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Full Length Research Paper

Seasonal and spatial variations of dissolved carbon and nitrogen in the Santos estuarine system, Southeastern Brazil

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We investigated the concentrations of nutrients carbon and nitrogen in Santos Estuarine System (SES). The SES is located in the region of Baixada Santista (Santos, Brazil) and is ecologically and economically important due to biological diversity, high levels of metal pollution and sewage, and the presence of the port considered the largest and most productive in Latin America. For the preparation of the nutrient flow model, limnological and oceanographic data were obtained in water and sediment of 27 stations distributed in SES between 2000 and 2008. Significant contributions especially of organic carbon and nitrogen were observed from the communities living around the estuary and the Santos bay. Equations were developed to explain the flow of nutrients based on the type estuary, tidal flows and channel. The SES was classified as a partially mixed system. The results showed that the system has a conservative behavior to salinity and non-conservative to carbon and nitrogen.

Key words: Carbon, nitrogen, modeling, salinity, nutrients flow.

INTRODUCTION

The carbon cycle is the most complex of all biogeochemical cycles, and more than 97% of carbon present in ocean water is present as dissolved inorganic, especially as CO_2, HCO_3^- and CO_3^{2-}, called total dissolved inorganic carbon (DIC) and total CO_2. Levels of dissolved organic carbon (DOC) in marine and continental waters are associated with the decomposition or oxidation process, which contains organic compounds like amino acids, monosaccharides, polysaccharides, humic substances and proteins. The nitrogen exists in many forms due to the large number of oxidation states can take. Nitrogen can be found in the aquatic environment as nitrate (NO^{3-}), nitrite (NO^{2-}), ammonium compounds (NH_3 and NH_4^+), nitrous oxide (N_2O) and organic forms (urea, amino acids and peptides).

Biogeochemical cycles of carbon and nitrogen in water are mainly associated with the tides, the abiotic and biotic processes, climatic conditions and associated ecosystem function (Cox et al., 2002). The knowledge about the nature and cycling of nutrients in estuarine systems allows for better estimates of carbon transport to the coastal zone and ocean (Pettine et al., 1998; Trefry et al., 1994). Estuaries are important routes for transfer of dissolved and particulate materials from the mainland to the coastal zone and ocean. The flow of nutrients into the estuaries is so intense and dynamic, the result is a strong interaction between the biotic and abiotic system, resulting in a high local biodiversity. The rivers carry and distribute nitrogen in estuaries, whose source can be natural or anthropogenic depending on the degree of

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Abbreviations: SES, Santos estuarine system; **DIC,** dissolved inorganic carbon; **DOC,** dissolved organic carbon; **DIN,** dissolved inorganic nitrogen; **DON,** dissolved organic nitrogen; **POC,** particulate organic carbon; **POM,** particulate organic matter; **PON,** particulate organic nitrogen.

preservation of the surrounding forest, of the intensity of erosion and leaching processes, as well as of the impact resulting from anthropogenic activities. In local and regional scales there are indications of an increase in levels of C, N and P from rivers to coastal and ocean (Howarth et al., 1996; Meybeck, 1993), and this increase in concentration of nutrients has contributed to an increase in the eutrophication process and degradation of coastal marine ecosystems, especially in estuarine areas.

It becomes necessary to measure the mass balance and the transformation of materials through groundwater, rivers, estuaries and coastal waters, in order to estimate the reservoirs of nutrients and understand how to process the flow paths as well as the advancement of degradation of coastal waters. Thus, we sought to apply all the information gained from the experiment in a flow model, whose objective was to answer the behavioral tendency of the ecosystem studied, as well as serve as a representative for other similar systems, especially in relation to geomorphology and aspects biogeochemical. Among the various models used for nutrient flow, the mass balance model is one of the most highly regarded when it comes to quantify the concentrations of the elements involved. In this case, some protocols for the construction of the database are suggested, in which case the methodological protocols used LOICZ - Land-Ocean Interactions in the Coastal Zone, which propose a typology of consistent database, and allows for comparison with databases various types of coastal and marine environments (Gordon Jr. et al., 1996; Smith and Crossland, 1999; Smith, 2002; Jorgenson and Brown, 2005; Le Tissier et al., 2006; Kannen and Burkhard, 2009; Lantuit et al., 2009; Streletskaya et al., 2009), was designed to estimate the flows of C, N and P in coastal areas around the world. According to Smith (2002), the role of the coastal oceans in the global C-N-P cycle is one of the major and most challenging questions that LOICZ is evaluating.

Through this research, we sought to observe and better understand the transport and mass balance of carbon and nitrogen by water and sediment compartments. For that it was researched the capture of those elements by the rivers that make up the mesh of the Santos estuarine system to the edge of the continental shelf ocean.

MATERIALS AND METHODS

Study area

Santos Estuarine System - SES (23º50'S and 24º S; 46º15'W and 46º30'W) is located in the Baixada Santista, coast of São Paulo State, Southeastern Brazil. This region is ecologically and economically important because of the great biological diversity originating from the Atlantic Forest biome, the presence of mangrove strands, whose role both in species diversity as in nutrient cycling is already well known, and high levels of pollution and contamination, coming mainly from the port and industrial complex, which together produce solid waste and effluents, including sewage, which are deposited in the channels of SES. The main beaches of southeastern Brazil, in terms of population density, are located exactly in the vicinity of the SES, in the municipalities of São Vicente, Santos and Guaruja. There is also the Port of Santos, the largest and most active port in Latin America, with intensive loading and unloading of goods and products, being the great center of runoff from Latin America to the world and vice versa. It should also highlight the industrial city of Cubatão, where are placed heavy industries, formed mainly by steel and metallurgy (Figure 1).

