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Trophic dynamics (Dissolved Inorganic Nitrogen-DIN and Dissolved Inorganic Phosphorus-DIP) in tropical urban estuarine systems during periods of high and low river discharge rates

CARLOS NORIEGA[1,2], **MOACYR ARAUJO**[1,2], **MANUEL FLORES-MONTES**[1] **and JULIA ARAUJO**[1]

[1]Departamento de Oceanografia/DOCEAN, Universidade Federal de Pernambuco/
UFPE, Av. Arquitetura, s/n, 50740-550 Recife, PE, Brazil
[2]Rede Brasileira de Pesquisas sobre Mudanças Climáticas Globais/Rede CLIMA, Av.
dos Astronautas, 1758, 12227-010 São José dos Campos, SP, Brazil

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Abstract: This paper focused on the use of the biogeochemical LOICZ (Land Ocean Interactions in the Coastal Zone) to investigate the dynamics of DIN and DIP nutrients among three highly urbanized tropical estuaries (Barra das Jangadas (BJ), Recife (RE) and Timbó (TB)), located in the northeastern region of Brazil. The input data were obtained through *in situ* measurements (2007) and governmental agency databases (2001-2007). The balances of the non-conservative elements showed that the RE and TB systems alternated between sources and sinks during the observation periods (0.2-0.8 mmoles DIP m^{-2} d^{-1} and 0.1-10 mmoles DIN m^{-2} d^{-1}). The metabolism rates in the systems indicated that the BJ system was autotrophic during the two observation periods (10-26 mmoles C m^{-2} d^{-1}), while the RE system was heterotrophic (9-12 mmoles C m^{-2} d^{-1}).

The river discharge rates observed during the period 2001-2007 showed averages ranging from 9.4±3.8 to 18.4±7.7 $m^3 s^{-1}$. Measurements of the trophic status in the RE system during 2007 characterized the system as eutrophic, thereby demonstrating high levels of chlorophyll-*a* and inorganic nutrients. The applications of balance sheets modeling proved to be very useful toward understanding the dynamics of estuarine systems dominated by large urban centers.

Key words: nutrients dynamics, estuarine, eutrophication, modelling, Brazil.

INTRODUCTION

The transport and release of carbon (C), nitrogen (N) and phosphorus (P) from land to the coastal oceans has become a matter of notable concern and interest during recent decades (Liu et al. 2010, Howarth et al. 1996, Nixon 1995). Understanding the nutrient and carbon cycles and their inward and outward fluxes within coastal ecosystems is imperative for the sustainable management of coastal resources. Due to the high densities of human life throughout watersheds along coastal zones, estuaries and coastal waters, ecosystems have become more vulnerable to anthropogenic impacts (Crossland et al. 2005). In addition, riverine nutrient inputs have increased dramatically as a consequence of urban

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Correspondence to: Carlos Noriega
E-mail: carlos.delnor@gmail.com
ORCid: 0000-0002-3590-6377

development, agriculture, and industrialization (Liu et al. 2010, Howarth, et al. 1996). The transport and biogeochemical cycles of C, N and P within coastal zones can be altered by human activities, thereby leading to nutrient enrichment, sewage runoff, hydrological changes, and increased amounts of carbon dioxide (Gordon et al. 1996, Wollast 1993). Environmental variations in the natural cycling patterns of these elements and their implications for the operational processes of estuarine systems should be investigated within a temporal and spatial context in consideration of the flux rates between the continents and their adjacent coastal systems.

Bays and estuaries are major sources of aquatic, terrestrial and atmospheric pollution in coastal regions that serve as transitional areas between the continents and the oceans. To understand the biogeochemistry of estuarine ecosystems, it is important to note that the hydrological system is the most important element in the biogeochemical cycle because it controls the retention of organic matter and dissolved inorganic nutrients derived from terrestrial environments or river discharge (Noriega and Araujo 2014). In this way, the maintenance of the ecological properties in an estuary depends on the balance between its capacity to absorb or export pollutants versus the magnitude of the estuarine input into the system. The intake of nutrients is intensified within estuaries located in highly and densely populated regions due to contributions from domestic and industrial effluents and urban outflow, as well as those from agricultural effluents.

In Brazil, half of the population is estimated to live within 200 km of the sea (IBGE). Several studies have shown that the main causes of pollution throughout the coastal zones of Brazil are related to population densification processes (Braga et al. 2000).

The Metropolitan Region of Recife (RMR) (Fig. 1), which is located in the coast of the state of Pernambuco, has three important estuarine areas, namely, Barra das Jangadas (13 km^2), Recife (26 km^2) and Rio Timbo (14 km^2), which also include mangrove areas and remnants of the Atlantic Forest. Most urban waste therein lacks adequate treatment, and both agriculture and livestock farming practices have intensified along the coastal region. Some isolated studies have already suggested that some of these areas are showing signs of incipient eutrophication (Guenther et al. 2016, Noriega and Araujo 2011, 2009). The systems adjacent to the RMR, including the Capibaribe River, Beberibe River, Tejipió River, Jaboatão River, Pirapama River, Pina Basin, and Timbó River, have experienced important ecosystem changes due to anthropogenic influences during the last century (Noriega 2010). In addition, the observed eutrophication is mainly associated with increases in the population, industrial development and agricultural activity on a smaller scale. The LOICZ (Land Ocean Interactions in the Coastal Zone) protocol represents the largest global and regional initiative for characterizing coastal zones through water, salt and nutrient balances along land-ocean interfaces (Gordon et al. 1996).

The main objective of this study was to temporally and spatially characterize three tropical estuarine areas through their nutrient (DIN and DIP), water and salt balances during periods of high and low fluvial discharge. Additionally, we aim to determine the trophic states of these systems through a water quality index. This study presents the first application of the LOICZ model at a larger scale in the northeastern region of Brazil.

