



Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

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

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ARTICLE INFO

Article history:
Available online xxxxx

Keywords:
Phosphorus
Sediments
Estuaries
Phosphogypsum
Geochemistry
Eutrophication

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 proprieties 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

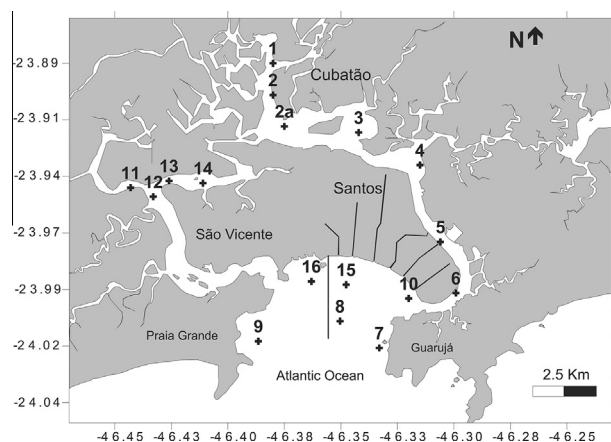


Fig. 1. Study area and sampling sites of the Santos–São Vicente Estuarine System, São Paulo, Brazil.

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