The Cubatão city has an industrial area remarkable, with some types of industries related to production of oil, production of manure and steel. As a result of intense industrial activity, much of the waste material are released in the channels that make up the mesh of the SES, found that mesh heavy metals, organic compounds, petroleum hydrocarbons and other (Braga et al., 2000).

The location of the port of Santos, as well as the industrial complex of Cubatão is strategic because it is close to the most developed region, industrialized and populous of the South America, the city of São Paulo. However, because the port was built in a mangrove area, where the sediment load is very high and therefore the rate of sedimentation, it is necessary that the main channel of the harbor is dredged annually. As a result, the material retained in the surface sediments returns to the water column, increasing the possibility of assimilation and consequent contamination of aquatic organisms, especially filter feeders such as shellfish.

Analytical procedures and model construction flow

Limnological and oceanographic data used to develop the flow model were obtained between the years 2000 and 2008 in 27 sampling stations distributed within the SES as follows: four stations near of industrial complex of Cubatão, six stations in Santos channel, eight stations in São Vicente channel, and nine stations in the Santos bay (Figure 1). Sampling followed the local seasonal pattern, and the sampling was conducted twice a year with total n = 416 samples to gauge the influence of ocean currents and the hydrological cycle in the estuarine system. All analytical procedures follow international protocols for the collection, preservation and analysis described in Strickland and Parsons (1968), Grasshoff et al. (1983) and Wetzel and Likens (2000). The methodological procedures for the determination of the parameters under investigation in the water column (surface and bottom) and surface sediment (up to 0.15 m) are summarized below. Water temperature (°C), pH and salinity (%) were measured with probes for multiparameter water quality WTW and YSI; density (g/cm^3) was calculated from the data of temperature and salinity of the water; free CO_2 and total CO_2 were obtained by titration with control of pH, using NaOH to raise the sample pH to 8.3 and HCl to reduce the pH to 4.3; total alkalinity (TA meq/l) and alkalinity carbonate (CA meq/l) were obtained by calculation from the potentiometric titration method in the analysis of total CO_2 and free CO_2, and calculated by Equations 1 and 2 (Parsons et al., 1984; Grasshoff et al., 1999). The dissolved inorganic carbon (DIC mg/l), also defined as dissolved CO_2 content, was calculated from the total amount of CO_2 per mole transformation according to Equation 3. The dissolved organic carbon (DOC mg/l) was determined by oxidation with potassium dichromate 1N and acid solution of [3 g Ag_2SO_4 + 1000 ml H_2SO_4 + 20 ml H_3PO_4 85% + 0.4 g NaF] and 1 ml of diphenylamine indicator solution, and titration was done according to determinations described by Aprile (2001), with a solution of iron sulfate and 0.5 N ammonia and detection limit of 0.001 mg/l. Dissolved inorganic nitrogen (DIN mg/l) represents the sum of the inorganic fractions in filtered samples (Equation 4), and ammonium (NH_3 mg/l) was determined by reaction with phenol and hypochlorite in alkaline solution catalyzed by sodium nitroprusside, and detection limit of 0.05 mg/l; nitrite (N-NO_2^- mg/l) was determined