MATERIALS AND METHODS

STUDY AREA

According to 2007 census data, the metropolitan region of Recife contains 3,436,000 inhabitants distributed throughout 14 municipalities that collectively comprise an area of 2785 km$^{2.}$. This area represents 2.83% of the total area of the state of Pernambuco, with a density of 1200 hab km^{-2},

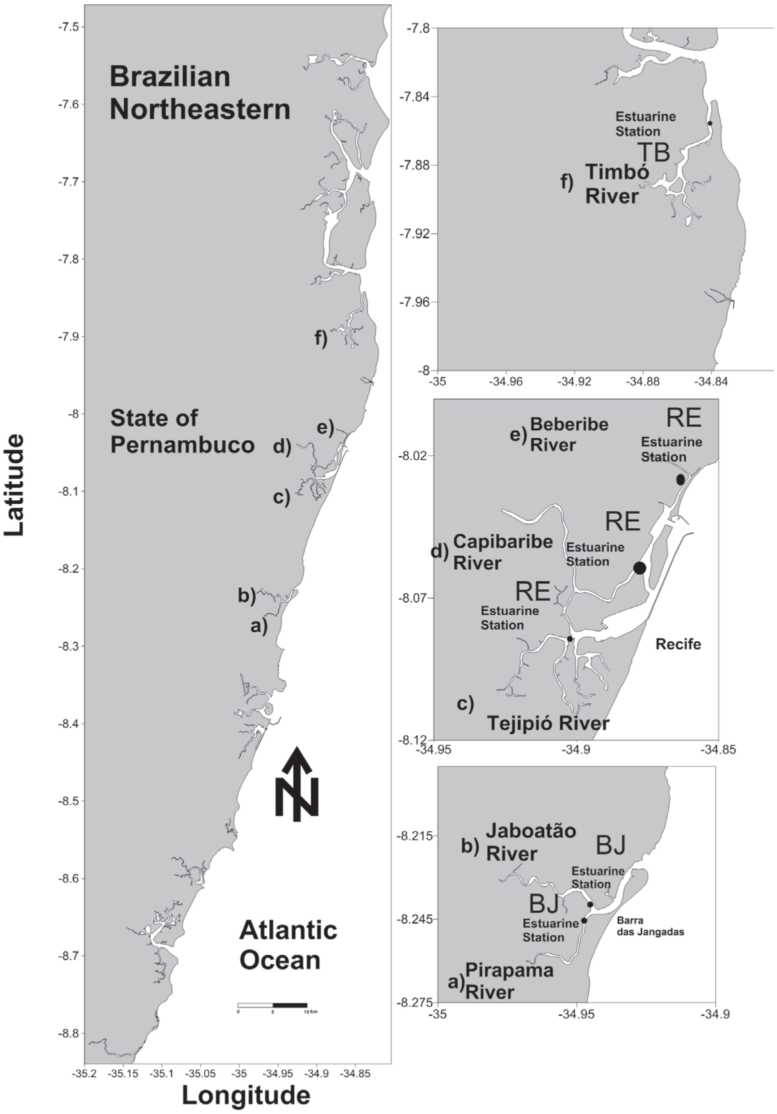

Figure 1 - Map of the coastal region of the state of Pernambuco showing the estuarine areas in this study (black circles indicate the estuarine observation stations). BJ, RE and TB indicate the estuarine regions this study.

a geometric growth rate of 1.50% / year and a 96.92% degree of urbanization (IBGE 2010). The four largest urban centers in the RMR, namely, Recife (1,422,905 inhabitants) and Jaboatão dos Guararapes (581,556 inhabitants), Olinda (367,902 inhabitants) and Paulista (262,237 inhabitants), constitute the largest integrated cluster. With an area of 218 km^2, Recife represents approximately 7% of the metropolitan area and contains 42% of the inhabitants in the RMR (IBGE 2010). The coastline of the three areas in this study is approximately 45 km long and includes the four municipalities with the highest concentration of inhabitants.

The three basins investigated in this study (Capibaribe, Beberibe and Tejipió) (Fig. 1) constitute an area of 509.47 km^2 within the RMR, while the basin of the Capibaribe River only occupies 4.52% of the total area in this region. The estuarine system of Barra de Jangadas is formed by the Jaboatão and Pirapama rivers and is located about 20 km south of the city of Recife (Fig. 1). This region has an area of approximately 13 km^2, an average depth of 2.5m, a maximum width of 250m (32,500x10^3 m^3) and a length of 8 km upstream following upstream by the main channel. The estuarine system of the Timbó River occupies an area of approximately 14 km^2, with mean depths of 3m (Noriega 2010).

CLIMATIC AND HYDROLOGICAL CHARACTERISTICS

The study area is located in the coastal region of the city of Recife (Fig. 1). The climate, which is classified as an As' on the Köppen scale, is characterized as warm and humid (i.e., "pseudotropical") and is moderated by the sea breeze. The pluviometric regime varies from 1500 to 2000 mm/year with a higher concentration from March to August. The river discharges in the study area ranged from 1.4 to 35 m^3 s^{-1}. The lowest discharges were recorded along the Beberibe River (1.4 to 4.9 m^3 s^{-1}) and the highest were observed on the Capibaribe River (10 to 35 m^3 s^{-1}) during the dry period and rainy period, respectively (Araujo and Ribeiro 2002). The groundwater discharge is small when compared to the discharge of the rivers.

According to Noriega and Araujo (2011) groundwater discharge corresponds to 3.6% of the total river discharge.

The semidiurnal tides varied between 1.0 and 1.6 m. The tidal limits were determined 5 km away from the first curve along the Beberibe River (Fig. 1), which is 5 km away from the mouth of the Tejipió River and 12 km away from the mouth of the Capibaribe River (Araujo et al. 1999).

RAINFALL AND RIVER DISCHARGE DATA (TEMPORAL SERIES)

Data from several stations and institutions that measure climatic variables were obtained for 6 basins (the Jaboatão, Pirapama, Capibaribe, Tejipió, Beberibe and Timbó Basins) to correlate the variations among them. We used hierarchical agglomerative cluster analysis (HAC) for identified the areas and months that showed similar characteristics. According to this analysis, we identify the regions and build our monitoring plan. Our study basins were: Recife (Capibaribe, Beberibe and Tejipió), Barra de Jangadas (Jaboatão and Pirapama) and Timbó.

One of the main hydrological characteristics of a river basin is its river discharge, mainly due to the fact that its river discharge varies strongly according to the seasonal climatic period. However, many basins, especially smaller basins, lack such information due to the absence of limnimetric measurements along their course. This difficulty was observed among most of the smaller basins throughout the state of Pernambuco. To resolve this problem, the Brazilian databases from the National Water Agency (ANA), State Plan for Water Resources Secretariat of Technology and Environment (SECTMA) and Secretariat of Water Resources of Pernambuco (SRH) were consulted. We also used the modified Schreiber model (Miranda et al. 2002) to obtain the discharge data for the areas without data. These months (March, June, October and December) were selected because they had statistically opposite characteristics. The climatology of fluvial discharges were obtained of 2001-2007 time series of river basins.

SAMPLING AND ANALYSIS

Samples were collected during March, June, October and December of 2007 during a total of four campaigns. For this study, we divided each estuarine region into 3 segments based on the longitudinal saline gradient classification proposed by McLusky (1993). The estuarine limit within the plume region was calculated based on the average salinity within the plume samplings.

