



Impact of harbour, industry and sewage on the phosphorus geochemistry of a subtropical estuary in Brazil



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ABSTRACT

The distribution of different forms of phosphorus in surface sediment from 17 sites were investigated by SEDEX method. The sites were divided into three sectors: Santos Channel (SC – influenced by harbour, fertilizers plants and phosphogypsum mountains), São Vicente Channel (SVC– domestic waste) and Santos Bay (SB – sewage outfall). The average percentage of each P fraction of the surface sediments in this region followed the sequence P–Fe (38%) > P_{org} (27%) > P_{exch} (13%) > Detrital – P (12%) > Auth – P (10%). P_{total} varied from 3.57 to 74.11 μmol g⁻¹ in both seasons. In SVC, P_{exch} ranged from 13% to 27% and P_{org} varied from 12% to 56%. These high percentages of P_{exch}/P_{total} (greater than 20%) may be related to low oxygen resulting from oxygen consumed by intensive organic matter decomposition as well as the salty water that leads to cation and anion flocculation. Also, the possibility of an influence related to the industrial source of P_{exch} is not ruled out. No significant seasonal differences were found among sites, except for sewage outfall, with changing in the grain size and hence, the P geochemistry. During the summer in the sewage outfall station, P_{org} represented 37% of P_{total}, which decreased to 13% in the winter. These results suggest that high percentages of organic phosphorus cannot be attributed only to autochthonous and allochthonous organic matter, but also to detergents and/or domestic waste. In contrast, spatial differences among sectors were observed, with the highest values of each fraction associated with sites near industrial and domestic waste activities.

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1. Introduction

Nutrient discharge is a serious global problem that affects coastal and estuarine areas proximal to sewage, waste, industrial, agriculture and harbour activities, leading to eutrophication. Consequently, the eutrophication seriously affects and changes the physical and chemical properties of the water column and sediments; these include changes in dissolved oxygen (DO) concentration, leading to hypoxia ($0.2 < DO < 2.0 \text{ mL L}^{-1}$) and anoxia ($< 0.2 \text{ mL L}^{-1}$) in the aquatic environment (Braga et al., 2000; Tribovillard et al., 2006). As a consequence, the excess nutrients cause the proliferation of algae and pathogenic organisms. Phosphorus has been considered as a key nutrient in eutrophication and primary production depends on the content of bioavailable phosphorus for phytoplankton in some coastal areas (Moturi et al., 2005; Coelho et al., 2004).

Sediments have been used as environmental indicators due to their capacity to accumulate and incorporate contaminants. Industrial and domestic wastes act directly on the studied estuarine system and adjacent mangroves, affecting biota and human health (Braga et al., 2000; Hortellani et al., 2005). According to Fisher et al. (1982), sediments provide approximately 28–35% P need in primary productivity in coastal marine areas.

To better understand sedimentary phosphorus role in the P biogeochemical cycle, sedimentary phosphorus speciation should be studied. In Brazil, some studies of phosphorus chemical speciation have been carried out in polluted environments (Carreira and Wagener, 1998; Moturi et al., 2005; Pagliosa et al., 2005) and in other regions as Laizhou Bay where occurs mariculture influence, (Zhuang et al., 2014) and Delhi (Moturi et al., 2005) However, no studies on phosphorus chemical speciation have been reported for estuaries or bays influenced simultaneously by fertilizer factories, harbour activities, domestic waste and sewage outfall as proposed here.

In this study, a sequential extraction method (SEDEX) (Ruttenberg, 1992) was employed to operationally discriminate

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five different forms of sedimentary P in the Santos–São Vicente Estuarine System. The purpose of this study is to investigate the contents and geochemical fractionation of P in surface sediments in a highly impacted estuary with several anthropogenic influences including industry, harbours, and domestic waste. In addition, this manuscript examines factors influencing the distributions of P species and determines the potential reservoirs of bioavailable P from sediments to the overlaying waters.

The contents of organic carbon, organic phosphorus and total nitrogen are related to the organic matter and may indicate eutrophication as well as, the physical and chemical properties of bottom water. The organic material content also provides information about assimilation/decomposition dynamics, which reflect the degree of deterioration in a given system.

2. Study area

The Santos–São Vicente Estuarine System is located in the São Paulo coastal area of Brazil at latitudes 23°53' and 24°01' and longitudes 46°22' and 46°19'. This region is considered to be an important economic region due to its harbours, industrial activity and tourism (Fig. 1).

The vegetation in the study area is characterised by an exuberant Atlantic forest and mangroves (Braga et al., 2000). The pluviosity is high and can reach 2500 mm y⁻¹. From January to March, the pluviosity has been reported to reach 760 mm (DAEE, 2006). The population is approximately 1,000,000, and this number almost doubles during the summer.

For study, the region was grouped by hydrodynamic and occupation similarities in three sectors. (1) Santos Channel (SC – Stations 1–6) possesses the largest harbour in Latin America and the main industrial activity in Brazil. Its sediment transport is characterised by riverine discharge with suspended solids from the Serra do Mar to Santos Channel with a unidirectional flux towards the Bay (Fúlfaro and Ponçano, 1976; Bonetti-Filho, 1995). (2) São Vicente Channel (SVC – stations 11–14) is characterised by low hydrodynamics surrounded by mangroves and small rivers that are influenced by domestic waste and industrial and harbour activities. SC and SVC receive large inputs of industrial and domestic waste including phosphogypsum from phosphate fertilisers that are transported by rivers from Cubatão to the channels (Oliveira et al., 2007). The phosphogypsum is accumulated as a byproduct of phosphoric acid production; the accumulation of this material continues along the port close to Cubatão city, where it is exposed to leaching due to the high rainfall (approximately 2500 mm y⁻¹). The phosphorus from phosphogypsum may be exported into

waterways, increasing eutrophication (Rutterford, 1994). Few studies have been conducted in this region to investigate eutrophication and sediment quality (Braga et al., 2000; Abessa et al., 2005). (3) Santos Bay (SB – stations 7–10 and 15–16) submitted to marine hydrodynamic, receives waters from both channels and submarine sewage outfall is present in the middle of the bay (station 8).

