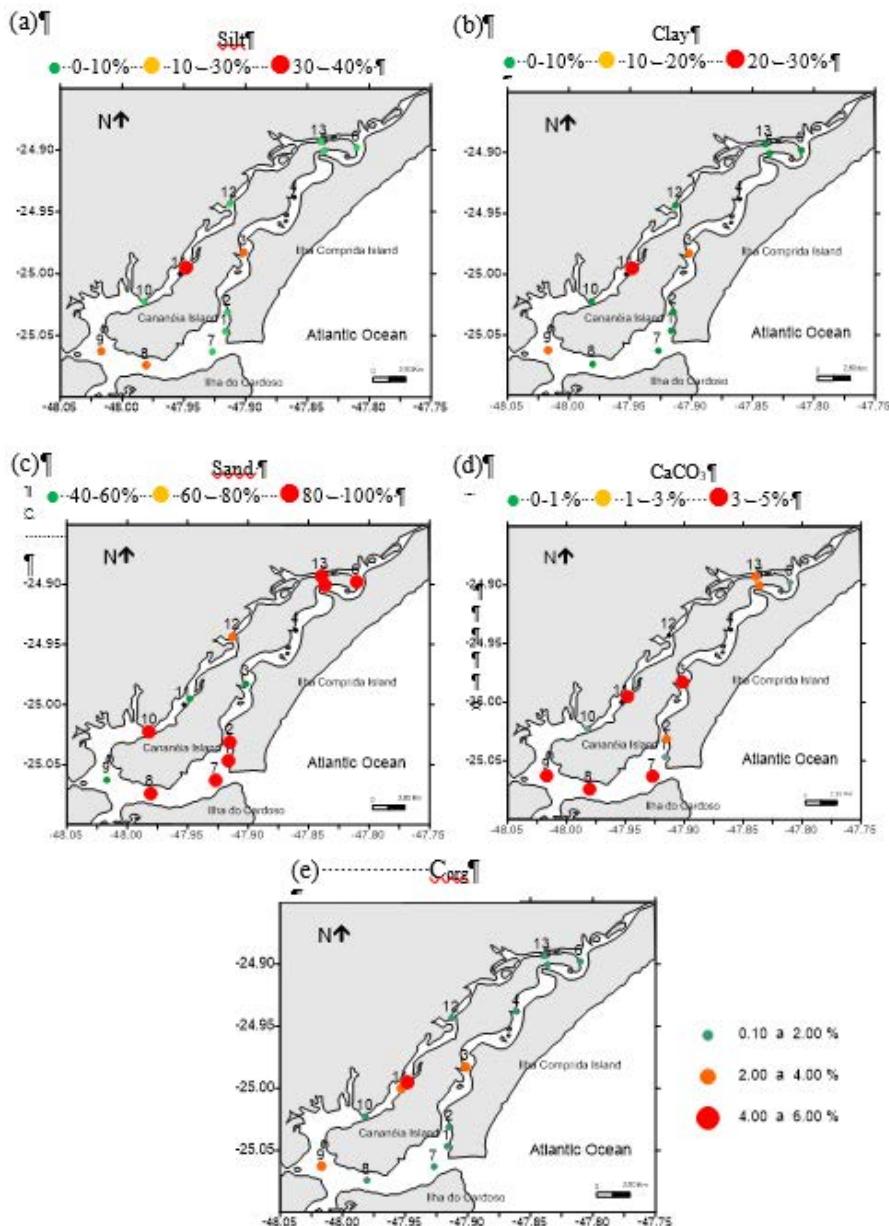


Figure 2. Grain sizes, biodetritic carbonate, and organic carbon percentages in surface sediments from Cananéia Island. Stations 4 and 11 were not determined. (a) silt, (b) clay (c) sand, (d) CaCO_3 and (e) Corg. Ranges of Corg were based on Romankevich's classification (1984): (0-2%-low), (2-4% medium), and (> 4% high).