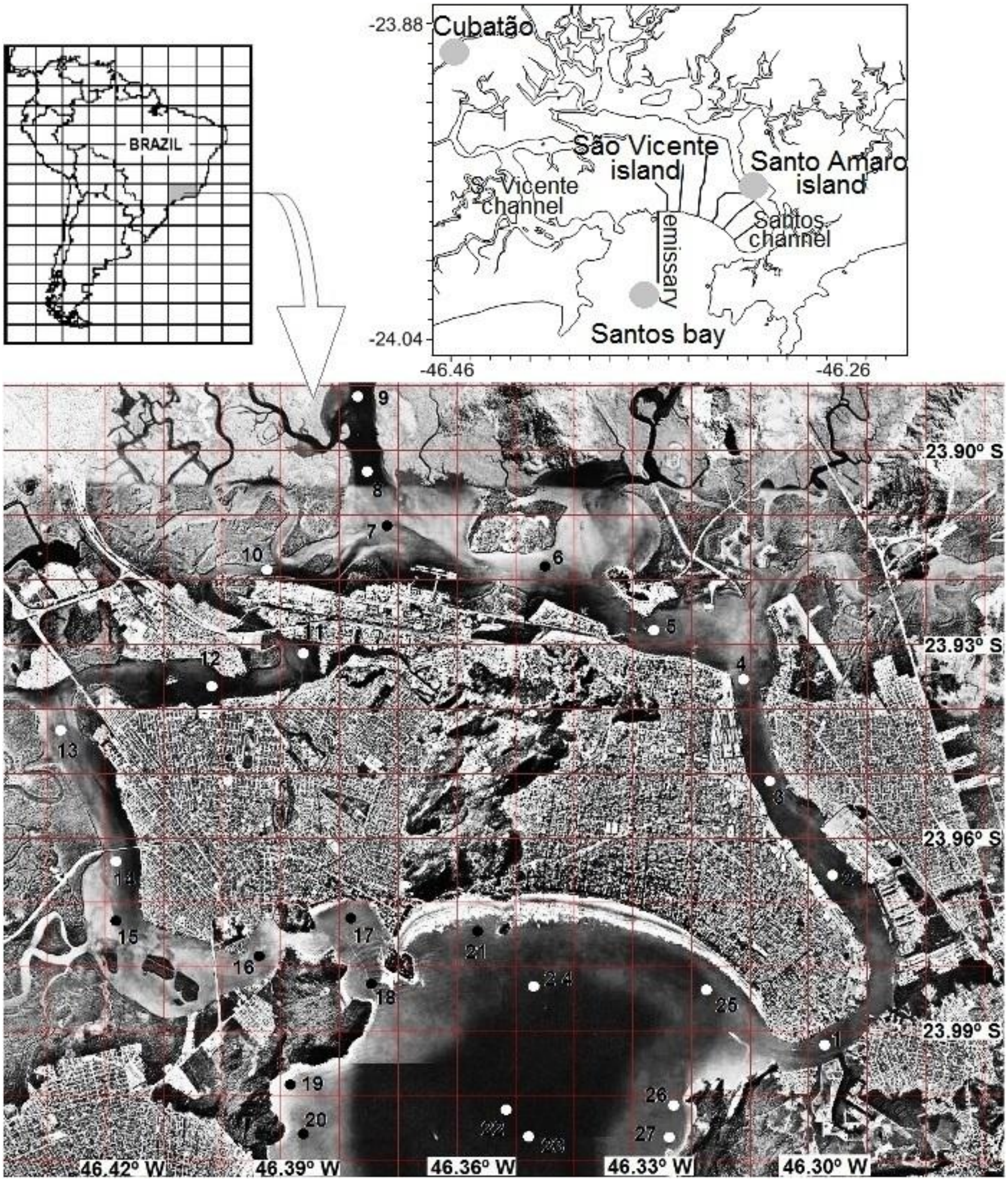

Figure 1. Santos estuarine system (Southeastern Brazil) with the location of sampling stations, and indication of the areas potentially polluting in the smaller map (gray circle) for the industrial Park Cubatão, Port of Santos and outfall.

in the presence of sulfanilamide prepared in acid solution and N-naphthyl ethylenediamine dichloro in alcohol solution with a detection limit 0.005 mg/l, and nitrate ($N\text{-}NO_3^-$ mg/l) was determined in cadmium column with reduction to nitrite in filtered and buffered samples with ammonium chloride, and detection limit 0.009 mg/l. Dissolved organic nitrogen (DON mg/l) was determined in samples filtered by the classical method of Kjeldahl distilling in the presence of 46% NaOH and H_3BO_3, and detection limit of 0.005 mg/l. The particulate organic matter (POM ug/g) in sediments was obtained by the method of oxidation with hydrogen peroxide (H_2O_2 30%) in hot plate at 80°C. The particulate organic carbon (POC ug/g) was calculated by equation 5, which shows the relationship between POC and POM, based on experiments to decomposition in tropical marine environment. The particulate organic nitrogen (PON ug/g) in sediments was determined by the Kjeldahl method of extraction, with a pre-digestion acid (H_2SO_4) of the samples with gradually increasing the temperature to 300ºC.

Equations applied in analytical procedures:

$$TA=\left[\left(\frac{V_{HCl}.N_{HCl}}{V_{sample}+V_{HCl}}\right)-\frac{1}{10^{pH}.fH^{+}}\right]\times K\times 10^{3}\Rightarrow TA=\left(2.5-1100\times\frac{1}{10^{pH}.fH^{+}}\right) \quad (1)$$

Where TA is total alkalinity (mEq.L^{-1}), V is volume of HCl and of sample, N is the normality of HCl, and K is the correction factor of the sample.

$$CA = TA - A \quad (2)$$

Where A is the dissociation constant of boric acid in mEq/l obtained in calculation table.

$$\sum CO_2 = CA\,x\,F_t \quad (3)$$

Where F_t is the correction factor for temperature and salinity obtained in calculation table.

$$DIN = [NH_3]+[NO_3^{\;-}]+[NO_2^{\;-}] \quad (4)$$

Where [X] is the concentration of element X in the sample.

$$POC = \frac{POM}{K_x} \quad (5)$$

Where K_x = 1.9 is a factor of proportionality in the tropical marine environment, and represented the average value of 2.1 suggested by Aprile (2001) and 1.7 of Siqueira et al. (2003) for the region.

The results were statistically analyzed using multivariate analysis, Pearson correlation analysis, considering $p < 0.05$ level of significance, and linear regression: a) to examine the degree of affinity between environmental variables; b) identify the correlation between the variables and the existing local human activities, and c) establish a pattern of carbon and nitrogen flow between compartments within the Santos Estuarine System. Isolines maps were constructed using Surfer 9.0 (Golden Software Inc.) and interpolation of data on maps was made using the kriging method.

The use of historical data was crucial to improve the mathematical model, which is much more accurate as they studied the event in a longer period of time. In this research, we chose to apply the model of mass balance. The mass balance models are considered functional tools, specially developed for decision-making, aiming at solving complex problems associated with the dynamics of an ecosystem and the various interactions between the biotic and abiotic systems. The simulation was established from historical data and based on protocols to flow of nutrients established by LOICZ - Land-Ocean Interactions in the Coastal Zone (Gordon et al., 1996). Among the main characteristics of this method are: the ability to work with secondary data, the minimum requirement of data, the broad applicability and uniformity of methodology and information on the process flow of nutrients (C, N and P).