3. Material and methods

3.1. Sampling and sample treatment

3.1.1. Bottom waters

Bottom water was sampled in February (Summer) and August (Winter), 2006. The sampled bottom waters were collected in Hydrobios[®] bottles for analyses of DO and ammonium (N-ammon.). Van Dorn bottles were used for sampling dissolved inorganic phosphate (DIP). The nutrient water samples were filtered using a preheated (450 °C for 4 h) Whatman GF/F membrane (47 mm), and the filtrate was analysed for DIP. Dissolved oxygen (D.O.) and Oxygen saturation (OS) was calculated by the equations of Aminot (1983).

3.1.2. Surface sediments

Seventeen surface sediment samples (0–5 cm) were collected with an inox van Veen crab in February (Summer) and August (Winter), 2006. The sediments were frozen at –20 °C and freeze-dried for 48 h. After drying, the sediment was ground to a powder with a mortar and pestle prior to chemical analyses of phosphorus speciation, organic carbon, total nitrogen and total iron. Grain size analysis was performed by the method of Suguio (1973).

3.2. Physical and chemical parameters

3.2.1. Bottom water analyses

Temperature was measured with a protected reversing mercury thermometer. Salinity was determined using a Beckman RS-10 induction salinometer. DO was measured by the Winkler method (Grasshoff et al., 1983) using a Metrohm[®] burette. OS was calculated by the equation of Aminot (1983). Ammonium was measured by the method of Tréguer and Le Corre (1975) DIP was measured by the colourimetric method using the molybdenum blue reaction (Grasshoff et al., 1983).

3.3. Surface sediment analyses

Sedimentary phosphorus species were determined by the sequential extraction scheme (SEDEX) in duplicate, as described by Ruttenberg (1992). In brief, the SEDEX consisted of five steps to separate the major reservoirs of sedimentary phosphorus into five pools: (i) loosely sorbed or exchangeable (P_{exch}); (ii) iron bound to oxy-hydroxides (P–Fe); (iii) Authigenic P (Auth – P) including carbonate fluorapatite (CFA), biogenic apatite (fish debris) and phosphorus-bound CaCO₃; (iv) Detrital-P, which is apatite of igneous or metamorphic origin (Detrital – P); and (v) organic P (P_{org}). The phosphate concentrations in all steps with the exception of step ii (P–Fe) were determined by the colourimetric method (Grasshoff et al., 1983) using a Genesys 2 spectrophotometer (Bausch & Lomb[®]). Sedimentary P–Fe in citrate–dithionite–bicarbonate (CDB) was determined using a combined CDB – MAGIC (magnesium-induced co-precipitation) method (Huerta-Diaz 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 NaOH solution. After separation by centrifugation and two washings with 10% NH₄OH solution, the

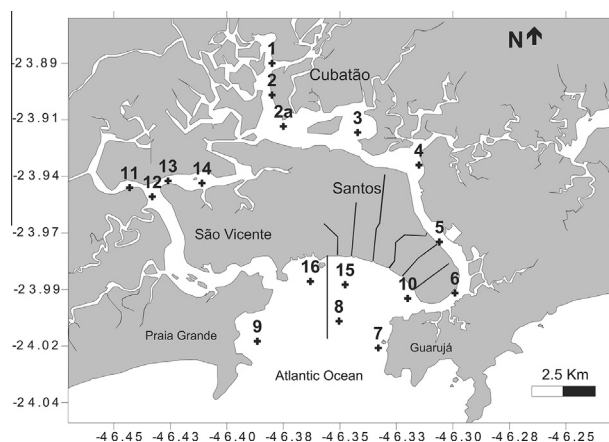


Fig. 1. Study area and sampling sites of the Santos–São Vicente Estuarine System, São Paulo, Brazil.

precipitate was re-dissolved in 10% HCl solution. The P concentration in the HCl extract was measured by the conventional colourimetric method as described above. The relative standard deviations of the replicates are less than 6%, 9%, 6%, 7%, and 5% for P-Fe, P_{exch} , Auth - P, Detrital - P 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. Total phosphorus (P_{total}) was considered as the sum of the five P forms.

To verify this method, we fractionated the Certified Reference Material Estuarine Sediment (NIST 1646) and also analysed P_{total} using the Aspila (1976) method for comparison with the P_{total} determined above.

Organic carbon (C_{org}), total nitrogen (N_{total}) and total sulphur (S_{total}) were determined with a LECO CNS 2000 analyser after the addition of 10% HCl to remove carbonates. The quantification limit for C_{org} , N_{total} and S_{total} was 0.003%.

Total iron was determined by instrumental neutron activation analysis (INAA); approximately 200 mg of sediment (duplicate samples) and approximately 150 mg of reference material were accurately weighed and sealed in pre-cleaned double polyethylene bags for irradiation. The samples and reference materials were irradiated for 16 h under a thermal neutron flux of $10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ in the IEA-R1 nuclear reactor at Institute of Nuclear and Energetic Researches (IPEN-SP). Two counting series were made after one week of decay and after 15–20 days. Gamma spectrometry was performed using a Canberra gamma X hyperpure Ge detector with resolutions of 0.88 keV and 1.90 keV for ^{57}Co and ^{60}Co , respectively. The methodology was validated by measuring the reference materials Buffalo River Sediment (NIST SRM 2704), Soil 7 (IAEA) and BEN (Basalt - IWG-GIT).

3.4. Data analysis

The Shapiro-Wink test was used to test the normality of the data, and the seasonal variation between summer and winter was determined by an analysis of variance (ANOVA). Principal components analysis (PCA) and Pearson correlation coefficients were used to verify the relationship between grain size and geochemical parameters.

4. Results

4.1. Bottom water quality

The bottom water results are listed in Table 1 (Supplementary data). The temperature of the bottom layer ranged from 24.64 to 28.00 °C in summer and from 21.06 to 23.50 °C in winter. In the interior of the system, the water was brackish, facilitating the increase of temperature in the summer.