ORGANIC CARBON (CORG)

C_{org} values ranged from 0.15 to 5.83%, with an average of $1.46 \pm 1.66\%$, with contents varying from low (0- 2%) to medium (2-4%), according

to Romankevich's classification (1984). The Mar de Cananéia region (stations 1 to 6) showed low levels of C_{org} (Figure 2e), except for station 3 (2.54%). In the Mar de Cubatão region (stations

10 to 13), sediments are predominantly sandy. C_{org} values totaled 2.92 and 5.83% in stations 11 and 11A, respectively. In Trapandé Bay, station 9 showed a concentration of 3.51%.

EXCHANGEABLE P (PEXCH)

In Cananéia, P_{exch} concentrations ranged from 0.16 to 2.07 $\mu\text{mol g}^{-1}$, with an average of $0.71 \pm 0.52 \mu\text{mol g}^{-1}$. The highest levels of P_{exch} were found in stations 3 and 9, with 2.07 and 1.25 $\mu\text{mol g}^{-1}$, respectively (Figure 3a). The percentages of P_{exch} in the whole system ranged from 7 to 25% (Figure 3c). The percentage decreased with marine influence. The highest P_{exch} percentages were in the Mar de Cubatão region (stations 4, 5, and 10 – Figure 3c). The lowest concentrations were found in Trapandé Bay, which suffers a tidal influence.

P BOUND TO FE OXIDES (P-FE)

P-Fe concentrations ranged from 0.74 to 4.40 $\mu\text{mol g}^{-1}$, with a mean of $1.92 \pm 1.26 \mu\text{mol g}^{-1}$ (Figure 3b). The highest levels were recorded at stations 3, 9, and 11A, and its presence is associated with stations with fine sediments. Continental contributions explain the significant percentages regarding Fe fractions. These ranged from 23 to 57% (Figure 3c), with the largest contributions being identified at stations 1, 2, 6, and 13.

P BOUND TO AUTHIGENIC APATITE (P-CFAP)

P-CFAP varied from 0.05 to 1.07 $\mu\text{mol g}^{-1}$, with an average of $0.37 \pm 0.31 \mu\text{mol g}^{-1}$. These greater contributions may be associated with the increase in P_{exch} (Figure 3a), which may favor the formation of authigenic apatites. The smallest contributions were found in the estuarine stations in summer.

P BOUND TO FLUORAPATITE (P-FAP)

P-FAP concentrations ranged from 0.11 to 0.97 $\mu\text{mol g}^{-1}$, with a mean of $0.42 \pm 0.30 \mu\text{mol g}^{-1}$ (Figure 3a). P-FAP offers a continental source of refractory P. Ruttenberg (1992) found high levels during the summer due to continental drainage, which configures a source of detrital sediments. As for the percentage of P-FAP in relation to P_{total} , the greatest contributions occurred in the most saline stations (1 and 7) and accounted for 19 and 22% (Figure 3c), respectively. Similar P-FAP percentages were observed by Berner et al. (1993). Silts may have higher P-FAP contents.

ORGANIC P (P_{ORG})

Organic P contents ranged from 0.31 to 7.71 $\mu\text{mol g}^{-1}$, with an average of $2.19 \pm 2.54 \mu\text{mol g}^{-1}$ (Figure 3b). The highest levels of P_{org} were observed at stations 9 and 11A (Mar de Cubatão), accounting for 50% (Figure 3c). The high percentage of P_{org} in these stations may be associated with their mud sediments.