RESULTS AND DISCUSSION

The isolines of organic and inorganic carbon and nitrogen to the water and sediment are presented in Figure 2. The concentrations of DIC (Figure 2A) in the water ranged between 2.67 and 32.16 mg/l, with average 24.39 ± 3.62 mg/l. The higher isolines were found in Santos channel between stations 5 and 8, and in the eastern part of the Santos bay between stations 25 and 27. There was a wide variation in the concentration of DIC in vertical profile (surface and bottom), this phenomenon is explained by the fact that surface waters contain between 10 and 15% less DIC than deep waters, a difference in the procedure of photo-assimilation carbon by living organisms, and by the streams of falling particles of dead organic matter and carbonate shells into the sediment (Grasshoff et al., 1999). DOC levels (Figure 2B) in the water ranged from 0.10 to 21.53 mg/l with an average 9.61±6.29 mg/l. The high variation of DOC, identified by the high standard deviation reveals a spatial variability of the types of solid waste and liquid effluents released in the SES. The organic shapes are mainly originated from domestic sewage spills in the region, as shown by the high values found at station 22, located at the outlet of the outfall, which ruled in the Santos bay untreated domestic sewage associated with urban stormwater in large part the cities of Santos and São Vicente. With respect to nitrogen forms, levels of DIN (Figure 2C) ranged between 0.04 and 4.71 mg/l, and average 0.61±0.59 mg/l. The higher concentrations were found in the area under the influence of the industrial complex of Cubatão, between stations 8 and 9, where predominated levels of ammonium and nitrite, the most common forms of nitrogen in non-natural water or municipal wastewater. The concentrations of DON (Figure 2D), the same way as with organic carbon, showed a pattern of a tendency to concentrate the highest levels of organic nitrogen in the vicinity of the outfall exit, between the stations 19, 20 and 22 (output emissary), 23, 26 and 27, all stations located in the Santos bay. DON concentrations in water ranged between 0.01 and 2.29 mg/l, with average 0.31±0.33 mg/l. Comparatively, the levels of carbon and nitrogen organic and inorganic were always significantly higher in the bottom waters than surface waters, due to the higher density in the deeper layers. In general, the Santos bay concentrated the highest levels of organic compounds, especially NH_3 forms, which represent a strong pollution by domestic sewage. In general, the nitrogen in the organic matter varies with the type of organism. According to Braga et al. (2000), autotrophic organisms require inorganic nitrogen; ammonia ions on the one hand, nitrite and nitrate or molecular nitrogen on the other hand, and in some cases organic nitrogen. In coastal and estuarine systems, variations in concentrations or overload of nitrogen are an important factor in the evolution of ecosystems.

Concentrations of particulate organic carbon (Figure 2E) in surface sediments ranged between 900 and 38,638 µg/g, with average 19,658±10,548 µg/g, whereas

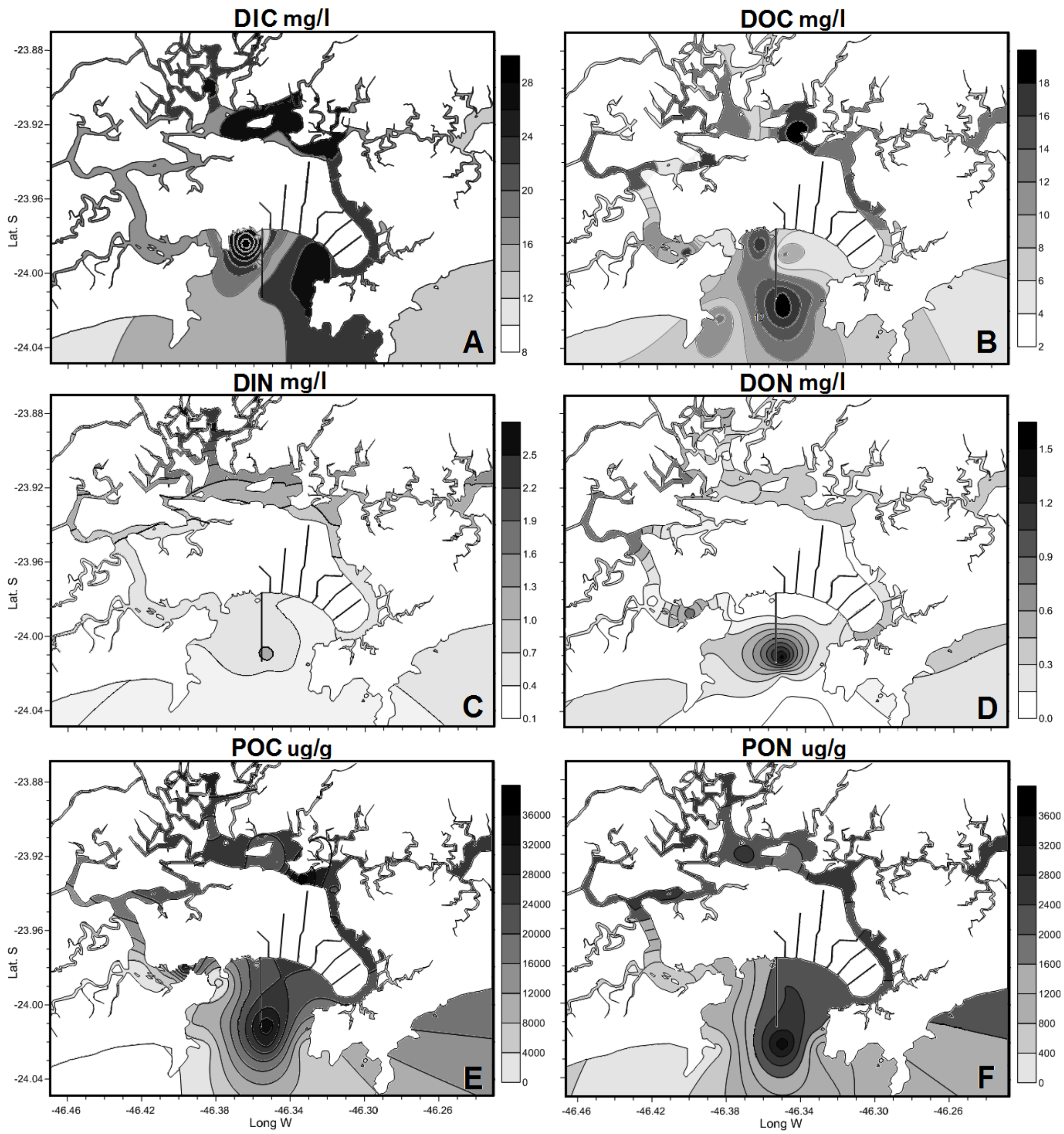

Figure 2. Isolines of carbon and nitrogen organic and inorganic to the water (DIC, DOC, DON and DIN) and sediment (POC and PON) compartments in Santos estuarine system.

the concentrations of particulate organic nitrogen (Figure 2F) ranged between 200 and 3550 µg/g, with average 1875±912 µg/g. The high standard deviations identified are explained by high variation in sediment composition and texture. In principle, higher levels of POC and PON were found on stations with predominantly muddy sediments rich in organic matter associated with clay, while the lowest levels were highly correlated with the stations with a predominance of sandy sediments and sandy clay. In general, in the sediment compartment the isolines concentrations of POC and PON tended to have higher levels in the Santos bay, near the outfall (station 22), and in the Santos channel where it is concentrated all the port activity loading and unloading of ships. The area under the influence of the industrial complex of Cubatão also showed higher values of POC and PON as a result of industrial and urban activities, such as the Village of Cubatão, an area of concern with various issues of public sanitation, including the treatment of disabled sewers.