Water temperature is one of the parameters that can influence the diagenetic processes. The ANOVA results, however, show that the temperatures were not significantly different; thus, considering the seasonal period and variance, temperature likely did not affect the phosphorus diagenesis. Spatially, the temperature was highest in the SVC and lowest in the SB. Brackish waters ($0.5 < S < 30$) were observed from stations 1 to 4 (high estuary of SC) and stations 11 to 14 (SVC), with higher values during the summer. The spatial distribution of salinity varied widely from 15.56 to 33.99 in summer and from 24.70 to 34.32 in winter; salinity increased moving from the middle part of the estuary to the bay. DO ranged from 1.09 to 4.75 mL L^{-1} during the summer and from 2.83 to 6.12 mL L^{-1} in winter. The OS ranged from 22% to 69% for both seasons.

N-ammonium concentrations varied from 0.32 to $39.08 \mu\text{mol L}^{-1}$ in summer and from 0.94 to $32.76 \mu\text{mol L}^{-1}$ in

winter. Decreased DO and OS values accompanied higher N-ammonium concentrations, particularly during summer, indicating intensive organic matter decomposition and denitrification. N-ammonium concentrations decreased moving from SC and SVC towards the bay, where the lowest values of N-ammonium were found.

DIP concentrations ranged from 0.83 to $8.30 \mu\text{mol L}^{-1}$ in summer and from 0.62 to $8.67 \mu\text{mol L}^{-1}$ in winter. As for N-ammonium, the highest concentrations of DIP were observed in the brackish water stations with low DO concentrations in both seasons. Braga et al. (2000) reported DIP concentrations reaching $24.52 \mu\text{mol L}^{-1}$ near factories and $1.00 \mu\text{mol L}^{-1}$ at SB.

Spatial differences among stations of the estuary were found in relation to salinity, DO, DIP and N-ammonium. In contrast, no seasonal differences in concentration were observed for the parameters of bottom waters (ANOVA, $p < 0.05$) (see Fig. 2).

4.2. Sediments

4.2.1. Grain size

The grain size values are listed in Tables 2 and 3 (Supplementary data). The SC (1–6) and SVC (11–14) stations presented high percentages of mud ranging from 32.1% to 98.2%. The highest levels of mud were found in the SVC, mainly at station 14, and SC stations 1, 2 and 2A. The sediments from SB were predominantly sand on the western side. Additional details about the grain size patterns in the Santos–São Vicente Estuarine System can be found in Azevedo et al. (2009).

With the exception of station 8 (sewage outfall), no significant seasonal differences were found. Station 8 is characterised by silty sand in the summer and by sand in the winter.

4.2.2. Sediment geochemistry

The sediment surface geochemistry is shown in Table 3. The highest values of phosphorus fractions, C_{org} , N_{total} , S_{total} and Fe_{total} were found in all SC stations (1–7) and stations 11–14, in the vicinity of industrial activity. The sediment geochemistry of the bottom waters showed spatial variations (ANOVA, $p < 0.05$).

In the SC, C_{org} varied from 2.1% to 6.3%, N_{total} from 0.2% to 0.4% and S_{total} from 0.2% to 1.5% during both seasons. The highest values were found at stations 1, 2, 2A, 12, 13 and 14. The values of Fe_{total} ranged from 1.5% to 5.5%.

The values in SB were lower than those of SC and SVC, ranging from 0.1% to 2.6% for C_{org} , 0.01–0.11% for N_{total} and 0.01–0.33% for S_{total} . For Fe_{total} , the values varied from 1.5% to 2.4%. No significant seasonal variations were found for C_{org} , N_{total} , S_{total} and Fe_{total} .

P_{total} ranged from 3.80 to $74.11 \mu\text{mol g}^{-1}$. The maximum value was found in station 1, in the vicinity of an industrial plant, in both summer and winter.

P_{exch} concentrations ranged from 0.24 to $9.36 \mu\text{mol g}^{-1}$ and accounted for 5.1–27.1% on a weight basis. The highest percentages of P_{exch} during the winter were found at station 5 (22%), 11 (27%) and 12 (20%).

P-Fe ranged from 1.09 to $37.68 \mu\text{mol g}^{-1}$ and accounted for 21–53% of P_{total} . The P-Fe percentage was the prominent form of P at all stations (Fig. 3B).

Auth-P varied from 0.36 to $10.64 \mu\text{mol g}^{-1}$ and accounted for 4–17% of P_{total} (Table 3); this fraction was the lowest form of phosphorus at all sites. The lowest percentages of Auth-P were found in SVC sediments (stations 12, 13 and 14), while the highest were found at stations 1, 3, 5 and 10.

Compared to different coastal areas throughout the world, the study area of this investigation has a low proportion of Auth - P/ P_{total} . In polar sediments, the Auth - P is the main phosphorus