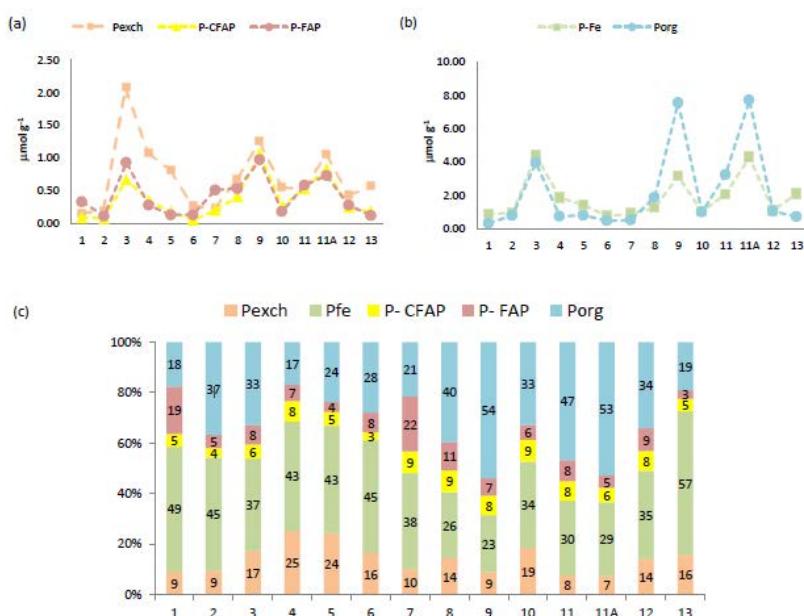


Figure 3. (a) Concentrations of P_{exch} , P-FAP , and P-CFAP ; (b) Concentrations of P-Fe and P_{org} . All concentrations are shown in $\mu\text{mol g}^{-1}$; (c) Percentages of P chemical speciation in Cananéia surface sediments.

TOTAL P (P_{TOTAL})

P_{total} ranged from 1.65 to 14.61 $\mu\text{mol g}^{-1}$ in the summer, with an average of $5.54 \pm 4.57 \mu\text{mol g}^{-1}$. In the winter, the values were slightly lower, ranging from 1.34 to 13.55 $\mu\text{mol g}^{-1}$, with an average of $4.83 \pm 3.86 \mu\text{mol g}^{-1}$. The highest values were found in sediments with more muddy characteristics, such as at stations 3, 9, and 11 A.

C_{ORG}/P_{ORG} RATIOS

The C_{org}/P_{org} ratios ranged from 242 to 907 in this study. According to Ruttenberg and Goñi (1997), the observed values of C_{org}/P_{org} molar ratios are corroborated with marine to mixed origin (80–300), soft plant tissue (300–1,300), and marine benthos (in the range of 550), as shown in Figure 4. The highest values are observed at stations 4 and 5 and the lowest are located at stations 7 and 13. The spatial distribution of the C_{org}/P_{org} molar ratio indicated continental sources in Mar de Cubatão. On the other hand, the values of C_{org}/P_{org} in Mar de Cananéia were indicative of mixed origin (marine and terrestrial). High values of the C_{org}/P_{org} molar ratio may be associated with the preferential remineralization process of P over carbon and refractory organic matter from the higher number of plants in estuaries and mangroves. Moreover, high values of the C_{org}/P_{org} molar ratio may be attributed to the increase in continental source of organic matter.

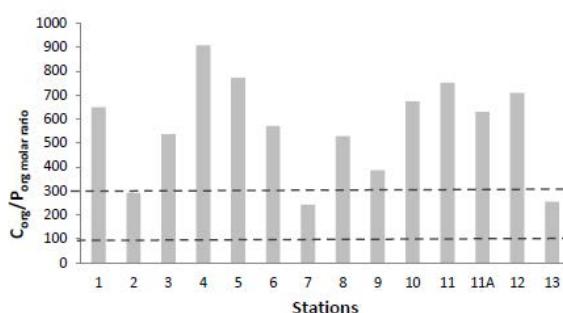


Figure 4. C_{org}/P_{org} molar ratios in Cananéia during the summer of 2006. The dashed lines are related to ranges from 80 to 300, indicating mixing organic matter origin. Above 300 is from the continental source and below 80 is the bacterial origin.

DISCUSSION

The Cananéia region belongs to the CIELC. This region is subject to a subtropical climate

