ORIGINAL ARTICLE

Distributions of total, inorganic and organic phosphorus in surface and recent sediments of the sub-tropical and semi-pristine Guaratuba Bay estuary, SE Brazil

Luiz Carlos Cotovicz Junior · Eunice da Costa Machado ·
Nilva Brandini · Rafaela Cristine Zem ·
Bastiaan Adriaan Knoppers

Abstract This study addresses the distribution of total phosphorus (TP) and its inorganic (IP) and organic (OP) fractions, grain-size and organic matter of surface and recent sediments, coupled to the behavior of total and dissolved inorganic phosphorus (TP and DIP) of the water column, of the semi-pristine Guaratuba Bay estuary, SE Brazil. Surface sediment samples were taken at 43 sites spread along the estuarine gradient and recent sediments from 3 short (35 cm long) cores from the upper, central and lower portions of the estuary, respectively. Highest TP and IP concentrations of surface sediments were detected within the upper sector and the transition zone between the upper and central sectors, all characterized by fine sediments, low salinities and water depths. In contrast, the lower sector and its narrow and deep tidal channel, subject to more intense tidal forcing, exhibited a higher fraction of sandy sediments with lower TP, IP and OP contents. In spite of the spatial variability in sediment grain size, IP corresponded to the major fraction of TP in all estuarine sectors and both TP and IP correlated significantly with the fine sedimentary (silt + clay) grain-size fraction. The fine surface sediments acted as a trap for IP at the fresh water–

low salinity interface, which also corresponded to the region of a DIP sink in surface waters. In general, the short sediment cores showed that TP and IP contents increased from 15 cm depths to the top layer. Published sedimentation rates from additional cores taken at the sites of the short cores of this study, implied that depositional alterations of TP and IP increased during the early 1970s, which corresponded to the onset of anthropogenic disturbances from crop plantations in the lowland plains of the river end-member and urbanization at the estuary's mouth and along the adjacent coast.

Keywords Phosphorus · Sediments · Semi-pristine estuary · Guaratuba Bay · SE Brazil

Introduction

The growing human population along the coastal zone has contributed to the enhancement of cultural eutrophication of fresh and marine water bodies set along the land-sea interface. Human effluent inputs of dissolved and particulate matter, inorganic and organic carbon (C), nitrogen (N) and phosphorus (P) from domestic, agricultural, and industrial activity, and fuel combustion, are the major drivers. Changes of the cycles of these bio-essential elements, primary productivity, dissolved oxygen consumption, flora and fauna biodiversity, fisheries yields and the deterioration of the water quality and ecosystem health and its services, correspond to the manifold impacts of cultural eutrophication upon aquatic water bodies (Vollenweider 1968; OECD 1982; Golterman and Oude 1991; Nixon 1995; Knoppers et al. 1999; Cloern 2001; Alvera-Azcarate et al. 2003; Huang et al. 2003; Coelho et al. 2004; Crossland et al. 2005; Whitall et al. 2007; Chai et al. 2006;

L. C. Cotovicz Junior (✉) · N. Brandini · B. A. Knoppers
Departamento de Geoquímica, Instituto de Química,
Universidade Federal Fluminense (UFF), Outeiro de São João
Batista, CEP 24.020-141, s/no, Niterói, RJ, Brazil
e-mail: lcc.junior@gmail.com

E. C. Machado · R. C. Zem
Centro de Estudos do Mar (CEM), Universidade Federal do
Paraná (UFPR), Avenida Beira-Mar, s/no Pontal do Sul,
Curitiba, PR, Brazil

Martin et al. 2010; Gireeshkumar et al. 2012; Cotovicz Junior et al. 2013; among manifold others).

Phosphorus, together with C, N, trace metals, vitamins, etc., corresponds to one of the essential major biogenic elements necessary for the sustenance of biological growth. Its main natural sources and release mechanisms from the watershed include rock weathering, soil erosion, mineral transport and organic matter degradation. Human activities, like mining of phosphate rock, P usage as a component of fertilizers in agriculture, detergents, animal feed supplements and other technical applications, has since the 1950s more than doubled P inputs to aquatic environments, affecting their metabolism, trophic state, water quality and proliferations of nitrogen-fixing cyanobacteria after exhaustion of dissolved inorganic nitrogenous nutrients (Tiessen 1995; Rast and Thornton 1998; Mackenzie et al. 1998; Ruttenberg 2005; Russell et al. 2008).

Phosphorus has, traditionally, also been considered as the prime limiting nutrient for the sustenance of primary production in fresh waters, in contrast to nitrogen in marine waters (Vollenweider 1968; Hecky and Kilman 1988; Nixon 1981; Golterman and Oude 1991). However, many estuaries and coastal lagoons of the humid tropical girdle are subject to spatial and temporal shifts between phosphorus versus nitrogen limitation. The magnitude and seasonal uni-modal pattern of freshwater inflow and associated suspended particulates, C, N and P composition and final inputs to the estuary, are related to the nature of wash-out from the watershed, the residence times of the estuarine waters and also the interaction between mangroves, the redox conditions of the upper layers of the sediments, and the renewal of surface pore waters by density displacement from advection of tidal more saline waters along the bottom, which may enhance the release of P to the water column (Knoppers 1994; Knoppers et al. 1999; Fisher et al. 2006; Bouwman et al. 2009).

Estuaries retain and accumulate a fraction of the river-borne particulates and associated macro and micro bio-elements by deposition in their sediments (Jennerjahn and Ittekkot 2002; Machado and Lacerda 2004; Sabadini-Santos et al. 2009). Manifold studies have shown that estuaries may act as important sinks for phosphorus, part of which, however, may also be gradually transported to the coast by surface sediment material cascading over longer time scales and the nature of the tidal regime (Meybeck 1993; Nixon et al. 1996; Fang 2000; Gireeshkumar et al. 2012). When dissolved phosphorus species enter an estuary and come in contact with low salinity waters, particularly within the ranges of 0–1 and 1–5, they become prone to intense particle-water interactions due to changes of the ionic strength operating at the particles surface and also the nature of their coatings (Bourton and Liss 1976; Morris et al. 1981; Turner and Millward 2002; Andrieux-Loyer

and Aminot 2001). Several processes in the oligohaline salinity zone may act in concert being responsible for the non-conservative behavior of, in particular, DIP. These processes include DIP adsorption onto the particle, co-precipitation with aluminum/iron oxi-hydroxides, inclusion of particulate P in organic floccules and aggregates, which eventually deposit on the sediment surface. Depending on the degree of advection, the particles may also be deposited slightly further downwards in the estuary. In contrast, P particle desorption and biological uptake account for the main processes acting in the less turbid higher salinity zones of the lower estuary (Bourton and Liss 1976; Morris et al. 1981; Turner and Millward 2002; Pagliosa et al. 2005).

The importance of sediments as a potential sink and/or a source of phosphorus has also been highlighted in shallow coastal areas, also linked to the redox conditions of the sediment-water interface and the efficiency of surface porewater wash-out by the process of density displacement during tidal intrusion of higher density marine waters (Fisher et al. 1982; Caraco et al. 1990). Furthermore, the sediment geochemical record can also indicate the quality and intensity of current and historical impacts on the aquatic system, as well as, to some degree evaluate anthropogenic impacts and help to ascertain its potential influence on the estuary's nutrient budget (Crossland et al. 2005; Yilmaz and Koç 2012).

This study describes the distribution of P in surface and recent sediments coupled to the behavior of P in the water column along the estuarine mixing zone of the semi-pristine Guaratuba Bay estuary, set at the southeastern Brazilian coast. Its watershed and estuary forms part of the Environmental Protected Área of Guaratuba (APA-Guaratuba, in Portuguese), which is also inserted in the Protected State Area of Boguaçu and Protected National Area of Saint Hilaire-Lange, governed by the Brazilian Environmental Legislation.