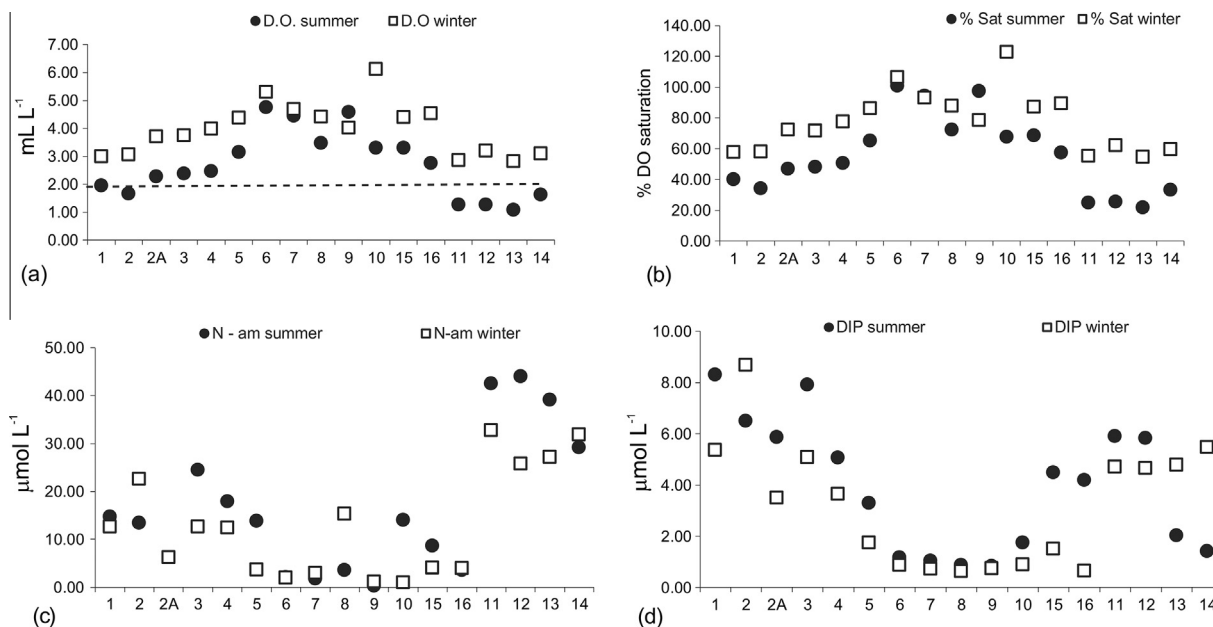


Fig. 2. Spatial distribution of dissolved oxygen (a), oxygen saturation (b), N-ammonium (c) and dissolved phosphate in summer (●) and winter (□), 2006. The line in (a) indicates the limit of 2 mL L^{-1} for oxyc waters.

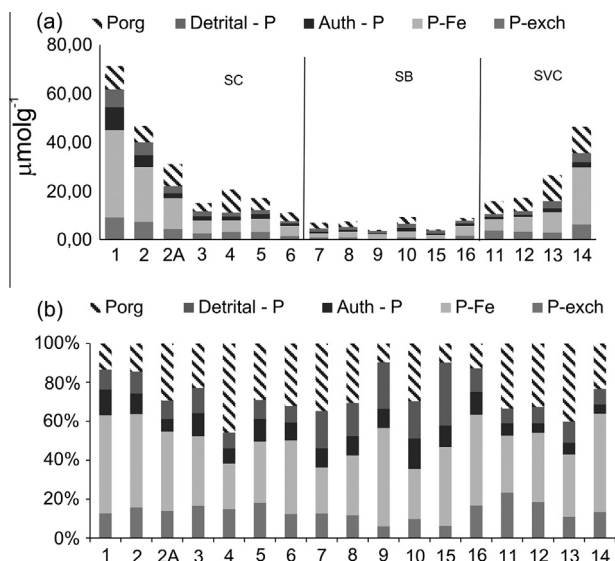


Fig. 3. (a) Mean concentrations ($\mu\text{mol g}^{-1}$) of P forms in summer and winter and (b) mean P percentages of P_{total} for surface sediments in the Santos–São Vicente Estuarine System; station 8 is not included, as will be discussed in Section 5.2.

fraction, with a mean of 36.9% in Antarctic surface sediments (Berbel and Braga, 2014) and Bering sediments (März et al., 2014).

Detrital - P varied from 0.94 to $7.21 \mu\text{mol g}^{-1}$ and accounted for 7–34% of P_{total} . The highest value of Detrital - P was found in stations 10 and 15, while the lowest values were found at all SVC stations. The high concentration of Detrital - P in SB is probably a consequence of the enhanced detrital phosphorus input due to both strong channel influences and sewer outfall.

P_{org} values ranged from 0.37 to $10.50 \mu\text{mol g}^{-1}$ and accounted for 10–47% of P_{total} . The highest concentrations as well as percentages were found at stations 4, 11, 12, 13 and 14 during the summer and at stations 4, 6 and 13 in winter. P_{org} represented the second largest pool of sedimentary phosphorus at all sites (see Fig. 4).

5. Discussion

5.1. Environmental conditions and geochemistry of surface sediments of the Santos–São Vicente Estuarine system

In the last 50 years, the Santos–São Vicente Estuarine System has received a large discharge of industrial and domestic waste with different compounds including dissolved nutrients (Braga et al., 2000), toxic metals (Siqueira and Braga, 2002; Hortellani et al., 2005; Azevedo et al., 2009) and hydrocarbons (Bicego et al., 2006). In the early 1980, the Santos–São Vicente Estuarine system was considered one of the most polluted estuaries of the world due to the release of untreated waste by several industries in the Cubatão (Martins et al., 2011).

In this study, bottom water and geochemistry data of surface sediments (C_{org} , N_{total} , S_{total} , P chemical forms and Fe_{total}) were evaluated in a highly impacted estuary on the Brazilian coast.

The PCA analyses (Fig. 5a and b) show three distinct regions with different influences in both seasons. Group I is characterised by the input of P_{exch} , Detrital - P, P-Fe and iron in muddy sediments (stations 1, 2, 2a and 4). Such associations reflect the strong continental influence and high anthropic activities such as industry, phosphogypsum mountains, steel factories and harbours.

Group II (stations 11, 12, 13 and 14) is characterised by high levels of C_{org} , N_{total} , S_{total} , DIP and N-ammonium along with high percentages of $P_{\text{exch}}/P_{\text{total}}$, low levels of DO and the highest levels of dissolved nutrients. The bottom waters from the SVC and SC stations are characterised by brackish waters (salinity < 30), high levels of DIP ($> 2 \mu\text{mol L}^{-1}$) and N-ammon and low DO ($< 2.0 \text{ mL L}^{-1}$) with no seasonal variations. This region is characterised by intensive domestic waste inputs with increasing anthropogenic organic matter. High N-ammonium, DIP, C_{org} , N_{total} and S_{total} concentrations associated with low DO and OS within sediments result from the decomposition of organic matter as these sites receive discharges of domestic waste. During the summer, all SVC stations presented hypoxic waters with OS percentages between 20% and 40% as well as high DO consumption due to the degradation of organic matter. The hypoxia in SVC waters seems to be seasonal because the DO concentrations exceeded