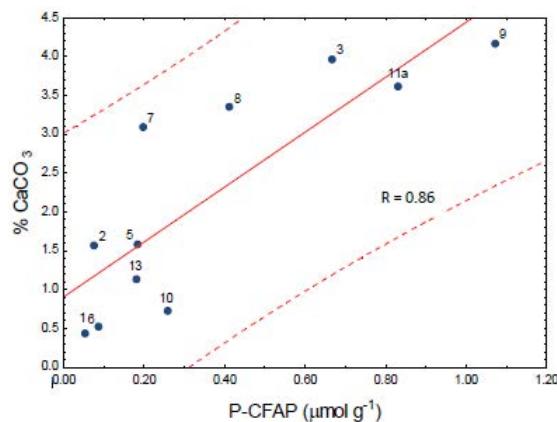
and supports important mangrove vegetation. The Summer of 2006 showed a typical subtropical climate with high pluviosity (533 mm in February 2006, CIAGRO - *Centro Integrado de Informações Agrometeorológicas* - Integrated Agrometeorological Information Center). During the summer, the waters are less saline in the vicinity of Trapandé Bay and in the southern region of Mar de Cananéia. This is due to the influence of the high rainfall that characterizes the southeast region of Brazil during the summer. Moreover, the Ribeira de Iguape River, in the northern region of the CIELC, has a greater influence on water salinity during the rainy period, during which fresh water is carried to the region of Cananéia Island. The sediments in the Cananéia estuary are characterized as sandy, with the presence of mud at some stations, such as 3, 9, 11, and 11A. These stations showed terrestrial sources such as humic substances (Millo et al., 2021), associated to low hydrodynamics, as observed by Saito et al. (2001) increasing the sedimentation of fine fractions. Despite these conditions, C_{org} values ranged from low (0–2%) to intermediate (2–4%); similar values were found by Tramonte (2016) and Millo (2021). The values of C_{org} showed significant correlations with the contents of mud, the species of sedimentary P, and CaCO₃. The correlation between CaCO₃ and C_{org} was significant, as shown in Table 2 ($r = 0.64$).

Moreover, CaCO₃ was also significantly correlated with P-CFAP ($r = 0.86$ - Table 2 and Figure 5), which may indicate the formation of authigenic fluorapatite carbonate or P adsorbed to CaCO₃. Regarding the components of sedimentary organic matter, the correlations of P species were very significant regarding C_{org} ($r \geq 0.60$).

The Pexch/Ptotal ratio in Mar de Cubatão was higher in stations in which the marine influence was lower. Stations 3, 5, 10, 12, and 13 more influenced by river waters (the Ribeira de Iguape, Iririáia-açu, and Itapitangui River), showing higher percentages of Pexch. Most of the contributions of the P fractions come from P_{org} and P-Fe, followed by Pexch, and mainly in stations 9, 11, and 11 A, which showed higher levels of mud and C_{org} (Figure 3c). On the other hand, P-CFAP and P-FAP occur at lower percentages than in other subtropical estuaries or bays (Table 4)

Table 2. Spearman correlations (in blue, $p < 0.05$) for sedimentary parameters from Cananéia surface 4 sediments.

| | Sand | Silt | Clay | %CaCO ₃ | C _{org} | P _{exch} | P-Fe | P-CFAP | P-FAP | P-Org | P-total | C _{org} /P _{org} |
|------------------------------------|-------|------|------|--------------------|------------------|-------------------|------|--------|-------|-------|---------|------------------------------------|
| Sand | | | | | | | | | | | | |
| Silt | -0.88 | | | | | | | | | | | |
| Clay | -0.83 | 0.93 | | | | | | | | | | |
| %CaCO ₃ | -0.82 | 0.85 | 0.79 | | | | | | | | | |
| C _{org} | -0.88 | 0.83 | 0.86 | 0.64 | | | | | | | | |
| P _{exch} | -0.84 | 0.87 | 0.88 | 0.77 | 0.64 | | | | | | | |
| P-Fe | -0.86 | 0.86 | 0.79 | 0.78 | 0.67 | 0.85 | | | | | | |
| P-CFAP | -0.81 | 0.81 | 0.82 | 0.86 | 0.86 | 0.75 | 0.79 | | | | | |
| P-FAP | -0.56 | 0.54 | 0.70 | 0.76 | 0.71 | 0.49 | 0.54 | 0.85 | | | | |
| P-Org | -0.96 | 0.92 | 0.86 | 0.82 | 0.93 | 0.67 | 0.77 | 0.87 | 0.67 | | | |
| P-total | -0.86 | 0.90 | 0.84 | 0.85 | 0.81 | 0.84 | 0.94 | 0.92 | 0.71 | 0.86 | | |
| C _{org} /P _{org} | -0.24 | 0.01 | 0.16 | -0.26 | 0.31 | 0.17 | 0.05 | 0.10 | -0.02 | 0.10 | 0.08 | |