Considering that salinity has a conservative behavior in coastal systems, and based on linear regression analysis shown in Figure 3, it was concluded that both total carbon (TC), result of adding the inorganic (DIC) and organic

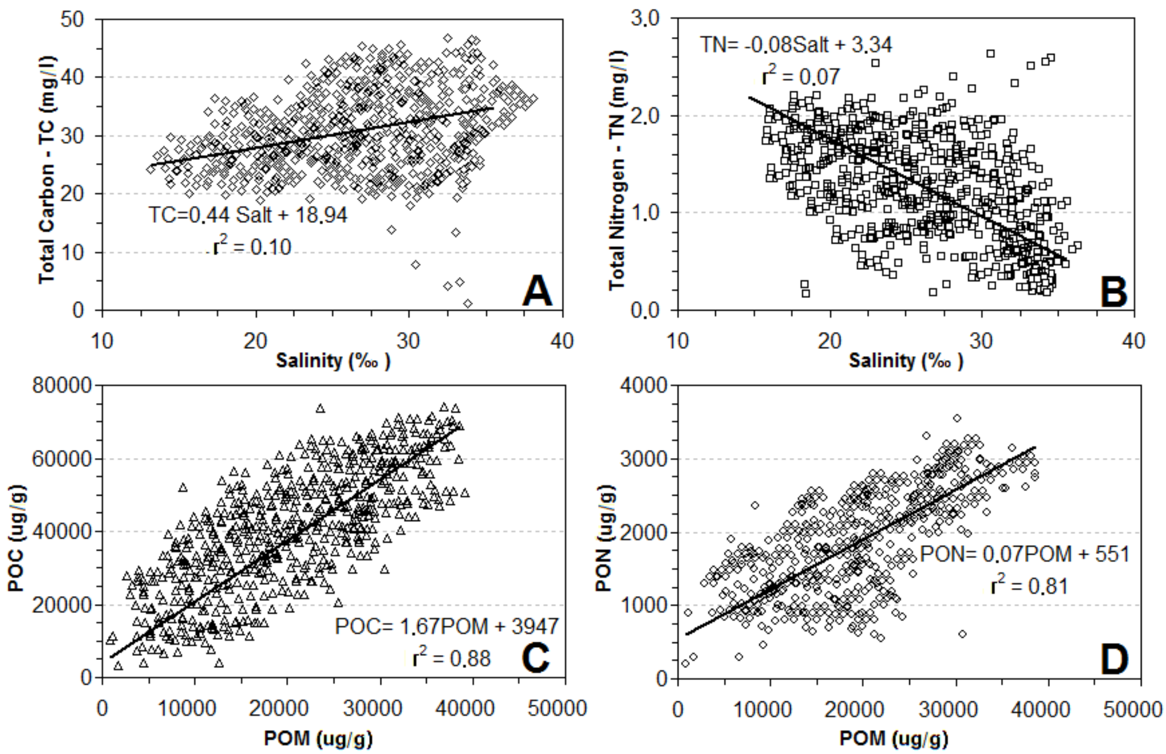

Figure 3. Linear regression analysis for correlation coefficient with $p < 0.05$ between salinity and total carbon (A) and salinity and total nitrogen (B) both the aquatic compartment, and correlation between organic matter and organic carbon (C) and organic matter and organic nitrogen (D) both in the sediment compartment.

(DOC) fractions, and total nitrogen (TN), the sum of DIN and DON fractions, did not have a conservative pattern in the aquatic system. The investigation of TC and TN revealed that its concentrations entering in the SES annually through of the Santos and São Vicente channels were of 1400 and 40 mg/l, respectively, while the levels of these elements that leave the system, by the connection between the Santos bay and the Ocean, were lower that 300 and 10 mg/l, respectively. This means that the SES accumulates carbon and nitrogen, which once not absorbed by the biota is stored in the sediment. According to the mass balance, the station 22, located at the outlet of the outfall, is permanent source of carbon and nitrogen, and depending on the tidal flow, this station can be considered as input (V_x) during the high tidal mark or as output (V_y) during the low tidal mark of TC and TN to the SES.

The correlation coefficients r^2 between TC and salinity and TN and salinity were low 0.10 and 0.07 respectively (Table 1, Figure 3A and B), indicating there is a variation in concentrations among these elements depending on the seasonality and of the flux of tides. Possibly, one part of the nutrients is assimilated by the intense local biota, and other part is added to the sediment, especially the muddy sediments present in the Santos and São Vicente channels. In general, the correlation among nutrients was weak in water, demonstrating independence between variables. The dissolved inorganic nitrogen and total nitrogen were highlights also with a strong positive correlation. The correlation coefficients determined for the regression analysis between POC and POM, and between PON and POM were significant with r^2 values 0.88 and 0.81 respectively (Table 1, Figure 3C and D), indicating a strong influence of particulate organic matter (POM) on the levels of carbon and nitrogen organics. In fact, in the channels where the concentration of organic matter was higher the levels of POC and PON were always high. An exchange may be occurring between the sources of marine and terrestrial organic matter prior to its disposal, caused by hydrodynamic parameters.