Materials and methods

The study area

The estuarine system of Guaratuba Bay (GB), Paraná State, is located in the southeastern coastal region of Brazil (25° $51'80'S$, 48° $38'20'W$; Fig. 1). The watershed and estuary are set within the sub-tropical humid coastal zone of SE Brazil. Its climate is of Köppen type Aw with warm wet summers (from October to March) and cold dry winters (from April to September). The inter-annual precipitation range varies between 2,000 and 3,000 mm at the lower, middle and upper premises of the watershed (Marone et al. 2004; Mizerkowski 2011). The estuary is about 15 km long,
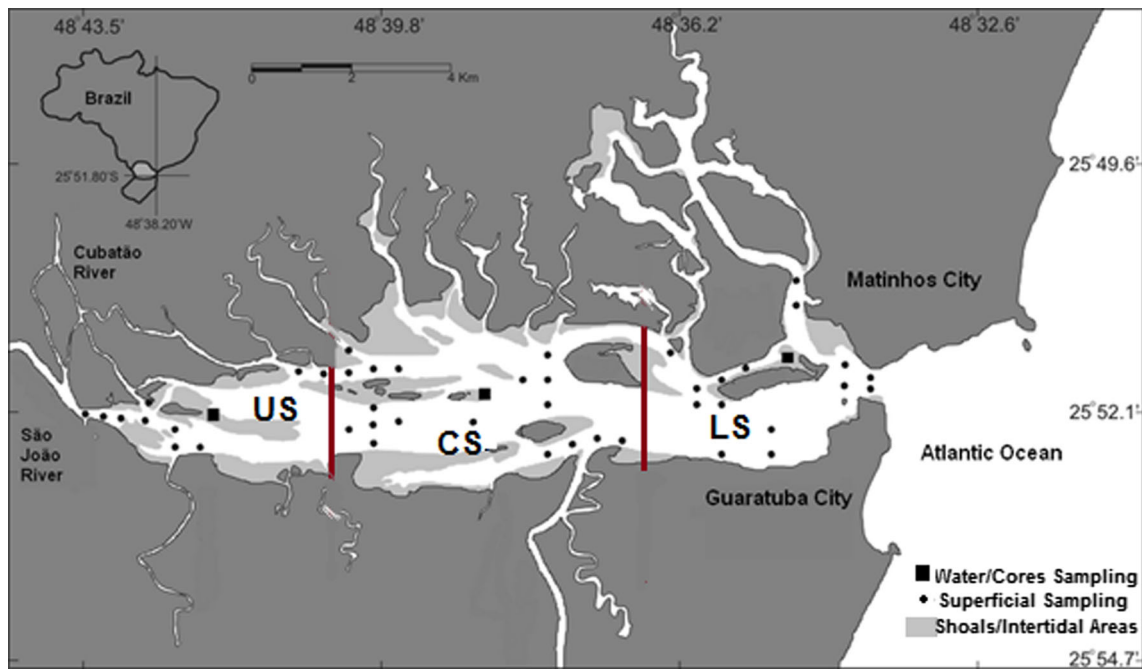
Fig. 1 Map location of the Guaratuba Bay. The *black circles* are the locations of the superficial collected samples; the *black squares* are the locations of the water/sediment cores collected samples. *US* upper sector (median depth 1.6 m); *CS* central sector (median depth 1.9 m); *LS* lower sector (median depth 5.6 m). The shoals/intertidal areas marked in the map have depths <2 m in the flood tide. The two red lines separate the sector domains

area of 48.57 km^2, 3.8 m mean depth, surrounded by grass plains and mangrove forests along its northern margin and subject to wash-out effects from micro-tidal pumping (1.5 m range) (Brandini 2008; Sanders et al. 2006). Two towns are located on opposite sides of the estuary's mouth, with Matinhos city (28,000 inhabitants) at the northern flank and Guaratuba city at the southern flank (30,000 inhabitants). In the summer months of January and February, the population can reach at 250,000 inhabitants along the coast. Localized banana and rice cultivation expanded since the early 1970s within the lowland plains of the main Cubatão and São João rivers, which desembouch at the upper estuary with a combined average annual discharge of approximately 80 m^3 s^{-1} (Marone et al. 2004). In spite of the local demographic expansion at the estuary's mouth and coast and subsistence agricultural practices in the river plains, Guaratuba Bay may be regarded as semi-pristine-estuary. It also lacks industries, the mangrove system remains untouched and the dense forests of its high relief drainage basin are protected by environmental law.

Sampling strategy

Surface sediments

The surface sediment samples were collected in June 2005 using cable operated Van Veen grab and GPS positioning

of the sampling stations ($n = 43$). The 43 sites covered the main axis of the estuary and also some tidal plains and river mouths (Fig. 1). For each sample, 2 cm of the superficial layer of the sediment was carefully removed with a spatula, stored in polythene bags and frozen until further analyses of total, inorganic and organic phosphorus in the laboratory. One fraction of each sample was separated ($\sim$150 g) and stored in the refrigerator for the immediate analyses of sediment grain size and organic matter.

Core sediments

Acrylic tubes with a diameter of 7 cm and a length of 21 cm were pre-washed with hydrochloric acid 10 % and distilled water. These were used to collect short sediment cores at three sampling stations set at the upper, central and lower sectors of the estuary, respectively. All the cores were sliced at intervals of 0–2, 2–5, 5–8, 8–11, 11–16, and 16–21 cm. Sampling was performed in September 2005 (winter, dry season) and March 2006 (summer, wet season), during low neap tide. At each point, one core was used to determine physical characteristics, grain size percentage and organic material concentration, and two cores were used to determine the inorganic, organic and total phosphorus concentration. The cores were transported from the estuary to the laboratory in vertical position and stored in a cool room at 4 °C.

Water

During coring, surface water samples were collected in order to determine the following variables: temperature (T), salinity (S), pH, dissolved oxygen (DO), Chlorophyll-a (Chl-*a*), suspended particulate matter (SPM), inorganic dissolved nutrients and total nutrients (nitrate-NO_3, nitrite-NO_2, ammonium-NH_4, phosphate-PO_4, silicate-$Si(OH)_4$, total phosphorus-TP and total nitrogen-TN).

Further information on the distribution and behavior of pH, S, TP and DIP along the estuarine mixing zone were obtained from data compilation of an annual cycle performed in the years of 2004, 2005 and 2006 by Brandini (2008). The figures of the mixing curves for pH, DIP and N:P ratios are included in the electronic supplementary material.

Analytical procedures

The phosphorus analyses in sediments were determined by the procedure described by Aspila et al. (1976). Total P of the sediment was determined by igniting 0.5 g of sediment at 550°C in a muffle furnace and henceforth extracted with 1 N HCl after shaking for 16 h. The inorganic P was determined by extracting sediment with 1 N HCl after 16 h shaking without the ignition. Organic phosphorus was determined by the difference between the total and inorganic fractions. All the wet analysis of phosphorus was done by using molybdate-reagent together with ascorbic acid (Grasshof et al. 1983). The absorbance was measured by a spectrophotometer, Shimadzu model UV-1601PC.

In order to evaluate the reproducibility of the method, one sample was replicated seven times using the procedures for the extraction of total phosphorus. The average concentration was 141.94 ± 2.81 µg g^{-1} (precision of 2 %). The accuracy of the method was validated utilizing the certified reference material (PACS 2), in which a medium ($n = 3$) of the 893.5 µg g^{-1} (accuracy of 7 %) was obtained.

The grain size analyses were carried out by the pipette analysis and sieving method according to Suguio (1973). The sand fraction (>63 µm) was removed by washing the sample through a 63 µm sieve. The silt (<63 and >2 µm) and clay (<2 µm) fractions were analyzed by the pipette method. The average diameter of the grains was calculated by the method of Folk and Ward (1957). Organic matter (OM) was measured as loss on ignition after combustion at 550 °C for 4 h (Jensen et al. 1992). The content of organic matter is obtained by the percentage difference in weight before and after the oxidation. The reproducibility of loss on ignition was 2.9 % (one sample was replicated five times to evaluate the precision of the method).

Temperature (T), salinity (S), dissolved oxygen (DO) and suspended particulate matter (SPM) were measured in situ with a YSI 6600 multiparameter sonde. The SPM and DO sensors were calibrated by the gravimetric and Winkler methods, respectively. The results were compared with the probe readings and SPM and DO values ($r^2 = 0.98$, $n = 8$; $r^2 = 0.92$, $n = 5$; respectively). The water samples for nutrients, Chl-*a*, TN, TP and SPM analysis were taken with a Niskin bottle and kept cold until processing and filtration (GF/F fiber glass Whatman filters). The water samples were stored in PE bottles and kept on ice in the dark until further processing in the lab directly after sampling. The Chl-*a* extraction followed the procedure of Strickland and Parsons (1972) and the nutrient analyses as described in Grasshof et al. (1983).

Results

Surface sediments

The grain size distribution of the superficial sediments was classified into clay, silt, and sand fractions (Table 1). The sediments in this study mainly consisted of fine sandy fractions from the central sector seawards along the sub-aquatic channel. The finer sediments were localized in the upper and partly the lateral premises of the central sector at the intertidal plains and close to the mangrove belts. The fine sandy fractions predominated in the regions with higher hydrodynamic forcing, like in the central-lower deep channel, near the oceanic inlet and at the river confluences. The general trend is the decrease of total and inorganic phosphorus fractions from the upper towards the central sector and lower sectors (Figs. 2, 3). The upper sector had higher values (330 ± 136.7; 234.8 ± 109.9; 95.2 ± 30.4 µg g^{-1}), followed by the central sector (261.3 ± 146.4; 195.0 ± 111.6; 66.3 ± 7.8 µg g^{-1}) and the lower sector with the lower values (114.9 ± 42.7; 91.3 ± 36.2; 23.6 ± 17 µg g^{-1}) for TP, IP and OP, respectively. IP dominated the surface sediments with 75.1 ± 9 % in comparison to TP. Note that in Fig. 2, the size of the circle is proportional to the phosphorus concentration. The white part of the circle refers to the inorganic fraction, while the dark part refers to the organic fraction. Figure 4 depicts that the difference between the organic and inorganic phosphorus increased along the salinity gradient. The upper, central and lower sectors presented the percentages of IP and OP to TP in the upper, central and lower sectors: 70.2 ± 5.2; 74.8 ± 7.4 and 79.2 ± 11.3 %, respectively.