The temperature and salinity (conductivity) parameters were measured using a CTD (Sea-

Bird Electronics SBE911plus, Sea-Bird Scientific Inc. ®). The salinity was also verified against the chlorinity, which was determined through $AgNO_3$ titration (Strickland and Parsons 1972). The local depth was determined using a digital echo sounder- Hondex PS-7® with a mark LCD screen and a resolution of 0.1 m. The depth of the visual disappearance of a Secchi disk was used to determine the water transparency.

The water samples were collected in Van Dorn bottles for further analyses of the dissolved oxygen (DO) and nutrient concentrations. The pH was measured relative to the NBS scale using a pH/ion analyzer and a Ross combination electrode (Orion ®) on board the vessel following sample acquisition using a pH/ion analyzer 350 and a Ross combination electrode (Orion ®). The precision and accuracy of the pH measurements were ±0.005 and 0.1%, respectively. The DO was analyzed using the Winkler method (Grasshoff et al. 1983) with a precision of ±1.3 µm. The relative oxygen saturation (%) in the water was calculated using the following equation for temperatures between 0 and 40°C and salinities between 0 and 40:

$$\% = \frac{DO}{DO^*} \times 100 \qquad (1)$$

where DO is the oxygen concentration in the sample and DO* is the oxygen solubility in the water at the same temperature and salinity using the UNESCO tables (1986).

The dissolved inorganic nutrients, dissolved inorganic ammonia + nitrite + nitrate (DIN), and dissolved inorganic phosphate (DIP) were analyzed according to Grasshoff et al. (1983) after the filtration of the samples using Whatman® GF/C 47-mm, with pore size of 0.45 µm glass fiber filters. The precision was ±0.02 µmol for nitrate, ±0.02 µmol for nitrite, ±0.02 µmol for ammonia, and 0.01 µmol for phosphate. The accuracy was ±2% for DIP, ±3% for nitrate and nitrite, and ±5% for ammonia.

Samples for analysis of chlorophyll-*a* were collected using a Van Dorn bottle (1 L) at the surface, and in the depth of the Secchi disk. The chlorophyll-*a* concentration was measured in the laboratory using a Micronal B280 spectrophotometer (Parsons and Strickland 1963, Wetzel and Likens 1991) with a precision of ±5 µg and an accuracy of 5%.

TROPHIC STATUS INDEX

The TRIX trophic state index proposed by Vollenweider et al. (1998) was used for a comparison between the chlorophyll-*a*, DO and nutrient concentrations across a wide range of situations by combining factors that are directly related to productivity, as represented in Eq. 2:

$$\mathrm{TRIX} = \left(\mathrm{Log} \times \left(\left(\mathrm{Chla}\right) \times \left|\mathrm{D\%DO}\right| \times \mathrm{DIN} \times \mathrm{DIP}\right) \times 1.5\right) / 1.2 \qquad (2)$$

where

TRIX: the index of the trophic state;

Chla: the concentration of chlorophyll-*a* (mg/m^3);

|D%DO|: saturation deviation of DO, or the absolute value of the deviation in the percentage of the DO saturation |100-%DO|;

DIN: dissolved inorganic ammonia + nitrite + nitrate (DIN) (mg/m^3); and

DIP: dissolved inorganic phosphorus (mg/m^3);

The constants 1.5 and 1.2 respectively represent the minimum values of the variables that comprise the TRIX index and the 10 levels of hierarchy within which it is drawn. Values between 2 and 4 correspond to a state of high water quality representative of low nutrient water, with a low trophic level. In contrast, values between 6 and 8 correspond to a poor state and are characteristic of highly productive waters with a high trophic level. Values between 4-5 correspond to moderately productive waters,. medium trophic level and good transparency of the waters. Values between 5-6 correspond to very productive waters, high trophic level and poor transparency of the waters.

The non-conservative balances associated with this index indicate the water-quality state in the study area.

INPUT DATA

Several databases from Pernambuco state and the Brazilian federal government (CPRH 2007, SRH 2008) were consulted in addition to previous research carried out in the study region between 2001 and 2007 (Noriega et al. 2005, Branco et al. 2002). Fluvial DIN and DIP concentrations were obtained from the CPRH database for the period 2001-2007, while the river discharge data were extracted from the state water resources report of SRH (2008). Missing data were estimated using the Schreiber model, obtained in Miranda et al. (2002). These surveys therefore constitute part of our work in the three areas studied. The last investigation carried out was a survey in 2007 that performed four data collections in the areas of the RMR (i.e., the Tejipió, Pina, Beberibe and Capibaribe Basins) during the months of March, June, October and December among the fluvial, estuarine and oceanic regions (Fig. 1).

STATISTICS OF THE FLUXES OF THE DISSOLVED INORGANIC NUTRIENTS AND FLUVIAL DISCHARGES

Through hierarchical agglomerative cluster analysis and principal component analysis, we identified the areas and months that showed similar characteristics. We use the XLSTAT ® 2010 software for the statistical analyzes mentioned above.

We analyzed the three areas statistically to observe the similarities between them. We tested for the normality through the Shapiro-Wilk and Anderson-Darling tests with $\alpha = 0.05$, which resulted in the rejection of the null hypothesis for normality within the analyzed series. As our data corresponded to three separate areas, we selected the Kruskall-Wallis test for tests involving more than two samples. The months with low and high river discharge rates were identified through a statistical hierarchical agglomerative cluster analysis of their similarities using Pearson correlation coefficients for all of the months within the 2001-2007 time series.

Additionally, a non-parametric Kruskal-Wallis test ($p < 0.05$) followed by a Dunn test was applied to the non-conservative DIP and DIN flows and the river discharge throughout the three areas.

MASS BALANCE

To characterize the changes in the water flow, salinity and nutrients (C, N and P) between the estuarine zone and the adjacent sea, a mass balance model was used following the guidelines of the LOICZ project (http://www.nioz.nl/loicz/info.htm; Figs. S1, S2 – Supplementary Material). The LOICZ protocol represents the largest global and regional initiative for characterizing coastal zones through water, salt and nutrient balances along land-ocean interfaces (Gordon et al. 1996).

The balance among C, N and P proposed by Gordon et al. (1996) was intended to be used to determine the metabolism of a coastal ecosystem under investigation, thereby identifying the sources or sinks in C, N and P. In general, this model is based on calculations of the salinity and water flow and the determination of the fluxes of the elemental nutrients. The results of these balances along with stoichiometric bases provide estimates of various processes, including production, respiration, nitrogen fixation and denitrification. Eq. 3 presents a simplified diagram characterizing the fluxes of matter. It should be noted that the theoretical description of the model presented below, which was based on Gordon et al. 1996, can be accessed at http://data.ecology.su.se/MNODE/.

$$dM/dt = \sum \text{inputs} - \sum \text{outputs} - \sum(\text{production} - \text{consumption}) \quad (3)$$

In Eq. 3, dM/dt represents the change in mass of any material in function of time. The balance in the LOICZ protocol assumes that the materials are conserved. In a steady state, the differences between the materials exported from the system (outputs) and the materials imported into the system (inputs) are described via processes that occur within the system (production-consumption).