**Figure 5.** Scatterplot of CaCO₃ x P-CFAP with confidence interval 95% in dashed lines.

According to Paludan and Morris (1999), a considerable fraction of the P from rivers is carried to the sea in the form of suspended particulate material, and its composition is modified by increasing salinity and pH. According to these authors, the contribution of P-Fe decreases as P-CFAP and P_{exch} increase toward the sea. This can be explained by changes in the surface charge regarding Fe oxides/hydroxides, which occur in response to increasing pH and salinity as water moves from brackish to saline areas and which can prevent phosphate from being adsorbed into Fe oxides/hydroxides (Zwolsman, 1994). Additionally, the resuspension caused by tides may result in higher oxygen penetration from the overlying water to the bottom sediments. Hence, the diffusion

of oxygen into the overlying and pore waters can initiate Fe oxidation (Zwolsman, 1994; Berbel et al., 2015). P_{org} and P-Fe were the predominant fractions in the sediments of all stations (Figs. 6a and 6b), which favor the formation of Fe oxide-hydroxides from continental sources. Regarding P speciation, the studied region can be divided into two parts: (i) Mar de Cananéia, with a predominance of P-Fe due to the influence of riverine sediments from the Ribeira de Iguape River (Fig. 6a) and (ii) the Trapandé Bay and Mar de Cubatão, in which P_{org} is the predominant form (Figure 6b).

The predominance of P_{org} may be related to the fact that Mar de Cubatão shows low hydrodynamics, which are associated with the contribution of organic matter from mangroves. The transformation and release of various P species in estuarine sediments are controlled by a series of biogeochemical processes and are associated with environmental conditions such as salinity, pH, dissolved oxygen, and sediment grain sizes, as in Berbel et al. (2015) in the Santos–São Vicente Estuarine System. In oxic conditions, P release is driven by organic matter remineralization and the adsorption of dissolved phosphates in sediments. On the other hand, under hypoxic and anoxic conditions, Fe from oxyhydroxide reduction releases P and form authigenic minerals as P-CFAP (Paytan and McLaughlin, 2007; Mort et al., 2010; Marz, 2014; Berbel et al., 2015; Yang et al., 2019). Nevertheless, P-FAP and P-CFAP are the most refractory P fractions.

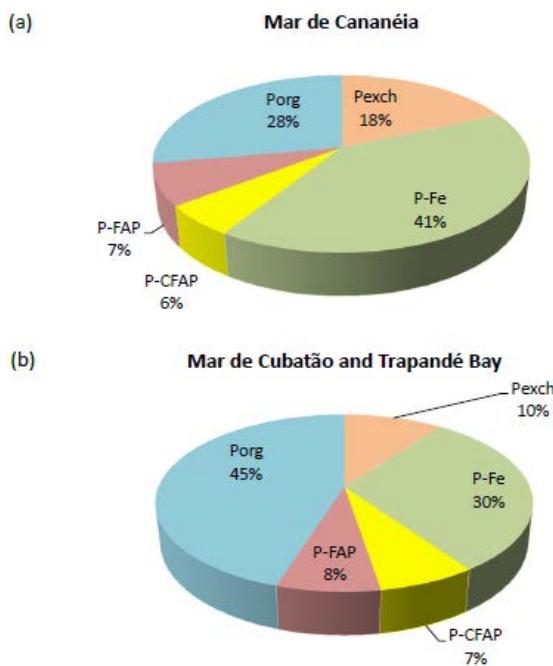


Figure 6. (a) Average of P species in Mar de Cananéia (%); (b) Average of P species in Mar de Cubatão and Trapandé Bay (%).

In contrast with other studies of continental shelf and polar environments (Berbel and Braga, 2014; Marz et al., 2015), the main P species in the surface sediments of Cananéia are P-Fe and P_{org} . Although Santos-São Vicente Estuarine System shows high levels of P chemical speciation – as in Table 3 – the percentages of each fraction are similar in relation to P_{total} . (Table 4)

P SPECIATION GEOCHEMISTRY IN THE CANANÉIA ESTUARY

P fractionation in the study region depends on environmental factors such as continental sources, hydrodynamics, and redox conditions. For instance, in Antarctic sediments, P-FAP and P-CPAP are the main fractions because of the predominance of physical weathering (Berbel and Braga, 2014; Marz et al., 2014; Mao et al., 2021). These results show that P-FAP and P-CPAP are highly correlated (Figure 7), thereby indicating that P-CPAP comes from a continental source, as observed by Solomon et al. (2020).