The organic matter (OM) presented a wide range of variation with a maximum of 13.7 % in the upper sector, whereas in four stations the values were <1 %. The

Table 1 Values of fine fraction percentage (<63 μm; silt + clay), silt, clay, organic matter (OM), total phosphorus (TP), inorganic phosphorus (IP), organic phosphorus (OP) and GPS position (UTM geographic coordinate system, Datum WGS 1984) of the superficial sediments according to the sector of the estuary

| Sector	Station number	Latitude (S)	Longitude (W)	IP ($\mu g\ g^{-1}$)	OP ($\mu g\ g^{-1}$)	TP ($\mu g\ g^{-1}$)	OM (%)	Silt (%)	Clay (%)	Fine fraction (%)	Sand (%)
Upper	1	7136,968.25	728,044.53	124.1	70.9	195.0	3.7	0.0	0.0	0.0	100
	2	7136,917.25	728,407.91	140.5	83.3	223.9	0.2	0.0	0.0	0.0	100
	3	7136,882.28	728,761.87	171.2	90.2	261.5	4.4	5.1	0.0	5.1	94.8
	4	7136,834.52	729,247.46	247.4	113.7	361.2	3.5	7.1	4.0	11.2	89.7
	5	7136,302.45	729,850.2	227.5	88.8	316.3	4.2	7.2	4.1	11.4	89.5
	6	7136,656.06	729,846.89	168.9	73.4	242.4	6.8	13.4	7.2	20.6	79.3
	7	7137,265.21	729,308.06	232.2	107.3	339.6	2.2	4.1	2.0	6.1	93.8
	8	7136,299.16	730,353.86	118.4	33.1	151.5	1.5	3.0	4.0	7.0	92.9
	9	7137,823.9	732,334.8	306.8	120.0	426.9	3.6	23.8	3.1	26.9	73.0
	10	7137,775.93	732,838.5	394.4	141.7	536.1	11.2	13.5	4.1	17.6	82.3
	11	7138,250.55	733,342.54	450.9	123.8	574.8	13.6	11.0	10.0	21.0	79.0
Central	12	7137,799.91	733,342.19	335.1	73.5	408.6	5.3	8.2	7.2	15.5	84.5
	13	7136,656.06	733,346.89	192.8	68.3	261.1	4.5	11.4	5.1	16.6	83.3
	14	7136,375.05	733,845.43	138.6	46.1	184.7	1.7	7.0	2.0	9.1	90.8
	15	7136,751.36	733,831.45	219.4	81.1	300.5	7.4	9.5	10.6	20.1	79.8
	16	7137,094.18	733,843.48	381.5	141.6	523.1	10.6	47.8	4.1	52.0	47.9
	17	7137,877.86	733,841.07	278.3	113.9	392.3	8.1	13.4	10.3	23.7	76.2
	18	7137,877.86	734,346.85	403.7	26.2	430.0	10.6	23.1	12.0	35.2	64.8
	19	7136,816.62	734,347.22	208.8	61.3	270.1	3.6	5.1	5.1	10.3	89.6
	20	7136,804.62	735,848.07	348.1	202.1	550.2	6.5	14.8	9.5	24.3	75.6
	21	7137,656.06	736,846.89	143.1	38.8	181.9	3.1	5.0	1.0	6.0	93.9
	22	7138,156.06	737,346.89	123.7	65.6	189.4	3.3	8.1	9.2	17.3	82.6
	23	7137,656.06	737,346.89	162.3	67.2	229.6	2.7	8.2	8.2	16.5	83.4
	24	7137,156.06	737,346.89	171.9	59.4	231.4	2.3	2.0	3.1	5.1	94.8
	25	7136,156.06	737,346.89	124.0	50.5	174.6	5.1	9.0	7.0	16.0	83.9
	26	7136,358.93	737,844.49	97.4	29.9	127.3	12.5	3.9	3.0	6.9	93.0
	27	7136,477.68	738,343.23	45.9	15.6	61.6	1.6	2.0	1.0	3.0	96.9
	28	7136,430.63	738,846.19	51.2	7.7	58.9	1.1	1.0	1.0	2.0	97.9
Lower	29	7138,200.58	739,818.04	83.7	43.2	127.0	3.2	4.1	4.1	8.2	91.7
	30	7137,480.00	740,345.63	75.3	41.8	117.1	1.3	5.1	6.0	11.2	88.7
	31	7137,156.06	740,346.89	69.4	24.2	93.6	2.0	4.0	4.0	8.1	91.8
	32	7136,156.06	740,846.89	72.2	51.8	124.0	3.8	4.1	4.1	8.2	91.7
	33	7137,156.06	740,846.89	62.2	15.0	77.3	4.2	3.0	2.0	5.0	95.0
	34	7137,656.06	740,846.89	71.7	32.8	104.6	2.8	3.1	1.0	4.1	95.8
	35	7137,893.68	741,331.36	91.3	4.8	96.2	1.5	1.0	1.0	2.0	97.9
	36	7136,156.06	741,846.89	165.4	60.7	226.2	2.6	9.2	2.0	11.2	88.7
	37	7136,656.06	741,846.89	84.3	17.6	101.9	0.1	1.0	2.0	3.0	96.9
	38	7139,656.06	742,346.89	45.7	16.0	61.7	0.7	0.0	0.0	0.0	100
	39	7139,156.06	742,346.89	131.3	13.2	144.6	0.8	1.0	1.0	2.0	97.9
	40	7137,958.88	743,329.82	106.9	20.8	127.7	1.9	2.0	1.0	3.0	96.9
	41	7137,536.95	743,315.88	43.5	11.9	55.4	2.5	1.0	0.0	1.0	98.9
	42	7137,474.37	743,842.48	121.4	9.3	130.8	2.2	1.0	0.0	1.0	98.9
	43	7137,701.01	743,841.79	136.5	10.4	146.9	6.2	0.0	0.0	0.0	100
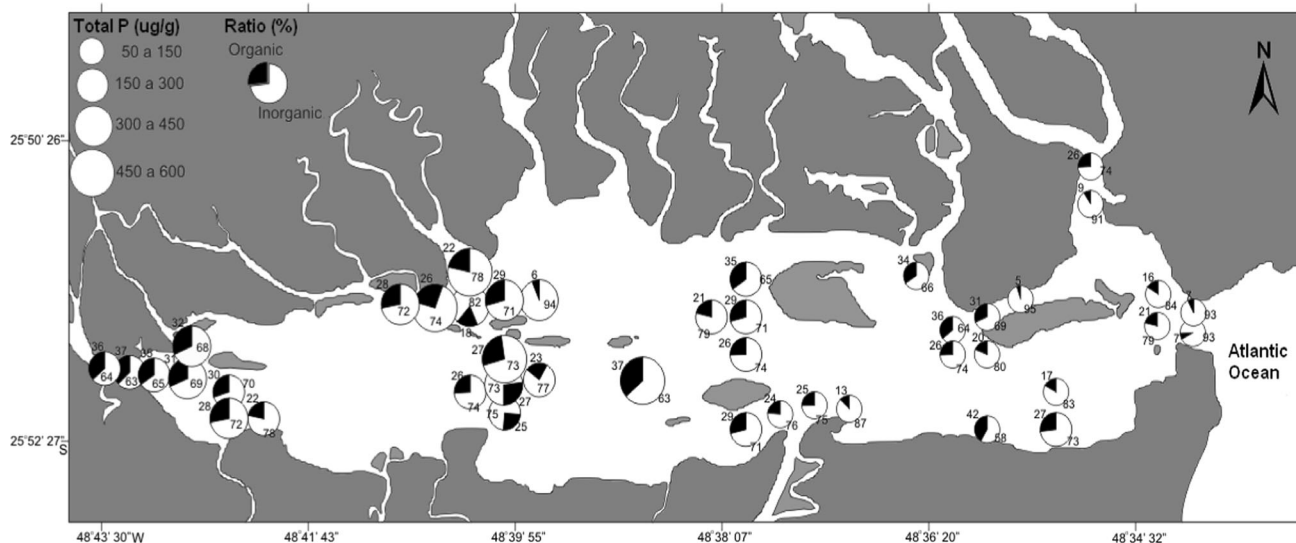
Fig. 2 Spatial map distribution of the P in the superficial sediments of the Guaratuba Bay. Note that the *full circle* represents the concentration of the Total Phosphorus, the *white part* is the inorganic and the *dark part* represents the organic fraction
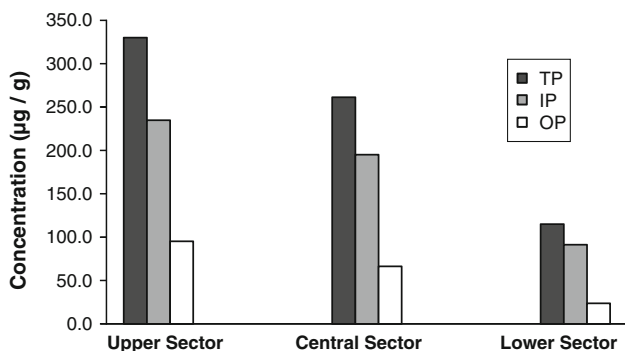

Fig. 3 Mean values of concentration of the total (TP), inorganic (IP) and organic (OP) phosphorus in the upper, central and lower sectors of the Guaratuba Bay
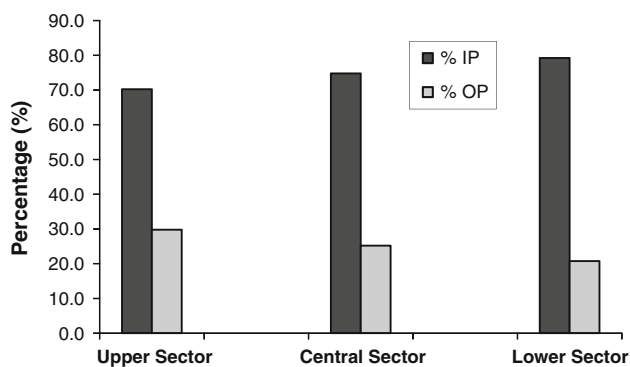

Fig. 4 Mean values of the proportion of inorganic phosphorus (IP) and organic phosphorus (OP) in the upper, central and lower sectors of the Guaratuba Bay

sediments in the upper and central sectors showed similar organic matter contents (5.0 ± 4.1 % and 2.4 ± 1.6 %, respectively), and in the lower sector the organic content was a smaller percentage (2.4 ± 1.6 %).