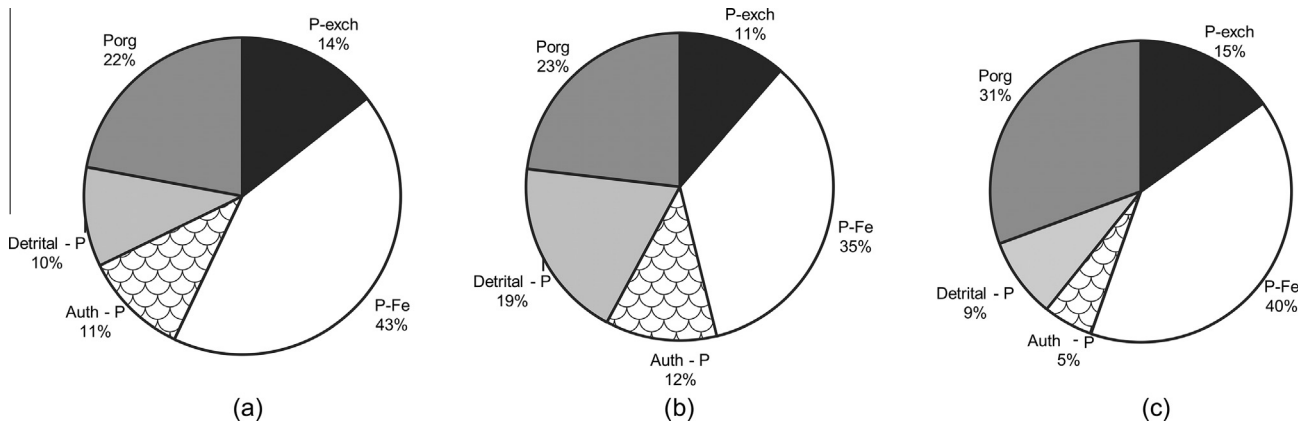


Fig. 4. Mean of P percentages in three sectors of the Santos São Vicente estuarine system and Santos Bay considering summer and winter 2006).

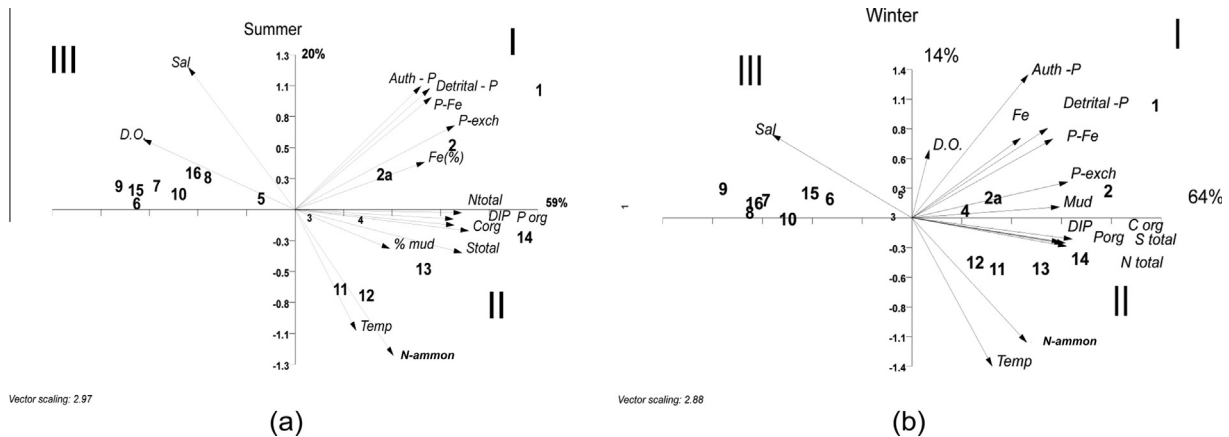


Fig. 5. Principal components analysis (PCA) of the Santos–São Vicente Estuarine System data considering (a) summer and (b) winter periods of 2006.

2.0 mL L^{-1} during the winter, with saturation percentages varying from 57.9% to 106.5%, indicating oxic waters. This seasonality of the DO concentrations may be related to the warm water temperatures, which influence the solubility of the gas. Conversely, anthropogenic influence is likely the main reason for the extremely low DO contents due to tourist and industrial activities, as found in the SC (54.7–62.3%). Oxygen is consumed in the surface sediments by the decomposition of the carbon of dead phytoplankton that sinks down.

The SC and SVC are positioned in an area that has limited water circulation along with the presence of industrial, harbour and domestic waste activities. Low water circulation favours the deposition of fine-grained sediments. In addition, mangroves retain part of transported material from the continent and release silty-clayed fractions to the channels, contributing to the accumulation of contaminants in the estuary.

In the surface sediments, high concentrations of phosphorus fractions were accompanied by enhanced DIP, and significant correlations were found between DIP and P_{exch} , $P\text{-Fe}$, Auth - P , Detrital - P and P_{org} ($r > 0.70$, $p < 0.0001$). This indicates the possibility that DIP results both from industrial activities and the organic matter decomposition of domestic waste. The correlation between DIP and Detrital - P may result from the large amount of input that the SC and SVC receive via streams carrying contaminants from phosphogypsum leaching and steel and manure factories in the Cubatão industrial district. Oliveira et al. (2007) analysed the

mineralogy and chemical composition of phosphogypsum from phosphate rocks of alkaline massif and surface sediment of the Mogi River at Cubatão. XRD analyses of phosphogypsum mineralogy indicated residues of Al – bound phosphates of Ca, Sr, Ba, REEs (rare earth elements) and strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$). The chemical composition of phosphogypsum revealed high contents of Si, Fe, Ca, P, Ti and light rare earth elements (LREEs).

Sediment transport is influenced by tidal influence and unidirectional flux from high estuary at stations 3, 4 and 5. As a result, a break in energy was observed, resulting in silty – clayed sediments at stations 4 and 5 (Fúlfaro and Ponçano, 1976) and contributing to high concentrations of P forms, C_{org} , N_{total} and Fe_{total} .

Balchand and Nair (1994) and Moturi et al. (2005) reported high percentages of P_{exch} in salty waters. In contrast, this study observed high phosphorus levels in the exchangeable phase in sediments under low saline regions, with extremely high P_{exch} percentages at the SVC stations ($>20\%$) due to the high discharge of nutrients from domestic sewage and industrial waste. $P\text{-Fe}$ and $P\text{-Al}$ are also considered to be closely related to anthropogenic activities (Jensen et al., 1995; Zhuang et al., 2014); the results of this study are in agreement with these reports as $P\text{-Fe}$ is the predominant form of sedimentary phosphorus and is found in high concentrations mainly at the Cubatão industrial district and the SVC. At these stations, $P\text{-Fe}$ accounted for more than 40% of P_{total} .