Eq. 4 defines the role of any system with a specific balance as a liquid source or sink for a particular material (C, N or P) and is defined as follows:

$$\Delta Y = (dY/dt + dV/dt) - \sum V_{in} Y_{in} - \sum V_{out} Y_{out} \qquad (4)$$

The units of ΔY are mass per unit time and are generally represented in millimoles or moles per day, while V represents the flow (m^3), and Y is the concentration of the element. The following sections describe the information obtained from literature, and the findings from our observations and estimates. The availabilities of C, N and P within estuarine systems are strongly related to their transport processes (i.e., sinking, advection, and water inflow from external sources). Our first modeling process incorporates physical data and flows. Subsequently, the chemical budgets of N and P are presented, and their implications on the metabolism rates of the ecosystems in different sectors of the estuarine system are discussed.

RESULTS

RAINFALL AND FLUVIAL DISCHARGES

Through hierarchical agglomerative cluster analysis and principal component analysis, we identified the areas and months that showed similar characteristics. These areas exhibited few differences among themselves, but the results showed that the three central basins (i.e., the Capibaribe, Beberibe and Tejipió Basins) corresponded to the same group, which is the same case for the southern group (the Jaboatão and Pirapama Basins). Thus, the three areas were treated as separate groups relative to their climatic characteristics (Fig. 2).

The time series for the basins follow a similar annual pattern with the least fluvial discharge (m^3 d^{-1}) occurring during the month of December and the highest discharge rate occurring in June. March and October were intermediate months of high and low discharge rates, respectively. The months with low and high river discharge rates were identified through a statistical hierarchical agglomerative cluster analysis of their similarities using Pearson correlation coefficients for all of the months within the 2001-2007 time series (Fig. 3).

The river discharge rates observed during the period 2001-2007 showed averages ranging from $815\times10^3\pm332$ to $1591\times10^3\pm672$ m^3 d^{-1} (9.4 ± 3.8 to 18.4 ± 7.7 m^3 s^{-1}). The largest water flows throughout the year were observed in the Recife Basin. Over the course of a year, this system showed peaks between $2500\text{-}3000\times10^3$ m^3 d^{-1} (29.0-34.7 m^3 s^{-1}), primarily in the months corresponding to the rainy season. These discharge rates presented a mean value of 18.4 ± 6 m^3 s^{-1} during this period for this river basin. The time series in the Barra das Jangadas Basin showed an average value of 12.6±4

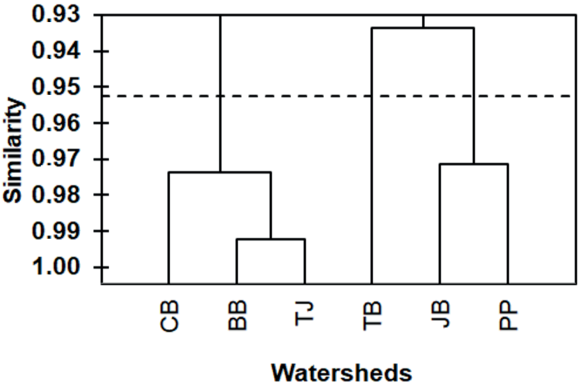

Figure 2 - Dendrogram of the associations among the basins using the rainfall series. CB: Capibaribe River; BB: Beberibe River; TJ: Tejipió River; TB: Timbó River; JB: Jaboatão River; PP: Pirapama River.

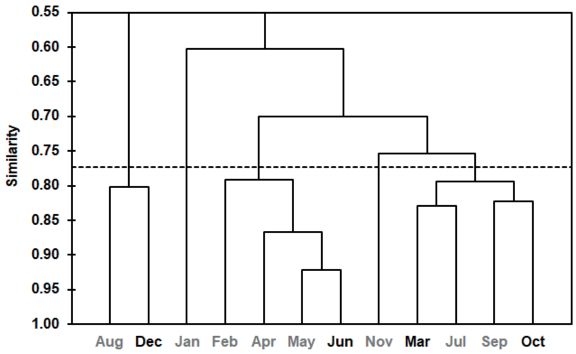

Figure 3 - Dendrogram of the associations between the months using the time series of fluvial discharge data. The months in black bold were studied in 2007.

m^3 s^{-1}, while the mean value for the Timbó River was 9.4±4 m^3 s^{-1} (Fig. 4a). A new series containing monthly values was obtained for each of the three areas while taking into account the occurrence of the annual cycle (Fig. 4b). Fig. 4b shows the differences among the three basins with respect to the magnitudes of their fluvial fluxes. Another important feature is the grey square area in the graph that is related to the rainy period. During the rainy season, the river discharges are larger, which is a historical fact that has been confirmed by other research carried out in the study region (Noriega et al. 2005, Grego et al. 2004, Araujo and Ribeiro 2002).

The observational period follows the historical trend of river discharges in the region and shows that the months with the highest and lowest rainfall amounts were June and October, respectively.

FLUXES OF PHOSPHORUS AND NITROGEN

The calculated and modeling results of the DIP and DIN fluxes ($mmoles.m^{-2}.d^{-1}$) within the estuaries are shown in Fig. 5a, b, c, d, e, f, respectively, for the months with low and high river discharge rates (m^3 d^{-1}) in the 2001-2007 time series in the Barra das Jangadas (BJ), Recife (RE) and Timbó (TB) Basins. Fig. 5a shows that the BJ system was a sink of DIP (negative DIP flux values) throughout the year, while the Timbó and Recife river systems oscillated between sources and sinks of DIP (positive and negative flux values, respectively) relative to the coastal zone (Fig. 5b, c). The estuarine fluxes of DIP fluctuated between +1.5 and -1.5 mmoles m^{-2} d^{-1} during the time series analyzed with the model. These fluxes (ΔDIP) oscillated with small amplitudes centered around zero and responded inversely to increases and decreases in the fluvial discharge. The fluxes in the rivers (positive fluxes) followed the variations in the river discharge rates (mainly in the BJ Basin) with values lower than 1.6 mmoles m^{-2} d^{-1}.