Table 3. Comparative values of P chemical species in some environments from Brazil. All concentrations are in $5 \mu\text{mol g}^{-1}$. Nd= not determined Ref : references

| | P_{exch} | P-Fe | P-CPAP | P-FAP | P_{org} | P_{total} | Ref. |
|--|------------|-----------|-----------|------------|-----------|-------------|----------------------|
| $\mu\text{mol g}^{-1}$ (mean or range) | | | | | | | |
| Sepetiba Bay (polluted area, mean) | 7.92 | 19.44 | 1.25 | 8.77 | 9.47 | 46.85 | Dias, 2006 |
| Jaguaribe river | nd | 0.36-1.12 | 0.24-1.18 | <0.02-0.78 | 0.82-1.87 | 2.67-3.61 | Marins et al., 2007 |
| Santos – S. Vicente (mean) | 3.67 | 11.29 | 2.42 | 2.64 | 6.92 | 26.94 | Berbel et al., 2015 |
| Guapimirim Estuary | 0.03-1.93 | 0.79-1.71 | 0.68-1.01 | nd | nd | 3.18-7.13 | Vicente et al., 2016 |
| Itapocoroy Bay (mean) | 0.92 | 0.05 | 6.68 | 0.06 | 0.05 | 7.78 | Souza et al., 2022 |
| Cananéia (mean) | 0.71 | 1.85 | 0.36 | 0.41 | 2.12 | 5.54 | This study |

Table 4. Percentages of P chemical species in relation to P_{total} in some environments from Brazil. Nd= not determined

| | P_{exch} | P-Fe | P-CPAP | P-FAP | P_{org} | References |
|------------------------------------|------------|------|--------|-------|-----------|----------------------|
| %P forms/ P_{total} | | | | | | |
| Sepetiba Bay (polluted area, mean) | 17 | 41 | 3 | 19 | 20 | Dias, 2006 |
| Jaguaribe river | nd | 30 | 24 | 6 | 40 | Marins et al., 2007 |
| Santos – S. Vicente (mean) | 13.8 | 38.6 | 8.9 | 9.2 | 29.5 | Berbel et al., 2015 |
| Guapimirim Estuary | 3.4 | 26.0 | 26.3 | nd | nd | Vicente et al., 2016 |
| Itapocoroy Bay (mean) | 11.75 | 0.64 | 86.33 | 0.48 | 0.06 | Souza et al., 2022 |
| Cananéia – this study | 12.5 | 37.0 | 6.9 | 6.3 | 37.0 | This study |

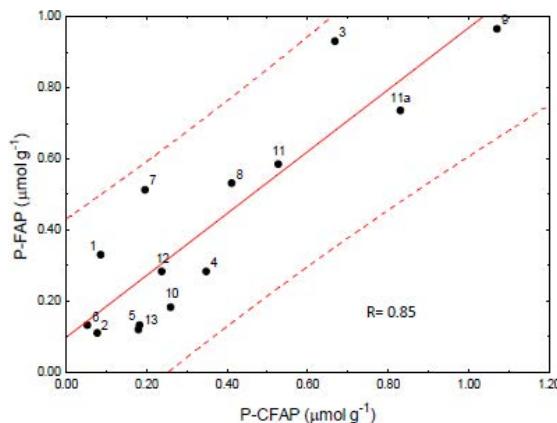


Figure 7. Scatter plot of P-FAP and P-CFAP with confidence interval 95% in dashed lines

High levels of C_{org} are usually accompanied by high P_{org} concentrations (Andrieux and Aminot, 1997; Barcellos et al., 2005; Berbel et al., 2015; Acharya et al., 2016). C_{org} is considered an indicator of organic matter inputs and shows positive correlations with P_{exch} , P-CFAP, P-FAP, and P_{org} . The fact that C_{org} is correlated with P-FAP, as shown in Table 2 ($r = 0.71$), may be attributed to

organic matter from a continental source. In fact, the obtained mean of C_{org}/P_{org} exceeded 300.