Sediment cores

The distribution of the mean values for the cores collected in the upper, central and lower sectors of the estuary is summarized in Table 2. The cores of the upper sector of the estuary exhibited the highest values for all the variables. The cores in the central and lower sectors showed similar characteristics for the grain size, OM, and phosphorus concentrations. In general, the total and inorganic phosphorus concentrations increase from bottom layer to surface layer in the upper and lower sectors, with maximum values of 442, 331 and 110 µg g^{-1}, respectively, for TP, IP and OP. In the central sector the observed pattern was different. The organic P fraction showed no vertical gradient in contrast to the inorganic and total P, with oscillations along the core. In all cores, the inorganic phosphorus fraction was higher than the organic one, but in different proportions if the sector is analyzed, for example: the upper sector had the higher mean values for the inorganic fraction (73.5 %), followed by the lower sector (69.9 %) and finally the central sector. Sanders et al. (2006) calculated the sedimentation rate by the ^{210}Pb chronology at the same core sites of this study. The sedimentation rates of the upper, central and lower sectors were 4.5, 3.9 and 4.3 mm year^{-1}, respectively. The bottom layer at 35 cm depth revealed an average age of approximately 82 years in the upper sector, 84 years in the central sector and 78 years in the lower sector.

The sediments showed a predominance of fine sandy grains, with silt and clay particles composing nearly 27–38 % of sediments from the upper sector, and 11–20 % of sediments from the central and lower sector. The sediment cores in the upper sector showed higher percentages

Table 2 GPS position (UTM geographic coordinate system, Datum WGS 1984), mean values and respectives standard deviations of fine fraction percentage (<63 mm; silt + clay), organic matter (OM), total phosphorus (TP), inorganic phosphorus (IP) and organic phosphorus (OP) of the sediment cores collected ($n = 4$ for each sector)

Sector	Latitude (S)	Longitude (W)	Core depth (cm)	Fine fraction (%)	OM (%)	TP ($\mu g\ g^{-1}$)	IP ($\mu g\ g^{-1}$)	OP ($\mu g\ g^{-1}$)
Upper sector	7136,756.12	730,415.37	0–2	27.4 ± 3.1	6.0 ± 1.9	442.1 ± 115.2	331.8 ± 84.3	110.2 ± 38.4
			2–5	31.9 ± 5.0	7.4 ± 0.4	420.5 ± 121.4	314.6 ± 97.7	105.9 ± 25.9
			5–8	38.5 ± 8.0	7.4 ± 0.5	378.6 ± 102.7	286.3 ± 83.5	92.3 ± 22.9
			8–11	37.2 ± 6.1	8.5 ± 0.7	373.3 ± 104.0	266.5 ± 81.1	106.8 ± 25.6
			11–16	29.6 ± 11.7	8.5 ± 2.4	352.6 ± 92.7	272.2 ± 82.4	80.3 ± 29.9
			16–21	32.8 ± 4.4	8.5 ± 0.4	318.3 ± 168.1	214.5 ± 100.6	103.9 ± 74.0
Central sector	7137,946.04	736,230.21	0–2	14.5 ± 6.1	3.8 ± 1.4	165.8 ± 111.2	102.2 ± 57.8	63.5 ± 54.1
			2–5	16.0 ± 0.5	3.9 ± 0.2	215.9 ± 43.6	132.0 ± 38.9	83.9 ± 13.9
			5–8	16.4 ± 5.9	4.5 ± 1.1	197.2 ± 73.3	129.7 ± 52.4	67.5 ± 21.2
			8–11	17.5 ± 2.9	4.5 ± 0.8	140.9 ± 28.8	95.7 ± 21.1	45.2 ± 15.7
			11–16	20.0 ± 0.5	4.2 ± 0.1	165.4 ± 34.8	103.6 ± 35.2	61.9 ± 5.6
			16–21	11.9 ± 0.6	3.4 ± 0.5	168.0 ± 62.9	97.5 ± 27.1	70.5 ± 52.8
Lower sector	7138,143.44	742,306.70	0–2	13.1 ± 0.8	3.4 ± 0.9	228.7 ± 104.4	166.7 ± 67.5	62.0 ± 37.4
			2–5	11.5 ± 5.2	3.0 ± 1.4	221.1 ± 89.9	147.0 ± 78.0	74.0 ± 29.0
			5–8	11.3 ± 3.3	3.5 ± 0.5	191.1 ± 95.4	137.9 ± 69.6	53.3 ± 26.0
			8–11	13.8 ± 5.4	3.2 ± 0.4	189.1 ± 69.6	131.5 ± 63.2	57.6 ± 6.4
			11–16	15.1 ± 0.7	4.3 ± 0.6	162.3 ± 54.9	115.6 ± 43.4	46.7 ± 14.8
			16–21	19.9 ± 4.0	6.1 ± 3.3	169.5 ± 50.6	114.7 ± 36.8	54.8 ± 14.7

Table 3 Physico-chemical water properties of the Guaratuba Bay Estuary. The local water sampling collection was the same as of the cores

Sector/ period	T (°C)	S	DO (mg/L)	DO (%)	Chl-a (μg/L)	Seston (mg/L)	Si(OH)$_4$ (μM)	DIP (μM)	NO$_2$ (μM)	NO$_3$ (μM)	NH$_4$ (μM)	DIN (μM)	TP (μM)	TN (μM)	DIN:DIP Ratio	TN:TP ratio
US/Sept 05	17	0	6.2	93.2	2.6	19.5	100.51	0.39	0.17	9.49	2.42	12.08	0.72	15.26	30.97	21.19
CS/Sept 05	19	9	6.9	92.4	3.8	42.7	82.58	0.30	0.18	5.59	0.62	6.39	1.16	17.47	21.30	15.06
LS/Sept 05	19.5	24	7.3	104.0	3.0	43.5	33.91	0.24	0.14	2.88	1.41	4.43	1.40	9.94	18.46	7.10
US/Mar 06	28	0	3.8	57.9	7.3	35.7	122.01	0.04	0.11	1.94	1.96	4.02	1.37	9.49	100.5	6.93
CS/Mar 06	28.5	9	3.5	50.2	11.9	39.9	76.29	0.03	0.08	0.19	1.57	1.85	1.98	7.40	61.67	3.74
LS/Mar 06	28.5	25	5.9	83.7	9.9	42.7	35.53	0.17	0.09	0.18	0.96	1.24	1.48	8.53	7.13	5.76

US upper sector, *CS* central sector, *LS* lower sector

of fine grain size sediments than those of the central and lower sectors. Despite some fluctuations, the trend corresponds to a decrease in sediment grain size toward the top layers in the three sectors of the bay.

Water properties

The physical–chemical properties of the water were prone to some seasonal differences (Table 3). The temperature and Chl-*a* showed higher values in the summer, with a range between 17 and 28.5 °C and 2.6–11.9 μg L^{-1}, recpectively. The concentrations of PO$_4$, NO$_2$, NO$_3$, NID and TN were higher in the winter, with ranges of the 0.03–0.39,

0.08–0.18, 0.18–9.49, 1.24–12.08 μM, respectively. The spatial gradient was verified for some parameters, with the inner sector presenting the higher values for Si(OH)$_4$, PO$_4$, NO$_2$, NO$_3$ DIN, NT, DIN:PID and TN:TP ratios. TP and NH$_4$ were not subject to marked seasonal differences, with ranges of the 0.72–1.98 and 0.62–2.42 μM, respectively.