Fig. 5d, e, f shows that the BJ and TB systems served as DIN sinks, while the RE system oscillated between a source and a sink. The DIN estuarine fluxes ranged from -20 to +10 mmoles m^{-2} d^{-1} during the observational period using the LOICZ model. In the Recife (B) and Timbó (C) basins, the fluxes oscillated at lower rates relative to the BJ basin. These fluxes (ΔDIN) oscillated at rates greater than those of the ΔDIP and responded inversely to the discharges in the BJ and TB systems. In Recife (Fig. 5b, e), there was no direct relationship between the river discharge and DIN flux, except for a peak in 2007 during the discharge period.

The positive DIN fluxes in the rivers also accompanied the river discharge rates (mainly in the BJ Basin) with values lower than 20 mmoles m^{-2} d^{-1}.

FRESHWATER VOLUMES AND RESIDENCE TIMES IN THE SYSTEMS

Fig. 6a, b summarizes the percentage volumes of freshwater in the systems and their respective residence times (Equations 5 and 6 indicated in the Supplementary Material). The variation in the percentages between the low and high river discharges was <5% between the periods for the 3 regions studied. The residence times are used to understand the average speed of renewal and retention of material, particularly they are useful in

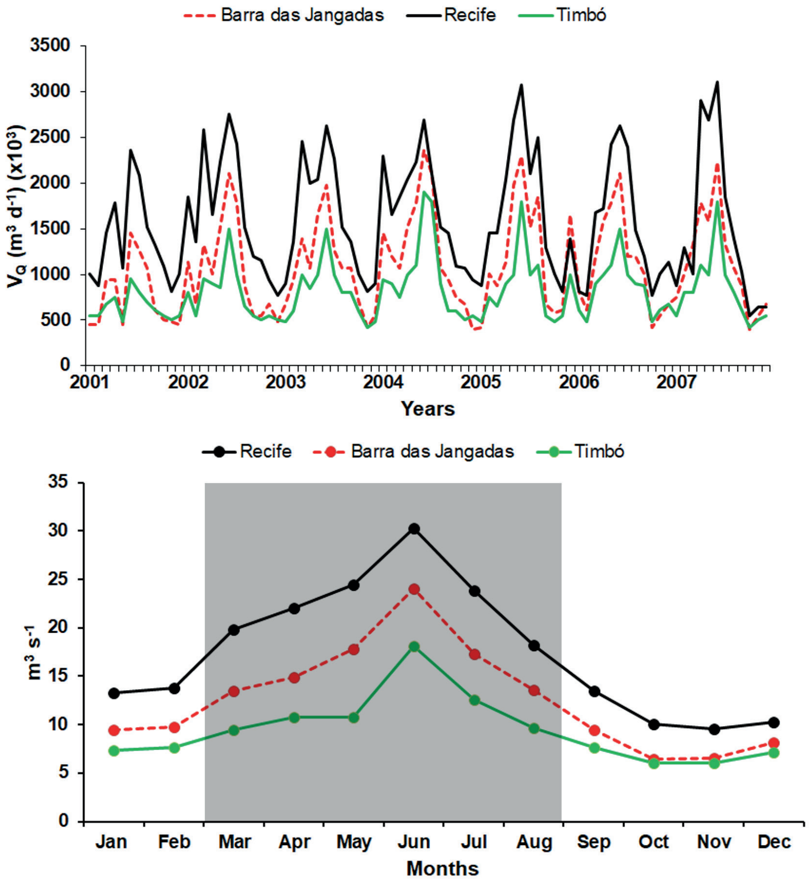

Figure 4 - 2001-2007 time series of river basin discharge data from the three river basins (**a**) and annual cycles constructed for the 2001-2007 time series of the river discharge data (in $m^3 s^{-1}$) for the river basins. The grey square region in (**b**) indicates the rainy season.

intercomparisons between estuaries. We observed that BJ had the shortest residence times among the 3 systems studied. The RE system shows the opposite, with long residence times between periods of high and low river discharge (Fig. 6a, b).

RELATIONSHIPS BETWEEN THE FRESHWATER PERCENTAGES AND THE NON-CONSERVATIVE DIP FLUXES

Table I shows the relationships between the percentages of freshwater in the systems and the non-conservative DIP fluxes, thereby representing the directions of the fluxes when the systems varied with respect to their discharge densities, which can control the metabolism of the system. The Timbó system showed the highest correlation between ΔDIP and the percentage of freshwater, while the BJ and RE systems showed variable relationships between the dry and rainy periods. Values of $R \geq 0.60$ represent a significant correlation between the data of the two variables tested (ΔDIP vs % freshwater).

STATISTICS OF THE FLUXES AND FLUVIAL DISCHARGE RATES

A non-parametric Kruskal-Wallis test ($p < 0.05$) followed by a Dunn test was applied to the non-conservative DIP and DIN flows and river discharge rates in the three areas (1: Barra das Jangadas, 2: Recife and 3: Timbó) during periods of high and low fluvial discharge (Fig. 7).