It is known the ability of organic matter to precipitate ionic elements through the mechanism of adsorption or complex formation. Because of this characteristic, and as a result of higher concentrations of organic matter are associated with muddy sediments, the port area (Stations 2 to 4) becomes the main area for adsorption of pollutants and contaminants in the sediments of the SES, particularly by metallic elements. The organic matter content in the Santos and São Vicente channels had a very similar behavior, while in the Santos bay this presented a heterogeneous behavior, in part due to the flow of tides that in the stations more distant from the outfall runs washing sediments seasonality, in each cycle of high tide. One factor that may have influenced the

Table 1. Pearson's correlation analysis* for the variables determined in the water column (surface and bottom) and sediment from the SES.

Variable	r (Pearson)	r^2	*p*	Variable	r (Pearson)	r^2	*p*
DICxDOC	0.2000	0.0400	0.0110	TCxDON	0.1712	0.0293	0.0297
DICxTC	0.8270	**0.6840**	0.0000	TCxTN	0.2315	0.0536	0.0032
DICxDIN	0.1804	0.0326	0.0219	TCxSalt	0.3163	0.1001	0.0000
DICxDON	0.1003	0.0101	0.2045	DINxDON	0.0277	0.0008	0.7263
DICxTN	0.2006	0.0402	0.0107	DINxTN	0.8240	**0.6790**	0.0000
DICxSalt	0.1166	0.0136	0.1401	DINxSalt	-0.1965	0.0386	0.0124
DOCxTC	0.8904	**0.7928**	0.0000	DONxTN	0.3067	0.0940	0.0001
DOCxDIN	0.2109	0.0445	0.0073	DONxSalt	0.1242	0.0154	0.1160
DOCxDON	0.1527	0.0233	0.0528	TNxSalt	-0.2646	0.0700	0.0060
DOCxTN	0.1654	0.0274	0.0358	POCxPOM*	0.9384	**0.8805**	0.0000
DOCxSalt	0.3279	0.1075	0.0000	POCxPON*	0.7794	0.6074	0.0000
TCxDIN	0.2565	0.0658	0.0010	POMxPON*	0.9010	**0.8118**	0.0000

*Variables for sediment; significant coefficients of correlations are marked in **bold** ($p < 0.05$), N= 416 and GL= 414.

results is the geomorphology of the region, with dozens of tiny channels and connections meander areas, always surrounded by mangrove vegetation. Sampling stations located in areas more sheltered from the action of tides showed low flow in the bottom, facilitating the accumulation of dissolved organic matter in sediments.

The organic pollutant loads from industrial sources exceeded the organic home-grown in the SES. According to Braga et al. (2000), the waters of Santos bay are contaminated by various industrial effluents, port waste dumps and domestic, those are released in the estuarine region and to come to bay through the Santos and São Vicente channels.

Carbon and nitrogen are two of the principal components of the organic matter. C/N ratios in sediments have aided to determine spatial and temporal variations of organic matter and lignin phenols in sources of organic matter to lakes (Mahapatra et al., 2011), as well as it is an alternative to identify fresh deposition of C and N from water column to sediment compartment. Plankton is rich in nitrogen forms and thus the C/N ratio is low, changing approximately between 5 and 9, including the deposits of organic matter in those organisms. Terrestrial vascular plants and their derivates in sediments have C/N ratios above 15, and high C/N ratios, above 24, can be considered as the mixing of terrestrial and autochthonous organic matter in sediments (Mahiques et al., 1999; Burone et al., 2003; Mahapatra et al., 2011), sometimes with contribution of macrophyte materials, implying, in this case, an increase of the remains partially destroyed of mangrove forests, with high content of plant fibers of cellulose and lignin. It is assumed that the mangrove vegetation is a strong supplier of nutrients, especially carbon to the water column and, consequently, to the sediment. Table 2 shows the range of variation of the rates C/N in the subareas that comprise the SES. The molar rate C/N had high variation in the aquatic compartment, between 7 and 106 with an average 46±26, while the rates for the sediment compartment varied between 1 and 22 with an average 10±4. The high amplitude of variation, especially in the aquatic compartment, indicated a general instability in the concentrations of carbon and nitrogen. The stations located in São Vicente channel and in part of the Santos bay were the main responsible for these high rates. This pattern of concentration of nutrients appears to be a consequence of the following factors: 1) marked reduction of the nitrogen fixed by excessive consumption in the sediment by benthic organisms, 2) growth of carbon compared to nitrogen by deposition of waste material from terrestrial organic matter of the basin drainage of Baixada Santista. Especially in the Santos bay because of the link with the sea, the biological material of marine origin is enriched in nitrogen when compared with terrestrial material. This probably caused a C/N ratio lower. The diagenetic processes of organic carbon change the rates C/N, which became higher.

Hydrodynamic model and nutrient budgets

To understand the processes governing the biogeochemical cycles in estuarine and coastal areas is necessary to know the local processes that control the flow of C, N and P. In areas partially or totally rich of mangrove and of the estuary, the dynamics of nutritional flow is intense and very fast. The processes of decomposition and releasing of organic matter are continuous and the ionic charge of elements released is very large, making these ecosystems among the most dynamic and intense in nutrient cycling. The marine biological productivity in surface waters is mainly controlled by the availability of macroelements, particularly nitrogen and phosphorus, and probably is not influenced

Table 2. C/N rates in water and sediment compartments of the SES.