Figure 8 shows the high positive loadings for P_{exch} , P-CFAP, P_{org} , P-CFAP, P-FAP, C_{org} , $CaCO_3$, clay, and silt. However, sand shows high negative loadings, indicating that grain size has a considerable impact on all P chemical speciation. All the P fractions are well correlated with silt and clay content, and this can be explained by the fact that mud sediments have a larger specific area than those of the coarser sediments, thus providing more binding sites for the adsorption of all P species, as occurs in São Vicente Estuarine System surface sediments (Berbel et al., 2015). Unlike in Mao et al. (2021), P-Fe and P-FAP show significantly positive correlations ($r = 0.54$ - Table 2), and these two P species are highly correlated with grain size, indicating that both P species are concentrated in the mud fraction. P-Fe is highly dependent on the redox conditions of adjacent water. The Cananéia bottom waters are highly oxygenated (77 to 102% saturation) according to Berbel (2008) and Sutti et al. (2023). Therefore, in surface sediments of this environment the Fe (III) reduction is unlikely.

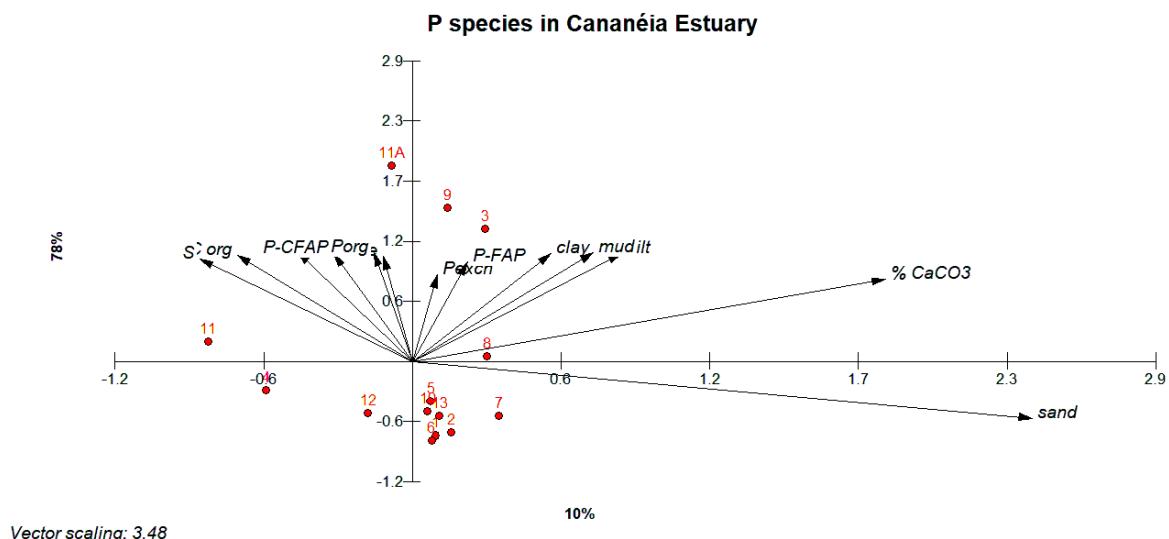


Figure 8. Principal component analysis of sediment parameters from Cananéia – summer 2006.

P-CFAP is highly correlated with P-FAP and $CaCO_3$, indicating that P-CFAP is from mixed sources, i.e., of marine and terrestrial origin. In marine waters, P combined with $CaCO_3$ and CFA can precipitate in interstitial water under brackish conditions (Gunnars

et al., 2004). At the same time, P_{exch} is formed by the adsorption of dissolved phosphate on the surface of fine-grained sediment (Andrieux and Aminot, 1997).