Discussion

The spatial variability of the grain size characteristics of the sediments of Guaratuba Bay results from a complex interaction between hydrodynamics, geomorphology and the estuarine bed. The shallow regions along the lateral

premises of the estuary, including the influence from mangroves, were likely formed due to lower physical forcing. The channel and deeper regions were subject to stronger advection due to tidal pumping. In accordance to the hydrological-geomorphological configuration and the sedimentological characteristic the estuary was divided into three main sectors; the upper, central and lower sectors (Zem et al. 2005). The upper sector is governed by fluvial processes and salinity gradients from about 0–10, the central sector, harbors the oscillating mixing zone from S of about 10–25, and is subject to the influence from mangroves. The lower sector is polyhaline to euryhaline. Marone et al. (2004), Brandini (2008) and Mizerkowski et al. (2012) also determined similar extensions of the three compartments from water property analyses and physical studies. Generally, the values for grain size fraction and the estuary depth decreased from downstream to upstream, showing lateral variations. The OM content in the sediment showed spatial variation, following the general pattern of particle size distribution of sediments, with the highest levels related to the fine fraction localized at the lateral depositional banks of the estuary, tidal flats (at the edges of the bay) and shoals (in protected areas of ebb tide conditions, mainly near small islands). These areas are characterized by shallow (<1 m) and poorly sorted sediments composed primarily of silts and very thin sands.

Pearson's correlations were calculated for the surface sediment parameters (Table 4). The total and inorganic phosphorus were correlated with the fine fraction ($r = 0.75$ and 0.76, respectively; Fig. 5), whereas the organic phosphorus and organic matter showed minor correlations with the fine grain size ($r = 0.62$ and 0.65, respectively).The inorganic phosphorus fraction was significantly correlated with total phosphorus ($r = 0.98$; $p < 0.001$) (Fig. 6).The spatial distribution of total and inorganic phosphorus concentrations in superficial sediments of Guaratuba Bay is governed by the grain size of the sediment. The particle size, in turn, is governed by the local hydrodynamics. The sediments in the area with high hydrodynamics have coarser grains, and are regions generally deeper and/or nearly the mouth of rivers and areas with greater influence of tides (near the mouth), where phosphorus levels are lower. The locations with lower hydrodynamics tend to adsorb phosphorus compounds. Finer grains with high specific surface areas-to-weight ratio have greater pollutant adsorption capacity, and sediments with higher portion of clay and silt grains have larger capacity to adsorb more P (Andrieux-Loyer and Aminot 2001; Frankowski and Bolałek 1997; Frankowski et al. 2002; Zhu et al. 2012). However, Borges et al. (2009) demonstrated that sediments with high anthropogenic disturbances lacked correlations between the TP concentration and the fine grain size fraction. This is due to the higher variability and magnitude of phosphorus inputs whereas grain size remained quantitatively stable and with similar grain size.

Zhou et al. (2007), studying the sediments of the Yangtze Estuary in China, encountered no TP variation in relation to the grain-size distribution. The authors discussed that the phosphorus in the sediments was mostly in the form of IP, with 80 % calcium-bound phosphate (Ca–P), i. e., the apatite inorganic phosphorus (AIP) and 20 % of non apatite inorganic phosphorus (NAIP), that are controlled by chemisorption on colloidal ferric and aluminum oxi-hydroxide (Fe/Al–P) coatings adsorbed on the surface of fine particles. Although Fe/Al-bound phosphate (Fe/Al–P) are closely related to fine-grained particles, Ca–P is evenly distributed in various grain-size classes (Andrieux-Loyer and Aminot 2001). Avilés and Niell (2005), in turn, encountered correlation between AIP and fine grain size ($r^2 = 0.75$, the same order of magnitude of this study), and the NAIP correlation with fine grain size that the authors encountered was more strong ($r^2 = 0.94$). Ribeiro (2006, unpublished work) showed that in Guanabara Bay (RJ) a neat spatial gradient in the concentrations Al and Fe was present along the fresh- and marine water end members and the three compartments of the bay itself, showing spatial gradient distribution similar to P in this study. The net removal of P and especially DIP in estuaries is typically driven by particle-water interactions, like adsorption, flocculation of humic-iron/aluminum complexes and biological uptake (Fox 1990; Turner and Millward 2002).

The hypothesis that the sediments of the upper sector trap IP of the water column is corroborated by the water properties of the system. The composite concentration salinity plots of the electronic supplementary figures, exhibits a clear removal of DIP between salinity of 0–8, being concomitant with a marked increase of pH in the same range (Electronic Supplementary Material 01). Morris et al. (1981) reported that the most intense removal occurs first between S from 0 to 1 and henceforth, between S from 1 to 5. Furthermore, the composite plot between DIP and salinity exhibited a typical concave non-conservative behavior down to the lower estuary, increasing again towards the tidal channel. The total removal of DIP was also from uptake by phytoplankton as shown by the Chl-a behavior (Mizerkowski et al. 2012). The higher IP concentrations of the sediments in the transition zone between the upper and central sectors, clearly implies that DIP adsorption onto fine particles and their subsequent deposition were coupled. Brandini (2008) also confirmed the non-conservative behavior of DIP along the salinity gradients. The Guanabara Bay exports nutrients to the ocean, but a large fraction is removed and accumulated inside of the Bay (Brandini 2008; Mizerkowski et al. 2012). The net deposition of P in sediments creates a relatively low P environment (Atkinson 1987). Preservation of phosphorus

Table 4 Pearson correlation matrix for inorganic phosphorus (IP), organic phosphorus (OP), total phosphorus (TP), organic matter (OM), silt, clay, fine fractions (silt + clay) and sand in the Guaratuba Bay estuary, Southern Brazil

	IP	OP	TP	OM	Silt	Clay	Fine fraction	Sand
IP	1.00							
OP	0.77*	1.00						
TP	0.98*	0.88*	1.00					
OM	0.70*	0.48	0.67*	1.00				
Silt	0.70*	0.59*	0.70*	0.58*	1.00			
Clay	0.59*	0.46	0.58*	0.56*	0.48	1.00		
Fine Fraction	0.76*	0.62*	0.75*	0.65*	0.96*	0.71*	1.0	
Sand	−0.76*	−0.62*	−0.75*	−0.65*	−0.96*	−0.71*	−1.0*	1.0

$N = 43$

* Correlations are significant at $p < 0.001$
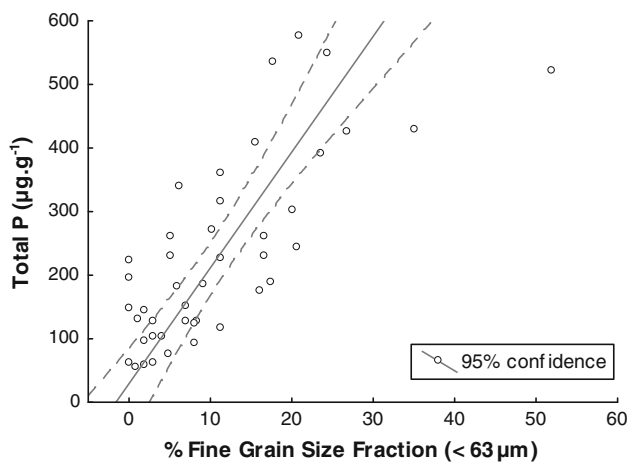
Fig. 5 Relationship between the total phosphorus and the fine grain size fraction in the superficial sediments of the Guaratuba Bay ($r = 0.75$; $p < 0.001$)
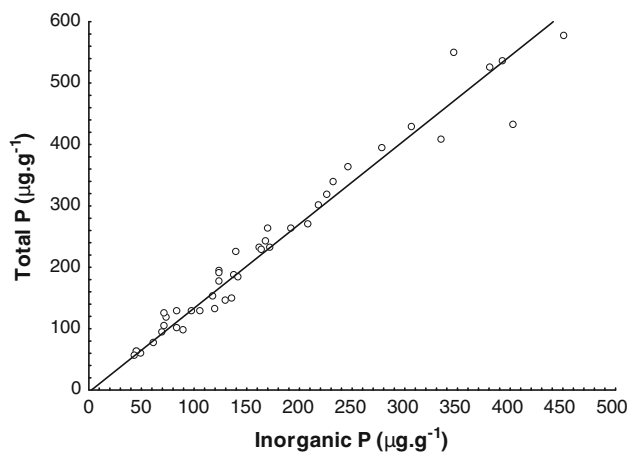

Fig. 6 Relationship between the total phosphorus (Total P) and the inorganic phosphorus (Inorganic P) in the superficial sediments of the Guaratuba Bay ($r = 0.98$; $p < 0.001$)

in sediments depends on several factors including the nature of phosphorus compounds, sedimentation rate, bioturbation, or irrigation by bottom current, bottom-water oxygen content and diagenetic processes (Aydin et al. 2009). Because these parameters vary in different sedimentary environments, burial flux of phosphorus may vary depending on the type of depositional environment like the salinity gradient, closeness of river runoff, hydrodynamic and geomorphological conditions (Atkinson 1987; Cha et al. 2005; Aviles et al. 2006).

The N/P molar ratio in the water column was highest in low saline upper sector. Nitrogen entering the estuary with high concentrations and IP adsorption and particle deposition must have been responsible for the high N/P ratios found. As such, this upper low salinity transition zone could be regarded as limited by nitrogen instead off P. Brandini (2008) and Mizerkowski et al. (2012) also showed this pattern, indicating strong limitation of the primary production by phosphorus in the upper sector (Electronic Supplementary Material 01). In the lower sector, however, nutrient limitation shifts towards nitrogen. Spatial and temporal shifts between P and N limitation has been reported for a variety of systems, particularly those set along the tropical girdle (Hecky and Kilman 1988; Knoppers 1994).