Area	Rate C/N water	Rate C/N sediment
Santos Channel	16-90	9-14
Cubatão	7-33	10-12
São Vicente Channel	20-90	1-22
Santos Bay	18-106	4-14

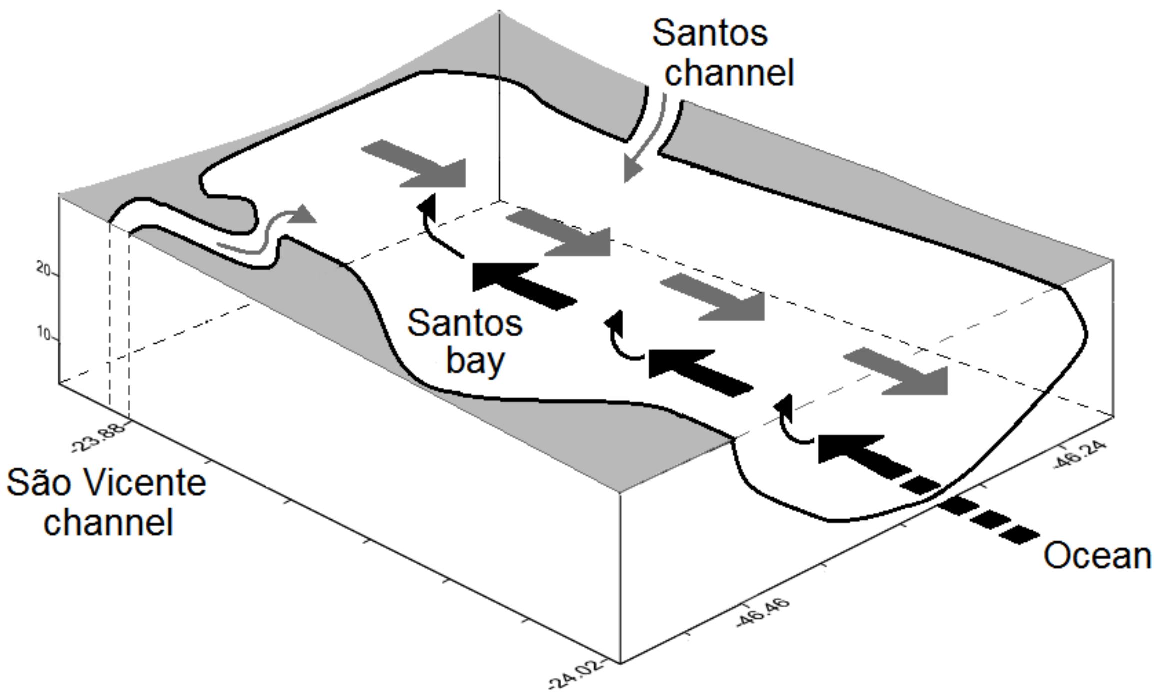

Figure 4. Simplified model of freshwaters and marine waters circulation in the Santos estuarine system.

by changes in inorganic carbon. For this reason, the flow of organic material is often not included in the models used to simulate the response of the oceans to increase anthropogenic discharges.

Equations were applied to the results to understand the fluxes based on the type of estuary, tides and channels, taking into account the density gradients that drive the patterns of circulation and mixing in the estuarine system. The SES was classified as a partial mixture system of water, which receives a supply of dense waters by the tide and layers of freshwater less dense and rich in organic material coming from the channels that border the swamp vegetation (Figure 4). In Santos bay, the tidal influence is greater, besides the flow from the channels can not dominate the circulation pattern, which in this case, occurs most often in a counterclockwise direction, partially removing the water bodies of the SES and discharging them into the ocean. Thus, the renewal of the waters of the SES is partial as these waters are carried by currents to the sea each tidal cycle. There is also a smaller circulation that occurs in the phases of low tide, also in counterclockwise, just inside the Santos bay.

The salinity gradient showed that the Santos channel at the port of Santos, has a greater influence of marine waters, regardless of what stage of high or low tide, shows stratification from station 1 to station 7. The water circulation occurs with marine waters flowing into the bay by the deeper layers, and freshwaters flowing in the bay by the more superficial layers. The São Vicente channel, for their localization, and morphological and morphometric characteristics, presents most part of the hydrological cycle a predominance of freshwaters coming from the rivers that supply the estuarine system. In fact, analyzing the degree of stratification in this channel, it is noted that from station 17 toward the interior of the estuary to station 9, the salinity drops to levels of brackish waters. Thus, the physical stratification imposed by the density is reduced gradually over the water column, contributing to the water mixture. The horizontal gradient of salinity in the bay is maintained by diffusive

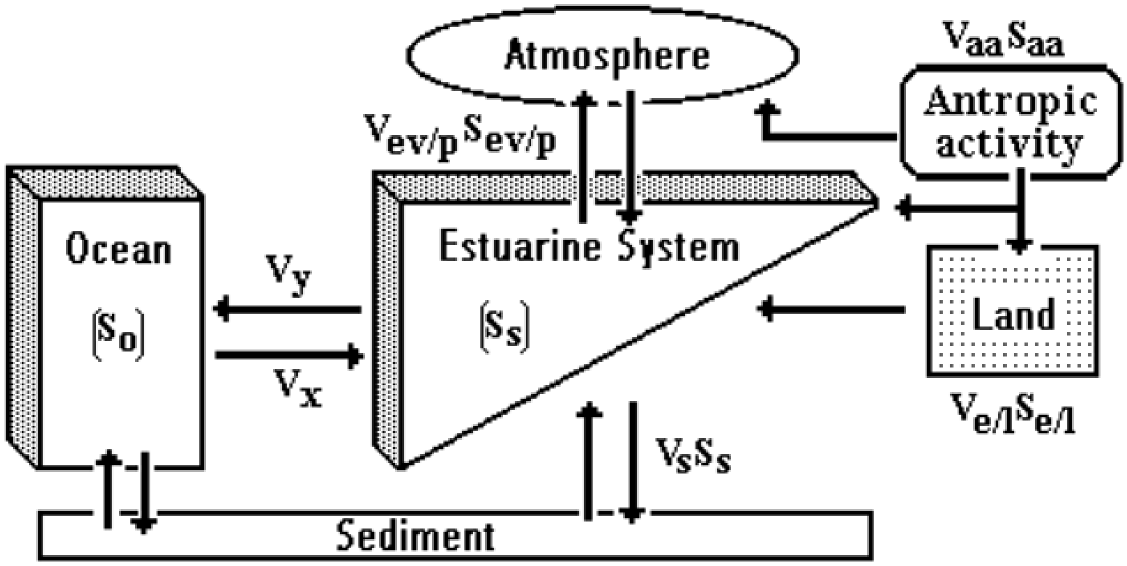

Figure 5. Flow model of carbon and nitrogen for the Santos estuarine system - SES, which is based on the analysis of mass balance of nutrients and conservative pattern of salinity in the system.

flux of salts to the sea due to the mix by the action of tides and winds.