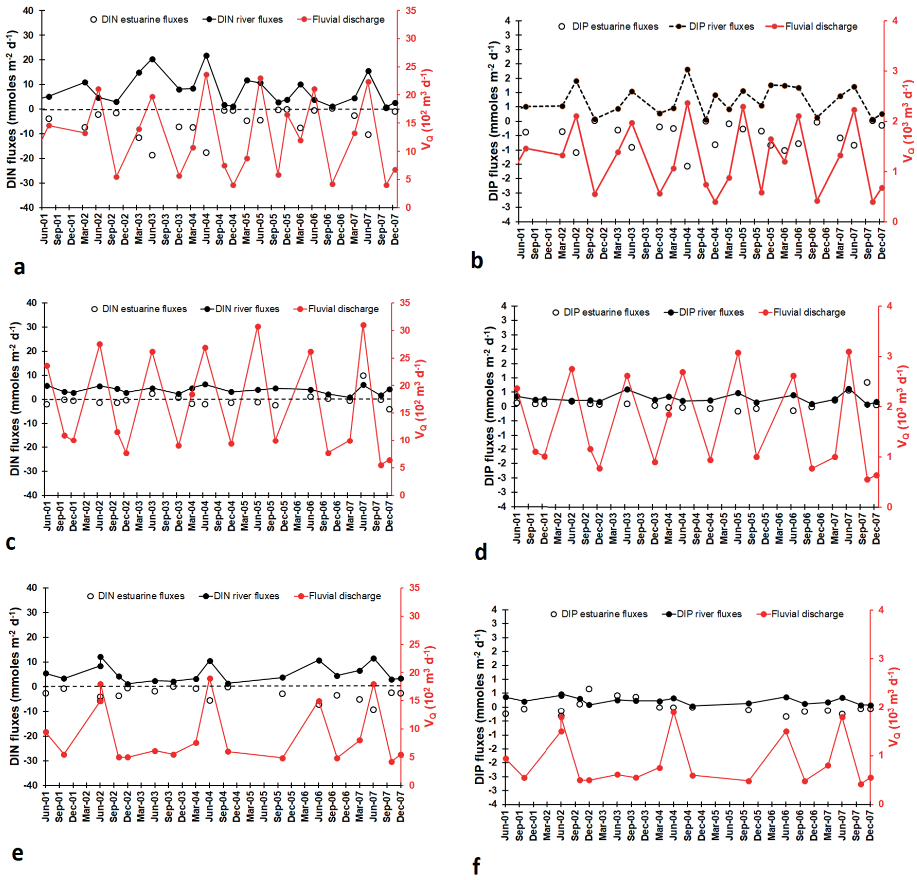

Figure 5 - Time series of the DIN and DIP fluxes (2001-2007) for the Barra das Jangadas (**a** and **b**), Recife (**c** and **d**) and Timbó (**e** and **f**) basins. The DIN and DIP estuarine fluxes were modeled, and the river fluxes and river discharge rates were calculated. Blue and green dashed lines indicate the zero value for the DIN and DIP fluxes, respectively.

The results showed significant differences among the DIP fluxes between the BJ and RE systems (H = 8.74, p <0.05) using the Dunn test. During the high discharge period, the BJ basin differed significantly from the other two areas (H = 18.9, p <0.05) (Fig. 7). The DIN fluxes did not show significant differences between the three areas during the dry period (H = 1.7, p <0.05), while the RE basin differed significantly from the other areas during the rainy season (H = 14.75, p <0.0006) (Fig. 7). The fluvial discharges (Fig. 7) showed significant differences between the two periods. The BJ and TB areas were significantly different from the RE region (H = 12.6 and H = 12.1, p <0.05, respectively).

Fig. 8a, b shows the results of the DIP and DIN balances. The balances indicate that the domain of the fluxes in the BJ system primarily constituted terrestrial loads regardless of the discharge period.

In the other two areas (Recife and Timbó), the fluxes exhibited alternating domains and were able to employ both terrestrial and oceanic exchange processes. According to Noriega and Araujo (2009), the BJ system showed the highest N and P loads of anthropogenic origin among 12 rivers studied between 2001 and 2005.

METABOLISM IN THE SYSTEMS

Phytoplankton-dominated oceanic systems are characterized by 106:16:1 (C:N:P) Redfield molar

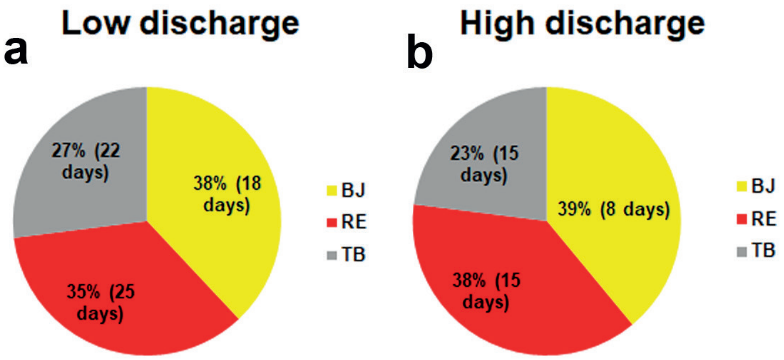

Figure 6 - Percentage of freshwater (%) and residences times (days) in the systems during periods of low (**a**) and high (**b**) river discharge. BJ: Barra das Jangadas; RE: Recife; TB: Timbó.

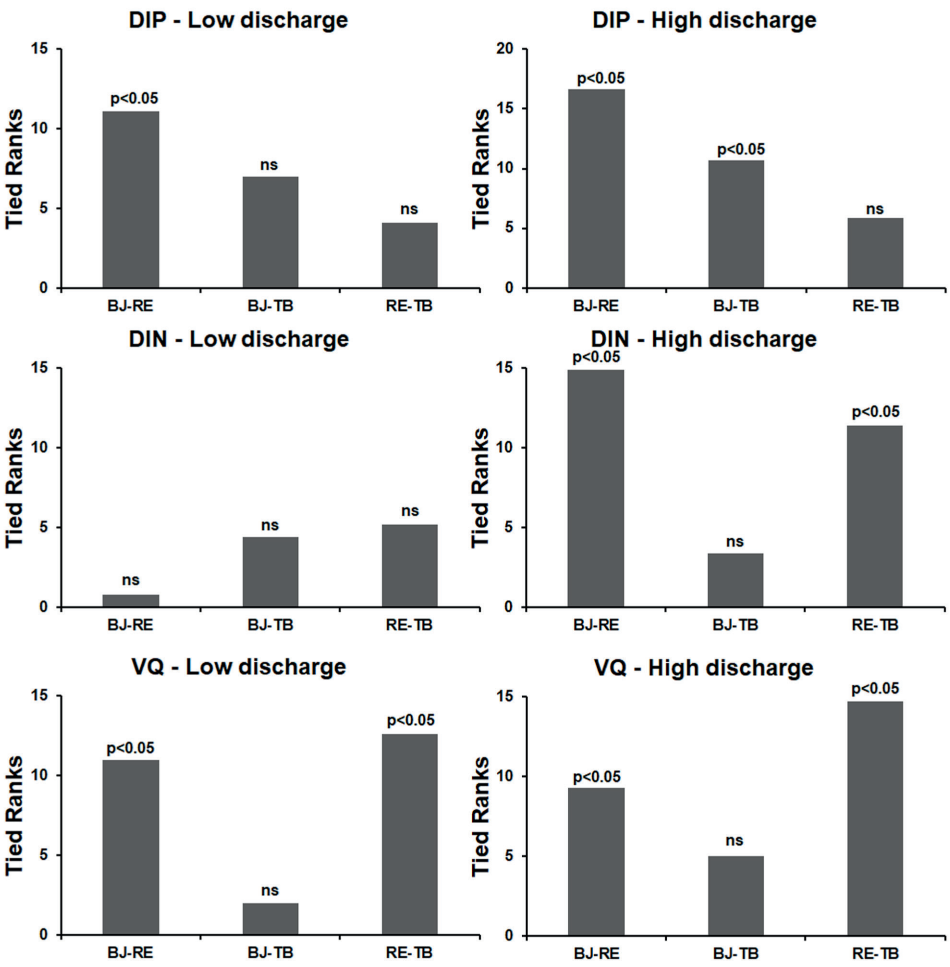

Figure 7 - Non-parametric DIP and DIN statistics between the Barra das Jangadas, Recife and Timbó basins during periods of both high and low fluvial discharge.