In all samples, the IP concentrations were higher than OP. The predominance of IP was found in many estuaries of Brazil and the world (Zwolsman 1994; Liu et al. 2004; Ashraf et al. 2006; Pagliosa et al. 2005; Marins et al. 2007). This is one of the most important features differentiating sediments from soils, in which organic forms predominate (Gunduz et al. 2011). This predominance of IP is explained by high rates of mineralization of OP in the water column without the participation of the sediment. The cycling of organic P has rapid turnover times, and is driven by decomposition, mineralization and assimilation by autotrophic production (Bouwman et al. 2009). The

accumulation of organic phosphorus can occur by rapid phosphorus burial, and a small fraction of OP would be incorporated into sediments. Another factor, not exclusionary, would be the great efficiency of remineralization of the OP in sediments.

There is correlation between OP and fine fraction sediment, but in small proportion if compared to the IP and TP fractions. Andrieux-Loyer and Aminot (2001) argued that the lack of the relation between OP and fine fraction sediment might be due, at least partially, to the fact that OP concentration in sandy sediments is also associated with larger particles (adsorbed in the form of bacterial films). Carol et al. (2012) did not encounter a link among the three fractions (sand, silt, clay) and OM. In summary, OM is a component that does not explain in a satisfactory way the presence of P in the system. Other factors seem to govern the distributions of the OP and OM concentrations in the estuary sediments. The distribution of OP in the sediments can be altered by the proximity of organic sources (rivers, swamps, sewage outfalls) and also by the high productivity in the water column (Clavero et al. 1999). The shallow depth of the water column can also favor OP regeneration (Faul et al. 2005). The higher organic fractions observed at some sites of the central sector and the lateral flats of Guaratuba Bay are probably related to additional sources of organic material such as the lateral input from mangroves especially along the northern margin of the system, which is more densely occupied by mangrove swamps than the southern margin mangrove and rivers. Mizerkowski et al. (2012) encountered the higher levels of chlorophyll-a (maximum values about 29 μg L^{-1}, related to the increase of the trophic status in the middle area of the estuary), indicating that this region is the most productive in the Bay. Brandini (2008) also showed that the central area is the most productive of the Bay due to the mangrove contributions, functioning as nutrient sink and organic matter source.

The concentrations of the IP and TP in sediment cores increased from bottom to surface in the upper and lower sectors. This vertical profile pattern reflects the recent influence from land as a source of sediments (Liu et al. 2004). The phosphorus gradient observed has also been observed in estuaries subject to urbanization and domestic effluent discharge (Borges et al. 2009).The results suggest an increase in the flux of phosphorus from the water column to the sediment possibly marking an onset anthropogenic influence in the sediments of the Guaratuba Bay. These increases toward the top of the cores are more evident in cores collected in upper and lower sectors, precisely the sectors that have some anthropogenic influence; the upper sector being an area that receives more direct influences from agriculture runoff (mainly rice and banana plantations) due to the proximity of the river, and the lower

sector being the region with the largest urbanization in its surroundings. Sanders et al. (2006) studied the sedimentation and accumulation rates in the Guaratuba Bay by ^{210}Pb profiles and the fluxes of the sediments from the water to the sediments have increased since the 1950 as a result of the beginning of anthropogenic activities in the watershed of the estuary. The authors also pointed that the local government does not have reliable information about the extent of the plantations within the lower Guaratuba Bay basin before the 1990s. Thereafter, the area of banana and rice plantations has increased steadily at 6 % per year. It is known that agricultural activity has been steadily increasing beginning from the second half of the 20th century. This growing trend appears to be accompanied by anthropogenic Hg concentrations. According to Godoy et al. (1997), this tendency in Hg fluxes is an indication of increasing agricultural practices, which have been using fertilizers that contain Hg as a sub-product. On the other hand, only about 45 % of the population of Guaratuba city, set partially at the estuary's mouth and spreads further along the coast, is not included in the sewage treatment system, and in the last decade the population growth was 17.72 % (SANEPAR 2003).

Mizerkowski (2011) classified the trophic states of Guaratuba Bay by the ASSETS Model (Assessment of the Estuarine Trophic Status) (Bricker et al. 2003) and TRIX index (Vollenweider et al. 1998). The indices classified the system as being mesotrophic, susceptible to higher anthropogenic input of nutrients and cultural eutrophication process, as the system exerts a low potential to dilute and export nutrients and low oxygen levels in some areas. This trophic status and assessment of the eutrophication in the Guaratuba Bay should be taken into account as a warning, given that the accumulation of the phosphorus in sediments is increasing. The P concentration ranges in sediments for other estuaries in Brazil and other countries suggest that the P concentrations in the Guaratuba Bay sediments were comparable with those in the regions that exhibit small to moderate anthropogenic influence (Table 5).

Conclusions

The TP and IP had significant correlations with the grain size, indicating that the particle size governs the distribution of P forms in sediments of the Guaratuba Bay. The shallow and low hydrodynamic regions tend to act as sinks of P (greater predominance in upper and central sectors), and appears generating P limitation in these regions (corroborated by high N:P values in this study and others focusing in the water properties). The OP and OM, in turn, had lower correlations with the particle size, suggesting that other processes can govern the organic content in the

Table 5 Comparison of the total, inorganic and organic phosphorus range concentrations (maximum and minimum values) of the Guaratuba Bay with other estuaries and coastal regions

System	TP (µg/g)	IP (µg/g)	OP (µg/g)	Reference
Guaratuba Bay (PR)—Southeast Brazil—semi-pristine estuary	98–546	53–388	30–203	This study
Jaguaribe River Estuary (CE)—Northeast Brazil—semi-arid coast, oligotrophic region	77–157	43–124	25–58	Marins et al. (2007)
Guanabara Bay (RJ)—East Coast Brazil—highly urbanized and eutrophized	172–1,551	81–1,396	40–241	Borges et al. (2009)
Coastal sediments from Rio de Janeiro (RJ)—Southeast Brazil—impacted from sewage disposal	370–2,286	243–1,814	127–703	Carreira and Wagener (1998)
Continental shelf of the Amazon River (AM)—North Brazil—highly tidal oscillation and freshwater influence, oligotrophic	46–366	7–301	6–211	Santos et al. (2010)
Cananéia-Iguape estuarine lagoonal system (SP)—Southeast Brazil—moderate anthropogenic impact, agriculture and deforestation	44–935	26–635	15–470	Barcellos and Furtado (2005)
Continental shelf of Santa Catarina State—Southeast Coast Brazil	38–580	25–406	3–72	Pellens et al. (1998)
Central region of the Great Barrier Reef continental shelf—Australia	167–576	125–341	53–267	Monbet et al. (2007)
Southwestern East Sea—Japan Sea—oceanic deep-water sediments	403–1,100	146–983	112–310	Cha et al. (2005)
Daliao River Estuary—China—temperate monsoonal zone, receiving about 1,200 million ton of industrial and domestic wastewater annually, contaminated	230–841	131–793	30–204	Wang et al. (2009)
Bohai and Yellow Sea—China—region surrounded by areas of high population growth and economic development	232–620	173–511	9–217	Liu et al. (2004)
Mondego Estuary—Portugal—temperate, large áreas of intertidal flats, eutrophic gradient	465–837	–	–	Coelho et al. (2004)
Golfo Norte da California—USA/México—high antrhopogenic influence	622–6,679	414–5576	58–551	Daesslé et al. (2004)
Cochin Estuary—India—Coastal area influenced by the back water sand, growing population and seasonal variations.	526–956	499–810	28–194	Ashraf et al. (2006)
Hooghly Estuary (Ganges)—India—Industrialized.	258–500	250–476	50–118	Vaithiyanathan et al. (1993)

estuary, as the primary production of the water column, the rapid remineralization of the OP to IP and the proximity with the sources of organic material. The concentrations of TP and IP showed, in general, a gradient increasing from downstream–upstream estuary.

The vertical profiles of the sediment cores indicated a trend of higher concentrations in the upper layers, suggesting an increase in the flux of phosphorus to the sediment in the last 30 years. The concentrations suggest the onset of detection of anthropogenic disturbances in the sediment using phosphorus as a proxy for domestic and agricultural pollution, serving as an indicator of previously unknown P behavior in a coastal region that is being exploited for agricultural development.

The phosphorus concentrations found in this study are within the range of values reported for sediments of some Brazilian estuaries and other coastal regions. Compared with other systems, the contents of the phosphorus in Guaratuba Bay is similar to oligo-meso-trophic regions.