Figure 4 shows schematically the flow of marine waters and freshwaters circulating inside the estuarine system. From this model, the circulation of water masses, and based on nutrient data, we developed a flux model of C and N based on the suggestions of Gordon et al. (1996) for an area previously defined. Furthermore, we took into consideration, for developing the model, the residence time of water in the system and routes of entry and exit of the estuary, including the atmosphere, land adjacent eroded or leached, and coastal and ocean systems. The sediment compartment was considered simultaneously as a reservoir and source of carbon and other elements, including metallic elements to the water. Thus, we have the following Equation 6 of conservation of mass:

$$\frac{dM}{dt} = \left(\sum In_i - \sum Ou_i\right) + \left(\sum P - \sum C\right) \Leftrightarrow \frac{dM}{dt} = 0 \qquad (6)$$

Where In_i is the inflow to the system; Ou_i is the outflows of the system, P is the production inside the system, and C is considered consumption (decomposition/oxidation and respiration).

A solution derived from Equation 6 and using the system flow shown in Figure 5 for the inputs of nutrients in the system (In_i) can be explained by the equation:

$$\sum In_i = V_{e/l}S_{e/l} + V_{ev/p}S_{ev/p} + V_sS_s + V_x + V_{aa}S_{aa} \qquad (7)$$

Where V is the nutrient load; and S is the charge of dissolved ions; *e/l* represents the nutrients from adjacent soil transported by the erosion and leaching processes; *ev/p* represents the evaporation and precipitation processes; S is the sedimentary flux; x is the nutritional flux from ocean to the estuary, and y is the nutritional flux from estuary to the ocean.

Equation 7 can be rearranged in order to estimate the anthropogenic activity in the region (V_{aa}), which can be used for any material in the water. We replace the flow of the ocean to the SES (V_x) in Equation 7, simplifying the expression to determine the total load on the system input (Equation 8):

$V_x = \dfrac{V_rS_r}{S_0 - S_s}$, and $S_r = \dfrac{S_0 + S_s}{2}$ we have ⇒

$$\sum In_i = V_{e/l}S_{e/l} + V_{ev/p}S_{ev/p} + V_sS_s + V_{aa}S_{aa} + \frac{V_r(S_0 + S_s)}{2(S_0 - S_s)} \Leftrightarrow$$

$$\sum In_i = V_iS_i + \frac{V_r}{2}\frac{(S_0{}^2 - S_s{}^2)}{(S_0 - S_s)^2} \qquad (8)$$

Where V_r and S_r are part of the residual volume of nutrients and ions in the system.

A solution based on the flow system shown in Figure 5 for the outputs of nutrients in the system (Ou_i) can be explained by Equation 9:

$$\sum Ou_i = V_sS_s + V_y \Leftrightarrow \sum Ou_i = V_sS_s + V_rS_r \qquad (9)$$

Of all the sources of input to the SES via anthropogenic, $V_{aa}S_{aa}$ is definitely the most important by volume, which is almost constant of discharges of effluents rich in inorganic (industrial sources) and organic (urban sources) compounds, as well as its high potential pollution and contamination. On the other hand, the flow or pulse of tide that is coming in and circulates through the Santos bay has an important role in the removal of excess waste transported by the connection of Santos and São Vicente channels, and also by the outfall, responsible for important contribution of organic compounds to the bay.

Conclusion

Within the study period, the volume of water circulated inside the SES was governed by the hydrological cycle (rainfall) with a strong influence of the pulse of tidal, not just in the bay, but also in all the large and small channels that make up the mesh of the estuarine system. The salinity gradient was conservative for all SES, while the variation in concentration of nutrients depended on much of the area of direct influence, considered in this research as the source of supply of nutrients, and the area of indirect influence, defined as the area that removes or modifies the concentration of the elements C and N in the water column and sediment: Could not find a conservative pattern of nutrients to the estuarine system as a whole, but the inorganic forms remained constant in certain parts of SES, especially in the region under direct influence of the industrial complex of Cubatão and port of Santos (Stations 3 to 9). In this case, the DIC has always remained at high concentrations in the water column in the space-time (Figure 2A), which indicates that there is in these stations one or more continuous sources of dump material rich in inorganic carbon. On the other hand, the Santos bay presented the highest variations in nutrient concentration along the current flow, a fact explained by local ocean dynamics. The data for the Santos bay has shown that it differs from Cubatão region and port area due to the tendency to conserve dissolved nutrients in the suspension. The effluent from the Cubatão city associated with solid waste in the port area are transported to the sea through the Santos and São Vicente channels, in particular the first, while in the bay and areas dominated by mangrove vegetation, the load of pollutants and contaminants is kidnapped, degraded and diverted to the food chain.

This study allowed understanding better the dynamics of nutrient flow due to the local hydrological cycle, especially under the influence of the pulse of tides. Thus, the results added to other work already developed in the region, may contribute to the management of industrial areas (industrial complex of Cubatão and port of Santos) and urban areas (Santos and São Vicente cities), to reduce pollutant loads and contaminants in the estuarine system.

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