Significant correlation was found between $P\text{-Fe}$ and P_{exch} . The release of phosphorus-bound iron oxy-hydroxides depends on

redox conditions. If the sediment presents oxic conditions, the formation of iron (III) oxides is favoured, and amorphous iron oxides that sorb anions and cations are formed. In reducing environments, iron (III) is reduced to iron (II), and phosphorus is released from Fe oxy-hydroxides.

In our study, the SVC and Cubatão industrial site (stations 1 and 2) presented hypoxic waters ($DO < 2.0 \text{ mL L}^{-1}$) and high sulphur contents. The released iron and phosphorus diffuse towards the oxygenated seawaters, and Fe and P re-precipitate as phosphorus-bound iron oxides.

Zhuang et al. (2014) found no correlation between P_{exch} and P_{org} , suggesting that there is no common source. Conversely, a strong correlation in this study was found between P_{exch} and P_{org} , indicating the strong influence of the diagenesis of organic matter.

The significant correlation (Fig. 6A) between Fe_{total} and C_{org} suggests that iron may be associated with organic matter, indicating that organic matter plays a significant role in the iron geochemistry. 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. As the saline water enters into the estuary, the interaction is enhanced due to the increase in electrolytes. The flocculation process is not limited to clays and organic complexes but also occurs in the soluble organo-metallic complex formed from humic materials and most of the metal ions (Rashid, 1985). Fig. 6B shows a significant correlation between Fe_{total} and S_{total} in both seasons; however, the outlier stations 13 and 14 exhibit high levels of C_{org} and S_{total} . These anomalies (Fig. 6A in circles) can indicate that the iron from steel factories does not reach the SVC as well as a strong influence of natural sewage disposal and other types of domestic waste, resulting in high concentrations of C_{org} and N_{total} . Conversely, the SC receives iron and sulphur inputs from industrial sites associated with low hydrodynamics in stations 1 to 3, resulting in low oxygen levels and high levels of S_{total} , Fe total and P-Fe in the surface sediment (Fig. 7).

The SC and SVC have high a sedimentation rate of 2.5 cm y^{-1} contributing to iron and phosphorus inputs, as demonstrated by the correlation between Fe_{total} and Detrital - P (Fig. 4A and B). Although the extremely high percentages of S_{total} and low DO indicate hypoxic conditions at the SC and SVC, the predominance of iron oxy-hydroxides at these sites suggests that 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.

The high percentages of P_{exch} and P_{org} at SVC stations during the winter suggest the strong contribution of not only decomposing organic matter but also domestic sewage discharge. Marine sediments exhibit P_{exch} percentages lower than 8% in continental shelves (Monbet et al., 2007) and coastal Antarctic sediments (Berbel and Braga, 2014). In estuarine sediments with little

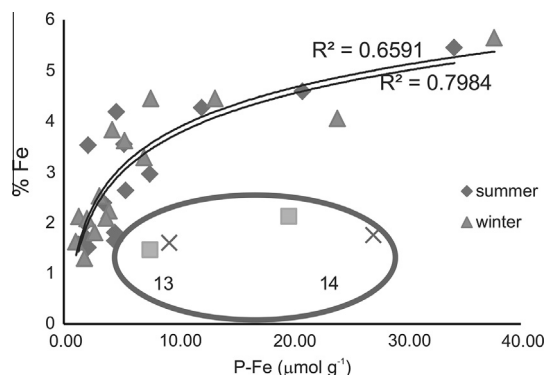


Fig. 7. The relationship between % Fe_{total} and P-Fe in Santos-São Vicente Estuarine System.

anthropic influence, the maximum P_{exch} percentage is 11% in the Cananéia Estuary of Brazil (Berbel and Braga, 2006) Fig. 8 shows the significant correlations observed between P_{exch} and P-Fe ($r^2 = 0.87$) and between P_{exch} and % mud ($r^2 = 0.71$).

These correlations may be explained by the greater surface area of fine particles, which results in more adsorption sites for phosphate ions on Fe oxides/hydroxides (Andrieux-Loyer and Aminot, 2001; Liu et al., 2004). The lack of a correlation between P_{exch} and the percentage of mud at stations 1, 2 and 14 (Fig. 8b) may indicate that continental influence from anthropic activities is a dominant control on phosphorus geochemistry, as reflected in the high levels of P-Fe, % Fe and % C_{org} .

The presence of enriched exchangeable and organic phosphorus provides a large reservoir of relatively labile substances that may eventually become an important source of phosphorus (Carreira and Wagener, 1998). Based on the calculations of these authors, we similarly estimate the labile phosphorus in the Santos harbour region. The area of Santos harbour (stations 1–5) is 7.8 km^2 , with average P_{exch} and P_{org} of $142 \mu\text{g g}^{-1}$ and $225 \mu\text{g g}^{-1}$, respectively. The average sediment depth and density are 1 cm and 2.4 g cm^{-3} , respectively. The size of the P_{exch} and P_{org} reservoirs are 27 and 42 t, respectively, resulting in a total of 69 t. Alternatively, if we include the P-Fe as labile P, the total P-Fe reservoir reaches 508 t, and the total P reservoir ($P\text{-Fe} + P_{\text{org}} + P_{\text{exch}}$) is 577 t.

Group III consists of the SB stations, with high OS and salinity, low mud percentage and dissolved nutrient concentrations and N-ammonium and DIP contents typical of coastal waters (except for station 8 – sewage outfall).

According to Fúlfaro and Ponçano (1976), SB is divided in two sectors: an eastern sector with silty sediments and a western sector with sandy sediments. As expected, the concentrations of forms of P, C_{org} , N_{total} , S_{total} and Fe_{total} at the eastern part of SB were higher than the sediments from western part.

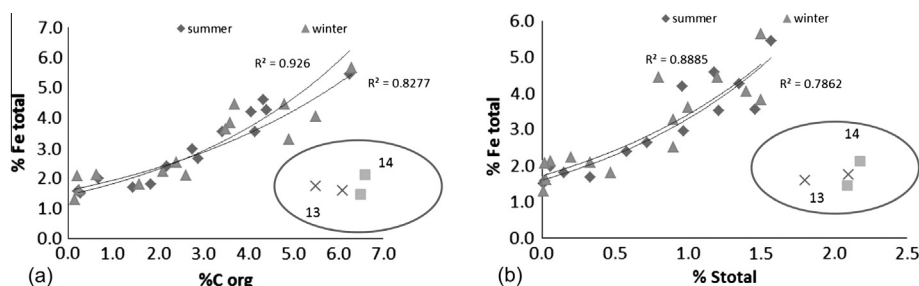


Fig. 6. Linear relationships between % Fe_{total} and C_{org} (A) and % Fe_{total} and % S_{total} (B).