References

Alvera-Azcarate A, Ferreira JG, Nunes JP (2003) Modelling eutrophication in mesotidal and macrotidal estuaries. The role of intertidal seaweeds. Estuar Coast Shelf Sci 57:715–724. doi:10.1016/S0272-7714(02)00413-4

Andrieux-Loyer F, Aminot A (2001) Phosphorus forms related to sediment grain size and geochemical characteristics in French Coastal areas. Estuar Coast Shelf S 52:617–629. doi:10.1006/ecss.2001.0766

Ashraf M, Edwin PL, Meenakumari B (2006) Studies on the seasonal changes of phosphorus in the marine environments off Cochin. Environ Int 32:159–164. doi:10.1016/j.envint.2005.08.006

Aspila KI, Agemian H, Chau ASY (1976) A semi-automated method for the determination of inorganic, organic and total phosphate in sediments. Analyst 101:187–197

Atkinson MJ (1987) Low phosphorus sediments in a hypersaline marine bay. Estuar Coast Shelf Sci 24:335–347

Avilés A, Niell FX (2005) Pattern of phosphorus forms in a Mediterranean shallow estuary: effects of flooding events. Estuar Coast Shelf Sci 64:786–794. doi:10.1016/j.ecss.2005.05.002

Aviles A, Rodero J, Amores V, Vicente I, Rodriguez I, Niell X (2006) Factors controlling phosphorus speciation in a Mediterranean basin (River Guadalfeo, Spain). J Hydro 331:396–408. doi:10.1016/j.jhydrol.2006.05.024

Aydin I, Aydin F, Saydut A, Hamamci C (2009) A sequential extraction to determine the distribution of phosphorus in the seawater and marine surface sediment. J Hazard Mater 168:664–669. doi:10.1016/j.jhazmat.2009.02.095

Barcellos RL, Furtado V (2005) Distribuição e características do fósforo sedimentar no sistema estuarino lagunar Cananéia-Iguape. Geochim Bras 19(1):22–36

Borges AC, Sanders CJ, Santos HLR, Araripe DR, Machado W, Patchineelam SR (2009) Eutrophication history of Guanabara Bay (SE Brazil) recorded by phosphorus flux to sediments from a degraded mangrove area. Mar Pollut Bull 58:1739–1765. doi:10.1016/j.marpolbul.2009.07.025

Bourton JD, Liss PS (1976) Estuarine chemistry. Academic Press, London

Bouwman AF, Beusen AHW, Billen G (2009) Human alteration of the global nitrogen and phosphorus soil balances for the period 1970–2050. Global Biogeochem Cycles 23:1–16. doi:10.1029/2009GB003576

Brandini N (2008) Biogeoquimica da Baía de Guaratuba. PhD Thesis, Universidade Federal Fluminense

Bricker SB, Ferreira JG, Simas T (2003) An integrated methodology for assessment of estuarine trophic status. Ecol Model 169:39–60. doi:10.1016/S0304-3800(03)00199-6

Caraco N, Cole J, Likens GE (1990) A comparison of phosphorus immobilization in sediments of freshwater and coastal marine systems. Biogeochemistry 9:277–290. doi:10.1007/BF00000602

Carol ES, Kruse EE, Tavani EL (2012) Physicochemical characterization of sediments from the coastal wetland of Samborombón Bay, Argentina. J South Am Earth Sci 34:26–32. doi:10.1016/j.jsames.2011.07.008

Carreira RS, Wagener AR (1998) Speciation of sewage derived phosphorus in coastal sediments from Rio de Janeiro, Brazil. Mar Pollut Bull 36(10):818–827. doi:10.1016/S0025-326X(98)00062-9

Cha H, Lee C, Kim B, Choi M, Ruttenberg K (2005) Early diagenetic redistribution and burial of phosphorus in the sediments of the southwestern East Sea (Japan Sea). Mar Geol 216(3):127–143. doi:10.1016/j.margeo.2005.02.001

Chai C, Yu Z, Song X, Cao X (2006) The status and characteristics of eutrophication in the Yangtze River (Changjiang) Estuary and the adjacent East China Sea, China. Hydrobiologia 563:313–328. doi:10.1007/s10750-006-0021-7

Cloern JE (2001) Our evolving conceptual model of the coastal eutrophication problem. Mar Ecol Prog Ser 210:223–253. doi:10.3354/meps210223

Clavero V, Jose J, Palomo L, Fernandez JA, Niell FX (1999) Water management and climate changes increases the phosphorus accumulation in the small shallow estuary of the Palmones River (southern Spain). Sci T Environ 228:193–202. doi:10.1016/S0048-9697(99)00045-5

Coelho J, Flindt M, Jensen H, Lillebo A, Pardal M (2004) Phosphorus speciation and availability in intertidal sediments of a temperate estuary: relation to eutrophication and annual P-fluxes. Estuar Coast Shelf Sci 61(4):583–590. doi:10.1016/j.ecss.2004.07.001

Cotovicz Junior LC, Brandini N, Knoppers BA, Mizerkowski BD, Sterza JM, Ovalle ARC, Medeiros PRP (2013) Assessment of the trophic status of four coastal lagoons and one estuarine delta, eastern Brazil. Environ Monit Assess 185:3279–3311. doi:10.1007/s10661-012-2791-x

Crossland CJ, Kremer HH, Lindeboom HJ, Crossland JI, Le Tissier MDA (2005) Coastal fluxes in the anthropocene. The land-ocean interactions in the coastal zone project of the international geosphere-biosphere programme series: global change—the IGBP series. Springer, Berlin

Daesslé LW, Camacho-Ibar VF, Carriquiry JD, Ortiz-Hernández MC (2004) The geochemistry and sources of metals and phosphorus in the recent sediments from the Northern Gulf of California. Cont Shelf Res 24(17):2093–2106. doi:10.1016/j.csr.2004.06.022

Fang TH (2000) Partitioning and behavior of different forms of phosphorus in the Tanshui estuary and one of its tributaries, Northern Taiwan. Estuar Coast Shelf Sci 50:689–701. doi:10.1006/ecss.1999.0604

Faul KL, Paytan A, Delaney ML (2005) Phosphorus distribution in sinking oceanic particulate matter. Mar Chem 97(3–4):307–333. doi:10.1016/j.marchem.2005.04.002

Fisher TR, Carlson PR, Barber RT (1982) Sediment nutrient regeneration in three North Carolina estuaries. Estuar Coast Shelf Sci 14:101–116. doi:10.1016/S0302-3524(82)80069-8

Fisher TR, Hagy JD, Boynton WR, Williams MR (2006) Cultural eutrophication in the Choptank and Patuxent estuaries of Chesapeake Bay. Limnol Oceanogr 51:435–447. doi:10.4319/lo.2006.51.1_part_2.0435

Folk R, Ward W (1957) Brazos river bar: a study in the significance of grain size parameters. J Sediment Res 27:3–26

Fox LE (1990) Geochemistry of dissolved phosphate in the Sepik River Estuary, Papua, New Guinea. Geochim Cosmochim Acta 54:1019–1024. doi:10.1016/0016-7037(90)90435-N

Frankowski L, Bolałek J (1997) Phosphate desorption from the sediments in the Pomeranian Bay (Southern Baltic). Oceanol Stud 1:205–214

Frankowski L, Bolałek J, Szostek A (2002) Phosphorus in bottom sediments of Pomeranian Bay (Southern Baltic—Poland). Estuar Coast Shelf Sci 54(6):1027–1038. doi:10.1006/ecss.2001.0874

Gireeshkumar TR, Deepulal PM, Chandramohanakumar N (2012) Phosphorous speciation in surface sediments of the Cochin estuary. Environ Monit Assess. doi:10.1007/s10661-012-2729-3

Godoy JM, Moreira I, Bragança MJ, Wanderley C, Mendes LB (1997) A study of Guanabara Bay sedimentation rates. J Radioanal Nucl Chem 227(1–2):157–160. doi:10.1007/BF02386450

Golterman HL, Oude NT (1991) Eutrophication of lakes, rivers and coastal seas. In: Hutzinger O (ed) The handbook of environmental chemistry, vol 5. Springer-Verlag, New York, pp 79–113

Grasshof K, Ehrhardt M, Kremling K (1983) Methods of seawater analysis. Verlag Chemie, Weinheim

Gunduz B, Aydın F, Aydın I, Hamamci C (2011) Study of phosphorus distribution in coastal surface sediment by sequential extraction procedure (NE Mediterranean Sea, Antalya-Turkey). Microchem J 98(1):72–76. doi:10.1016/j.microc.2010.11.006

Hecky RE, Kilman P (1988) Nutrient limitation of phytoplankton in freshwater and marine environments. Limnol Oceanogr 33:796–822. doi:10.4319/lo.1988.33.4_part_2.0796

Huang XP, Huang LM, Yue WZ (2003) The characteristics of nutrients and eutrophication in the Pearl River estuary, South China. Mar Pollut Bull 47:30–36. doi:10.1016/S0025-326X(02)00474-5

Jennerjahn TC, Ittekkot V (2002) Relevance of mangroves for the production and deposition of organic matter along tropical continental margins. Naturwissenschaften 89:23–30. doi:10.1007/s00114-001-0283-x

Jensen HS, Kristensen P, Jeppesen E, Skytthe A (1992) Iron: phosphorus ratio in surface sediment as an indicator of phosphate release from aerobic sediments in shallow lakes. Hydrobiologia 236:731–743. doi:10.1007/BF00026261

Knoppers BA (1994) Aquatic primary production in coastal lagoons. In: Kjerfve B (ed) Coastal lagoons processes. Elsevier, Amsterdam, pp 243–286

Knoppers BA, Carmouze JP, Moreira-Turcqo PF (1999) Nutrient dynamics, metabolism and eutrophication of lagoons along the east Fluminense coast, state of Rio de Janeiro, Brazil. In: Knoppers BA, Bidone ED, Abrão JJ (eds) Environmental geochemistry of coastal lagoon systems of Rio de Janeiro, Brazil. FINEP/UFF, Rio de Janeiro, pp 123–154