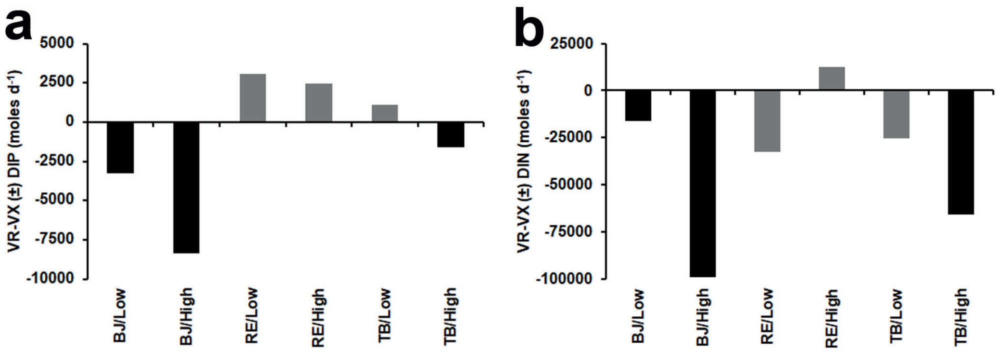

Figure 8 - Terrestrial-oceanic domain in the observed areas, BJ: Barra das Jangadas; RE: Recife; TB: Timbó for DIP (**a**) and DIN (**b**). Residual (black bars) and Mixture (grey bars).

TABLE I
Correlations between the non-conservative fluxes of DIP and % freshwater in estuarine systems during periods of high and low river discharge (Confidence interval: 95%, N = number of data).

Region	Correlation coefficient (R). Dry period.	Correlation coefficient (R). Wet period.	N
Barra das Jangadas-BJ	0.40	0.60	38
Recife (Capibaribe, Beberibe and Tejipió)-RE	0.72	0.50	34
Timbó-TB	0.73	0.80	30

ratios, while systems under urban influence have 40:12:1 (C:N:P) ratios (SanDiego-McGlone et al. 2000). With this information and considering the results for terrestrial-oceanic domains, we established the metabolism rates for the systems (i.e., production-respiration) with their respective fluxes at the CO_2 water-air interface according to the equation of Gordon et al. (1996). For the nitrogen fluxes, we used another equation by Gordon et al. (1996), in which the nitrogen fixation and denitrification are equivalent to the following: (Fixation N - Denitrification = ΔDIN observed - ΔDIP × (N: P)). The corresponding results are shown in Table II.

These results suggest that the systems varied between autotrophy and heterotrophy, indicating that they are both producers and consumers of organic matter (Equation 9). The estuarine system of Recife seemed to be a source of CO_2 for the atmosphere throughout the year, while the Barra de Jangadas system was a CO_2 sink. The Recife system appeared to be a self-depleting system of organic matter and nutrient exportation. For the nitrogen cycle, the RE and TB systems appeared to be sources of nitrogen via denitrification throughout the year with high rates during the low discharge period; meanwhile, the BJ system showed nitrogen fixation at low rates during both periods.

TROPHIC STATUS IN THE RECIFE SYSTEM

The concentrations of DIN and DIP nutrients associated with Chlorophyll-*a* and saturated oxygen represent the water quality status of the Recife area. Fig. 9 shows the results for the high and low discharge months during 2007. DIP, DIN, Chlorophyll-*a* and saturated oxygen are the basic parameters for the index of trophic state applied in this study.

The studied region presents as a eutrophic state, which is indicative of highly productive water and of a low environmental quality throughout the year of 2007.

TABLE II
Metabolism of systems through the stoichiometry of Gordon et al. (1996) (average values). BJ: Barra das Jangadas; RE: Recife; TB: Timbó.

Area/Discharge	Influence	Relation C:N:P	mmol C m^{-2} d^{-1}	mmol N m^{-2} d^{-1}
BJ/Low	Terrestrial	40:12:1	10	1.75
BJ/High	Terrestrial	40:12:1	26	0.17
RE/Low	Mixture	106:16:1	-12.7	-3.17
RE/High	Mixture	106:16:1	-9.54	-0.95
TB/Low	Mixture	106:16:1	-8.50	-3.09
TB/High	Terrestrial	40:12:1	4.40	-2.94

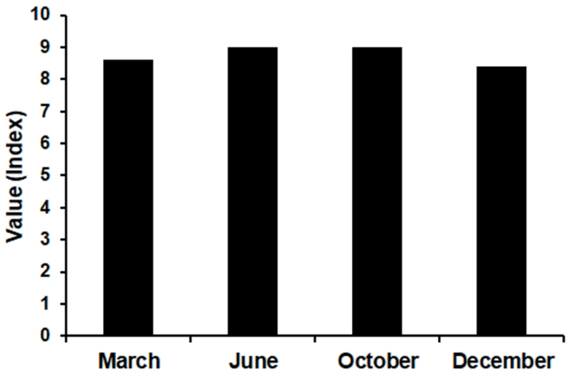

Figure 9 - Values of TRIX trophic status index in Recife-RE (Capibaribe, Beberibe and Tejipió) in 2007.

DISCUSSION

The non-conservative fluxes of DIN and DIP were analyzed through two temporal perspectives to obtain answers regarding the directionalities of these fluxes at the land-ocean and water-air interfaces.

Anthropogenic influences were evident and were experienced while observing the high concentrations originating from the hydrographic basins of each estuarine system (high concentrations of DIN and DIP). As reported by Noriega and Araujo (2009), the watershed loads in the state of Pernambuco were characterized by strong anthropogenic influences, which are evidenced by high N and P concentrations in the sewage and urban drainage. The largest inputs via wastewater were BJ and RE, which contributed 9800 t yr^{-1} of N and 1900 t yr^{-1} of P for the period 2001-2007. The urban runoff inputs were 220 t yr^{-1} of N and 47 t yr^{-1} of P, for the same period (Fig. 10a, b, d, f). Noriega and Araujo (2009) indicated that the anthropogenic loads exceed the natural loads of N and P in 96% in the hydrographic basins of the state of Pernambuco. We used this data and calculated the specific contributions for each system and period of study (2001-2007). We estimate that wastewater represents 69% and 64% of the total load of N and P in these 3 systems, respectively (Fig. 10a, b, c, d, e, f). When comparing anthropogenic emissions with natural sources, RE, BJ and TB provide 88% of N and 96% of P of anthropogenic origin for their hydrographical basins.

The highest concentrations of DIP and DIN corresponded to the Barra das Jangadas and Timbó systems, and the negative fluxes observed during the low and high discharge periods are evidence that the Barra das Jangadas estuarine system was a sink of DIN and DIP throughout the year. This characterizes a system that sequesters the difference between imported and exported material, thereby acting as a reservoir where the inputs in the system are larger than the outputs.