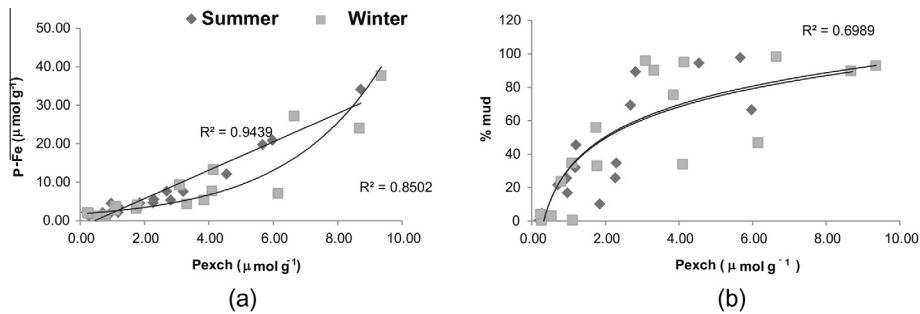


Fig. 8. The relationships between P-Fe and P-exch (a) and P-exch and % mud (b).

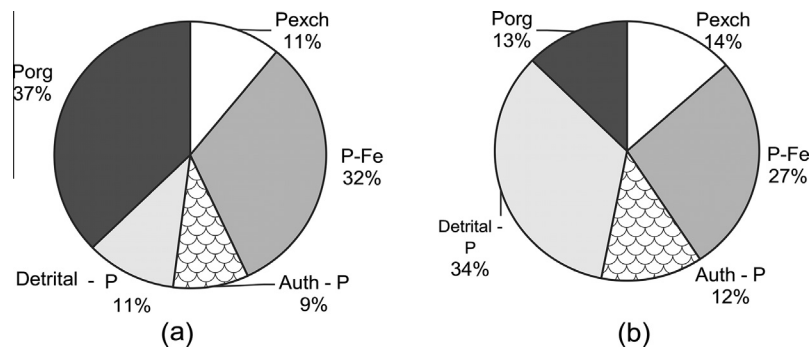


Fig. 9. Phosphorus geochemistry at station 8 in the (a) summer and (b) winter of 2006.

In contrast with this study, Detrital – P is the predominant form of P in Laizhou Bay and Zhangzi Island (Zhuang et al., 2014) P_{org} , which was the dominant form in this study.

5.2. Seasonal changes in phosphorus geochemistry in sewage outfall (station 8)

Changes in grain size were observed at station 8 (sewage outfall). The concentration of suspended solids in the effluent of Santos is high and considered to be above average for urban sewage. This information provides important information about the influence of sewage on grain size distribution.

According to Gonçalves and Souza (1997) and Braga et al. (2000), sewage has a typical composition with high contents of nutrients in the water around the diffusers. This suggests that the sewage discharge might cause the organic enrichment of the enrichment.

In this study, changes in the grain size and phosphorus geochemistry were observed. During the summer, P_{org} represented 37% of P_{total} , which decreased to 13% in the winter. A similar pattern was observed for the C_{org} concentrations, which decreased almost 100 times from 2.19% in the summer to 0.24% in the winter. Perretti and Braga (2006) found the same differences in grain sizes at the same station in summer and winter of 2005 (see Fig. 9).

In addition to contaminants such as dissolved and sedimentary nutrients, detergents are also present in sewage and can accumulate in the sediments (Field et al., 1995; Stoll et al., 1997).

Bosquilha (2003) found MBAS (methylene blue active substance) concentrations in seawater between 0.15 to 0.26 mg L⁻¹, which is considered a toxic to sea urchin embryos (Abessa et al., 2005). The same authors found values of MBAS from 7.33 to 22.96 µg g⁻¹ in surface sediments near the diffusers. These results suggest that the high percentages of organic phosphorus at station 8 (summer) and SVC stations (both seasons) cannot be attributed only to autochthonous and allochthonous organic matter, but are also related to detergents and/or domestic waste.

5.3. Total phosphorus values as a guideline for pollution assessment

This study proposes surface sediment phosphorus concentrations for the development of coastal management policies in areas with similar characteristics.

Baturin et al. (2003) and (Teodoro et al., 2010) suggest that P_{total} values higher than 22.6 µmol g⁻¹ (700 µg g⁻¹) indicate anthropogenic influence, and Zhang et al. (2008) suggest that P_{total} values for lake surface sediment lower than 16 µmol g⁻¹ of (500 µg g⁻¹) indicate unpolluted sediment. Intermediate values between 16 < P_{total} < 42 µmol g⁻¹ (500 < P_{total} < 1300 µg g⁻¹) indicate moderate pollution, while values higher than 42 µmol g⁻¹ (1300 µg g⁻¹) indicate polluted sediments. Table 4 shows the sedimentary phosphorus at some polluted sites.

No quality criteria was found in the literature for estuarine sediments but some reports of Environmental Agencies from Canada (Environment Canada, 2007) show values for total phosphorus (960 mg Kg⁻¹ – 30.97 µmol g⁻¹) in fluvial estuary of Saint Lawrence in the pre industrial period. Besides, Barcellos et al. (2005) reported maximum value of total phosphorus of 30.15 µmol g⁻¹ for surface sediments from a pristine estuary (Canaanéia – Iguape Estuary). Considering the value of 30.97 µmol g⁻¹, we can conclude that 4 of 17 sediments of Santos–São Vicente Estuarine system are highly contaminated in stations 1, 2, 2A and 14, i.e., 23.5% of total can be considered extremely high levels in relation to pre industrial period.

Recently, Robertson and Stevens (2013) have established values for phosphorus in sediments in New River Estuary (New Zealand) as is shown in Table 5.

Based on this classification, 53% of sediments from Santos–São Vicente Estuarine System may be considered fair–poor quality in relation to P_{total} .