P_{exch} is one of the most important species of inorganic P in sediments since it is available to biota

in overlying waters, and it is commonly adsorbed on the surfaces of oxides, hydroxides, and clay particles. In highly oxygenated waters, such as those of the Cananéia estuary, the P released from organic matter oxidation is partly adsorbed on the fine particles of sediments and partly diffused into the overlying water. The released P can be adsorbed into Fe oxyhydroxides, forming authigenic CFA. In estuarine environments, the movement of saline water during the rising tide likely influences the physical and chemical properties of the suspended materials, particularly the constituent colloidal and humic compounds from mangroves (Millo et al., 2021). As the saline water enters the estuary, this interaction is enhanced due to the increase in electrolytes. The flocculation process is not limited to clays and organic complexes; it also occurs in the soluble organo-metallic complex formed from humic materials and most metallic ions (Rashid, 1985; Ruttenberg, 1992). The significant correlation between C_{org} and P-Fe ($r = 0.67$) suggests that Fe may be associated with organic matter, indicating that organic matter plays a significant role in Fe geochemistry. The presence of P-Fe in the surface sediment is due to the fact that the preservation and remineralization of particulate Corg in marine sediments are directly linked to biogeochemical processes in the sediments that control the cycles of nutrients and other elements, as well as to the dissolution and precipitation of minerals (Berner, 1990; Daines et al., 2017; Chuang et al., 2021).

Regarding P-FAP, this P form is almost insoluble in coastal sediments in alkaline aquatic environments (Ruttenberg, 1992; Slomp et al., 1996). In coastal areas in which large rivers are discharged or physical weathering is predominant, such as in Antarctic environments, P-FAP is a dominant P fraction in sediments (Berbel et al., 2014; Acharya et al., 2016). P_{org} in surface sediments accumulate for short periods (Andrieux and Aminot, 1997), and it can be partially and biologically utilized by mineralization. On the other hand, regarding estuarine environments, the high percentages of P_{org} in the Cananéia estuary may be attributed to refractory organic matter from continental sources, as shown in the high C_{org}/P_{org} molar ratio.

During the mineralization of labile organic matter from the marine environment, P is released and transformed into P-CFAP or temporarily adsorbed onto the surface of minerals (clays and Fe oxyhydroxides) as P-Fe and P_{exch} (Slomp et al., 1996). These possible transformations are supported by the high correlations between P_{org} and P-CFAP, P-Fe, and P_{exch} in this study. Regarding environmental aspects, according to Zang et al.'s (2007) classification of lacustrine sediments, the Cananéia sediments can be considered unpolluted, as shown in Table 5.

Table 5. Comparing Cananéia surface sediments based on total phosphorus classification according to Zhang et al. (2007)

| % P total | P total ($\mu\text{mol g}^{-1}$) | Classification |
|-----------------|------------------------------------|---------------------|
| 0.05 | 16 | Non polluted |
| 0.05 < P < 0.13 | 15 < P < 42 | Moderately polluted |
| > 0.13 | > 42 | High polluted |
| This study | 1.65 to 14.61 | Non polluted |

CONCLUSION

Surface sediments from the Cananéia estuary show low concentrations of P species and C_{org} . The reasons for low concentrations of these parameters are two-fold: (i) high hydrodynamics, which contribute to the predominance of sandy sediments in most stations, and (ii) low anthropogenic sources. The main P chemical species in these sediments are P-Fe (38%) and P_{org} (32%) for all stations, thus confirming terrestrial and authigenic contributions. In muddy sediments from stations 3, 9, 11, and 11A, P_{org} was the main fraction, whereas P-CFAP and P-FAP accounted for low percentages (6–9 %), indicating mosaic sediment distribution and the "spots" form of organic matter deposition. In general, P speciation in the surface sediments from Cananéia showed the tendency for P to be retained due to the formation of Fe oxyhydroxides during the flocculation processes that occur because of the intrusion of the tide and the of Fe and phosphate ions from terrestrial sources due to river inputs via Valo Grande. Moreover, P speciation confirms the preserved condition of the Cananéia region, which is in the southern portion of the CIELC.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author.

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AUTHOR CONTRIBUTIONS

G.B.B.: Investigation; Writing – original draft; Writing – review & editing.
 V.G.C.: Methodology and Analysis; Writing – review & editing.
 E.S.B.: Supervision; Resources; Project Administration; Funding Acquisition; Writing – review & editing.

CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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