Liu SM, Zhang J, Li DJ (2004) Phosphorus cycling in sediments of the Bohai and Yellow Seas. Estuar Coast Shelf Sci 59(2):209–218. doi:10.1016/j.ecss.2003.08.009

Machado WT, Lacerda LD (2004) Overview of biogeochemical controls and concerns on trace metal accumulation in mangrove sediments. In: Lacerda LD, Santelli RE, Duursma E, Abrão JJ (eds) Environmental geochemistry in tropical and subtropical environments. Springer-Verlag, Berlin-Heidelberg, pp 319–334

Mackenzie FT, Ver M, Lerman A (1998) Coupled biogeochemical cycles of carbon, nitrogen, phosphorus and sulfur in the land-ocean atmosphere system. In: Galloway JN, Melillo JM (eds) Asian change in the context of global climate changelo. Cambridge Univ. Press, New York, pp 42–100

Marins RV, Paula Filho FJ, Rocha CA (2007) Geoquímica de fósforo como indicadora da qualidade ambiental e dos procesos estuarinos do Rio Jaguaribe–Costa Nordeste Oriental Brasileira. Quim Nova 30(5):1208–1214. doi:10.1590/S0100-40422007000500029

Marone E, Noernberg MA, Santos I et al (2004) Hydrodynamic of Guaratuba Bay—PR, Brazil. J Coast Res Special Issue 39:1879–1883

Martin GD, Muraleedharan KR, Vijay JG, Rejomon G, Madhu NV, Shivaprasad A et al (2010) Formation of anoxia and denitrification in the bottom waters of a tropical estuary, southwest coast of India. Biogeosciences Discuss 7:1751–1782. doi:10.5194/bgd-7-1751-2010

Meybeck M (1993) C, N, P and S in rivers: from sources to global inputs. In: Wollast R, Mackenzie FT, Chou L (eds) Interactions of C, N, P and S biochemical cycles and global change. Springer, Berlin, pp 163–193

Mizerkowski BD (2011) Assessment of the estuarine waters of the state of Paraná (Southern Brazil): descriptive approach, trophic status and monitoring techniques. http://d-nb.info/1013147367/34. Accessed 03 Nov 2011

Mizerkowski BD, Machado EC, Brandini N, Nazario MG, Bonfim KV (2012) Environmental water quality assessment in Guaratuba bay, state of Paraná, southern Brazil. Braz J Ocean 60(2):109–115. doi:10.1590/S1679-87592012000200001

Monbet P, Brunskill GJ, Zagorskis I, Pfitzner J (2007) Phosphorus speciation in the sediment and mass balance for the central region of the Great Barrier Reef continental shelf (Australia). Geochim Cosmochim Acta 71:2762–2779

Morris AW, Baie AJ, Howland RJM (1981) Nutrient distributions in an estuary: evidence of chemical precipitation of dissolved silicate and phosphate. Estuar Coast Shelf Sci 12:205–216. doi:10.1016/S0302-3524(81)80097-7

Nixon SW (1981) Remineralization and nutrient cycling in coastal marine ecosystems. In: Nelson BW, Cronin LE (eds) Nutrient enrichment in estuaries. Humana Press, New Jersey, pp 111–138

Nixon SW (1995) Coastal marine eutrophication: a definition, social causes, and future concerns. Ophelia 41:199–219

Nixon SW, Ammerman JW, Atkinson LP et al (1996) The fate of nitrogen and phosphorus at the land-sea margin of the North Atlantic Ocean. Biogeochemistry 35:141–180

OECD - Organization for Economic Co-operation and Development (1982) Eutrophication of water, monitoring, assessment and control. OECD publications, Paris

Pagliosa PR, Fonseca A, Bosquilha GE, Braga ES, Barbosa FA (2005) Phosphorus dynamics in water and sediments in urbanized and non-urbanized rivers in Southern Brazil. Mar Pollut Bull 50(9):965–974. doi:10.1016/j.marpolbul.2005.04.005

Pellens IC, Belloto VR, Kuroshima KN, Abreu JG (1998) Resultados preliminares da distribuição de fósforo e suas formas nos sedimentos da Plataforma Continental do Estado de Santa Catarina. Notas Tec Facimar 2:51–60

Rast W, Thornton JA (1998) Trends in eutrophication research and control. Hydrol Process 10(2):295–313. doi:10.1002/(SICI)1099-1085(199602)10:2<295:AID-HYP360>3.0.CO;2-F

Russell MJ, Weller DE, Jordan TE, Sigwart KJ, Sullivan KJ (2008) Net anthropogenic phosphorus inputs: spatial and temporal variability in the Chesapeake Bay region. Biogeochemistry 88:285–304. doi:10.1007/s10533-008-9212-9

Ruttenberg KC (2005) The global phosphorus cycle. In: Holland HD, Turekian KK (eds) Treatise on geochemistry. Elsevier Publishers, Amsterdam, pp 585–643

Sabadini-Santos E, Knoppers BA, Oliveira E, Leipe T, Santelli RE (2009) Regional geochemical baselines for sedimentary metals of the tropical São Francisco estuary, NE-Brazil. Mar Pollut Bul 58(4):601–634. doi:10.1016/j.marpolbul.2009.01.011

Sanders CJ, Santos IR, Silva-Filho EV, Patchineelam SR (2006) Mercury flux to estuarine sediments, derived from Pb-210 and Cs-137 geochronologies (Guaratuba Bay, Brazil). Mar Pollut Bull 52(9):1085–1089. doi:10.1016/j.marpolbul.2006.06.004

SANEPAR – Companhia de Saneamento Paranaense (Sanitation Company of Paraná State) (2003) http://www.sanepar.com.br. Acessed 25 June 2011

Santos ML, Saraiva ALL, Delfino IB, Antunes LC et al (2010) Avaliação das Formas de Fósforo nos Sedimentos Superficiais da Plataforma Continental do Rio Amazonas. Rev Gest Cost Integr 10(4):589–596

Strickland JDH, Parsons TR (1972) A practical handbook of seawater analysis. Fisheries Research Board of Canada, Ottawa

Suguio K (1973) Introdução à sedimentologia. Universidade de São Paulo, São Paulo

Tiessen H (1995) Introduction and synthesis. In: Tiessen H (ed) Phosphorus in the global environment, transfers, cycles and management. Wiley, Chichester, pp 1–6

Turner A, Millward GE (2002) Suspended particles: their role in estuarine biogeochemical cycles. Est Coast Shelf Sci 55:857–883. doi:10.1006/ecss.2002.1033

Vaithiyanathan P, Jha PK, Subramaniam V (1993) Phosphorus distribution in the sediments of the Hooghly (Ganges) Estuary, India. Est Coast Shelf Sci 37:603–614. doi:10.1006/ecss.1993.1076

Vollenweider RA (1968) Scientific fundamentals of the eutrophication of lakes and flowing waters, with particular reference to nitrogen and phosphorus as factors in eutrophication. OECD publications, Paris

Vollenweider RA, Giovanardi F, Rinaldi A, Montanari G (1998) Characterization of the trophic conditions of marine coastal areas with special reference to the NW Adriatic Sea; proposal for a trophic scale, turbidity and generalized water quality index. Environmetrics 9:329–357

Wang P, He M, Lin C, Men B, Liu Ruimin, Quan X, Zhifeng Yang Z (2009) Phosphorus distribution in the estuarine sediments of the Daliao River, China. Est Coast Shelf Sci 84:246–252. doi:10.1016/j.ecss.2009.06.020

Whitall D, Bricker S, Ferreira J, Nobre AM, Simas T, Silva M (2007) Assessment of eutrophication in estuaries: pressure-state-response and nitrogen source apportionment. Environ Manag 40(4):678–690. doi:10.1007/s00267-005-0344-6

Yilmaz E, Koç C (2012) A study on seasonal changes of phosphorus fractions in marine sediments of the Akyaka Beach in Gökova Bay, Turkey. Clean Technol Environ Policy 14(2):299–307. doi:10.1007/s10098-011-0402-0

Zem RC, Pathineelam SM, Marone E (2005) Morfologia e dinâmica de sedimentos na baía de Guaratuba, PR. http://www.abequa.org.br/trabalhos/0190_zem_et_al._abequa_2005_.pdf. Acessed 07 June 2012

Zhou J, Wu Y, Kang Q, Zhang J (2007) Spatial variations of carbon, nitrogen, phosphorous and sulfur in the salt marsh sediments of the Yangtze Estuary in China. Estuar Coast Shelf Sci 71:47–59. doi:10.1016/j.ecss.2006.08.012

Zhu Y, Zhang R, Wu F, Qu X, Xie F, Fu Z (2012) Phosphorus fractions and bioavailability in relation to particle size characteristics in sediments from Lake Hongfeng, Southwest China. Environ Earth Sci. doi:10.1007/s12665-012-1806-9

Zwolsman JJG (1994) Seasonal variability and biogeochemistry of phosphorus in the Scheldt Estuary, South-west Netherlands. Estuar Coast Shelf Sci 39:227–248. doi:10.1006/ecss.1994.1061