P_{total} concentrations at station 1 (68.47 µmol g⁻¹/2122 µg g⁻¹ in summer; 74.11 µmol g⁻¹/2297 µg g⁻¹ in winter) exceed the CONAMA (Federal Brazilian Environmental Law) alert values established for dredged sediments (64.5 µmol g⁻¹/ 2000 µg g⁻¹).

Table 4
Phosphorus speciations in surface sediments at polluted sites in $\mu\text{mol g}^{-1}$. The values in parentheses are the percentages of each fraction relative to P_{total} .

	P-exch	P-Fe	Auth-P	Detrital - P	P _{org}	P _{total}	
Ipanema Sewage Outfall (Brazil)	-	8.57–51.77	-	-	5.34–27.08	11.94–73.76	Carreira and Wagener (1998)
National Capital Territory (NCT) of Delhi (India)	5.16–19.68 (3.7–23.9)	0.97–7.74 (1.9–10.9)	33.87–45.16 (32.6–46.6)	15.16–81.61 (21.6–59.0)	3.23–9.03 (2.2–13.1)	69.68–138.39	Moturi et al. (2005)
Hinchinbrook Channel (Australia)	0.16 (1.5)	1.99 (17.8)	0.74 (6.6)	0.91 (8.2)	7.40 (66.0)	11.20	Monbet et al. (2007)
Rockingham Bay (Australia)	0.72 (5.4)	2.22 (16.6)	5.13 (38.4)	1.11 (8.3)	4.2 (31.3)	13.40	Monbet et al. (2007)
Missionary Bay (Australia)	0.75 (6.1)	0.79 (6.4)	1.31 (10.6)	1.17 (9.5)	8.30 (67.4)	12.30	Monbet et al. (2007)
Adriatic Sea – fish farm (Italy)	-	1.21–11.91 (12.9–40.1)	0.57–2.68 (5.6–12.4)	0.04–3.44 (0.4–18%)	0.10–13.00(18.7–40%)	19–135	Matičević et al. (2008)
Admiralty Bay (Antarctica)	1.56 (4.8)	4.20 (12.5)	11.77 (36.9)	13.9 (40.6)	1.69 (4.2)	32.31	Berbel and Braga (2014)
Laizhou Bay (China)	0.04–0.58(0.4–3.4)	0.18–1.64(1.1–9.4)	0.64–3.24 (5.2–19.2)	7.42–15.16 (13.4–55.0)	0.69–2.93 (4.8–17.3)	10.19–18.80	Zhuang et al. (2014)
Zhangzi Island (China)	0.07–1.11 (2.3–9.5)	0.64–1.61 (9.1–27.9)	0.28–3.13 (3.1–24.1)	0.53–6.57(20.0–65.8)	0.74–2.77 (11.0–31.1)	2.62–12.95	Zhuang et al. (2014)
Zhejiang (coastal sediment) (China)	-	1.96–4.05 (10.5–20.9)	1.14–2.83 (5.9–16.3)	10.25–13.93 (58.6–73.2)	1.06–3.35 (6.1–15.9)	17.00–21.94	Cong et al. (2014)
Changjiang estuary (China)	0.24–0.95 (1.4–5.3)	0.05–0.65 (0.3–3.7)	0.54–1.50 (2.9–9.6)	6.60–13.20 (40.6–73.9)	0.82–4.27 (5.5–26.3)	15.00–21.40	Meng et al. (2014)
This study	0.20–8.72 (4.9–27.1)	1.29–34.17 (20.9–53.2)	0.40–8.31 (3.9–16.6)	0.69–7.25 (5.1–34.2)	0.73–11.17 (9.2–46.8)	3.80–74.11	

* Values originally in $\mu\text{g g}^{-1}$ or mg Kg^{-1} were converted to $\mu\text{mol g}^{-1}$.

Table 5

Classification of surface sediments in the stations according to Robertson and Stevens (2013) classification based on total phosphorus concentrations in $\mu\text{mol g}^{-1}$.

Concentrations ($\mu\text{mol g}^{-1}$)	<5.5	5.5–16.0	16.0–32.0	>32.0
Sediment quality in relation to P_{total}	Very good	Good	Fair	Poor
Stations (this study)	9 and 15	3, 6, 7, 8, 10 and 16	2 a, 4, 5, 11, 12 and 13	1, 2 and 14

The P_{total} concentrations at station 1 ($68.47 \mu\text{mol g}^{-1}/2122 \mu\text{g g}^{-1}$ in summer; $74.11 \mu\text{mol g}^{-1}/2297 \mu\text{g g}^{-1}$ in winter) exceed the CONAMA (Resolução CONAMA, 2004 - Federal Brazilian Environmental Law) alert values established for dredged sediments ($64.5 \mu\text{mol g}^{-1}/2000 \mu\text{g g}^{-1}$).

6. Conclusion

The SC and SVC present bottom water characteristics typical of waters affected by eutrophication: low DO values and high levels of DIP and N-ammonium resulting from intensive organic matter decomposition associated with high the discharge of nutrients, primarily phosphate, from industrial, domestic waste and harbour activities and related to the low hydrodynamic of the estuary. As a consequence, the surface sediments exhibit very high concentrations of phosphorus species, C_{org} , N_{total} , S_{total} and Fe_{total} . The SVC sediments show extremely high percentages of $P_{\text{exch}}/P_{\text{total}}$ (greater than 20%) due to low oxygen resulting from oxygen consumed by intensive organic matter decomposition as well as the salty water that leads to cation and anion flocculation. Also, the possibility about the industrial source of P_{exch} is not ruled out.

Conversely, the surface sediments from the SC tend to retain phosphorus due to the formation of iron oxy-hydroxides during the flocculation processes that occur with the inflow of the tide along with iron and phosphate ions from terrestrial and industrial sources. Due to high nutrient discharge from different sources, the bottom water became hypoxic, primarily during summer, increasing the release of phosphorus. In terms of pollution assessment, this study shows that 53% of the surface sediments can be considered moderately polluted (35%) to polluted (18%). The unpolluted sediments are located mainly in the SB.

SB presented low quantities of organic matter and phosphorus although it harboured the same outfall sewer because of the presence of sandy sediments as a result of the hydrodynamics that contribute via dispersion of contaminants.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.marpolbul.2015.02.016>.

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