The fluxes in the Recife system showed variations throughout the observed time series. The system alternated between acting as a source and a sink of nutrients and exhibited slight DIP source and DIN sink trends. The DIP exported through the land-ocean interface contributed to the fertilization

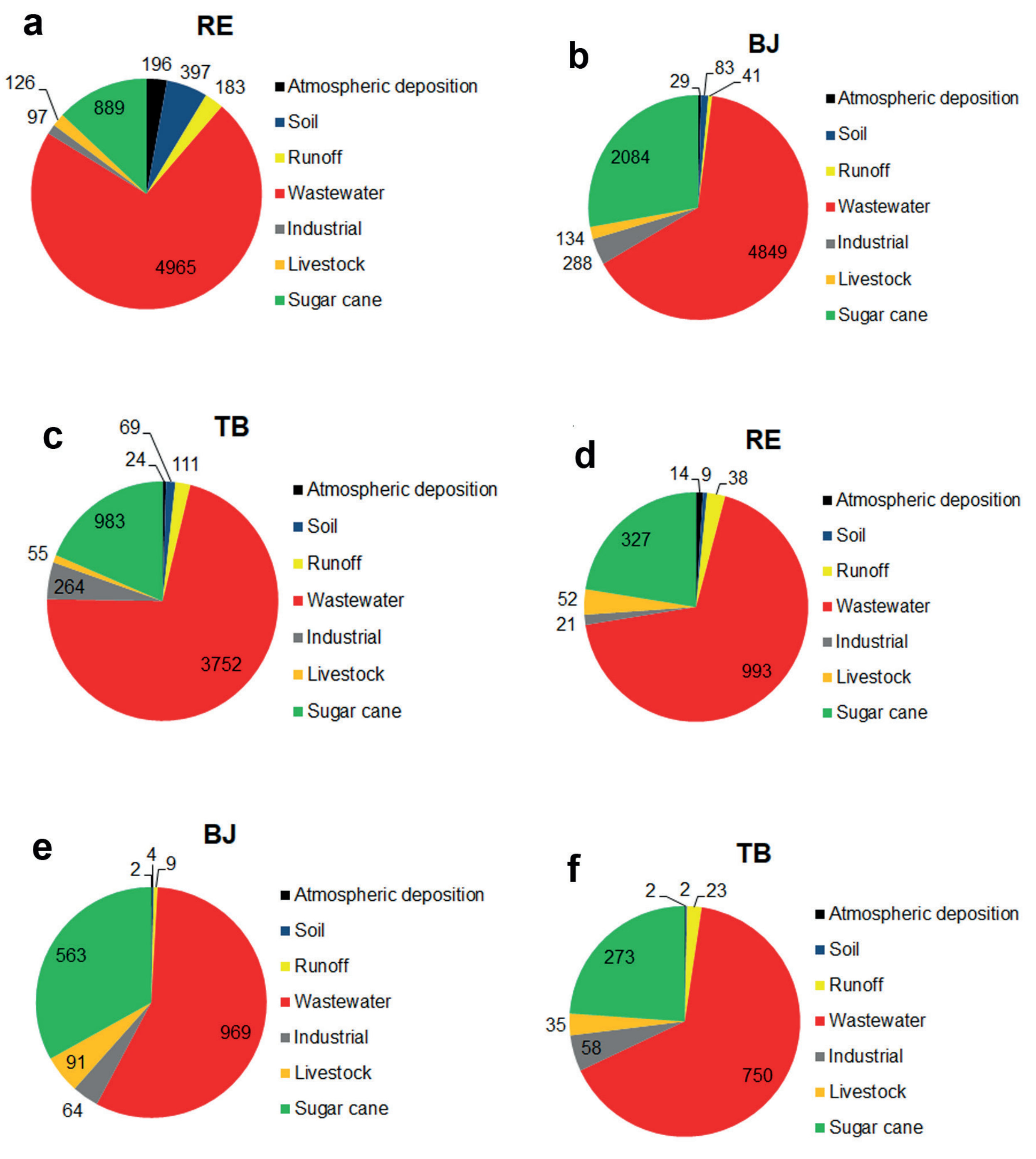

Figure 10 - Estimates of N (**a**, **b** and **c**) and P (**d**, **e** and **f**) emissions (t yr^{-1}) from natural and anthropogenic sources in the basins of RE, BJ and TB. The relative contribution (%) of each individual source is in parenthesis. Data obtained from Noriega and Araujo (2009).

of the adjacent coastal zone, while the DIP stored in the system could have been adsorbed into particulate material, sedimented or assimilated by the phytoplankton community, thereby contributing to the heterotrophy of the water column as shown in the correlations described above.

The Timbó system varied slightly between the retention and release of DIP but served as a DIN sink during the observed periods, thereby contributing to the internal processes in the estuarine system.

When comparing this study to other tropical systems, the fluxes showed values similar to those observed by Souza (2000) in the Sergipe River estuary in Brazil (ΔDIP= -0.15 and ΔDIN=-1.9 mmoles m^{-2} d^{-1}, respectively). However, in Cameroon estuarine system, Gabche and Smith (2001) observed higher magnitudes in ΔDIP (-7.0 mmoles m^{-2} d^{-1}) and ΔDIN (+73 mmoles m^{-2} d^{-1}) values than those recorded in our study.

The water balances showed that the systems differed by <5% between the low and high discharge periods and that the residence times were 18-25 days during periods of low discharge and 8-15 days during periods of high river discharge. According to Swaney and Smith (2003), small systems (<100 km^2) usually have residence times ranging from 1 to 100 days depending on the residual characteristics, mixing parameters and morphology of the system. The residence times associated with the non-conservative DIN and DIP fluxes were the main causes of the processes of element exportation or importation into the adjacent coastal zone. As shown in Table I, the systems tended to function as sinks when the percentage of freshwater increased (principally in the Timbó river system). Mineralization and benthic processes tended to prevail when the freshwater volumes and residence times were higher. The non-parametric Kruskal-Wallis statistic showed significant differences between the Recife river discharge rates with those of the Barra das Jangadas and Timbó systems, thereby illustrating the strength of the main hydrographic basin in the state of Pernambuco. A statistical analysis of the DIP loads was evidence for the strong influence of phosphorus in the Barra das Jangadas and Timbó systems. These two systems, which exhibited the highest DIP loads during the study period, are characteristic of systems that mineralize organic matter, in contrast to the Recife system. The DIN did not show significant differences between the systems during the periods of low discharge and was considered homogeneous among the three areas. During periods of high discharge, the DIN in the Recife system differed significantly from those in the other areas and exhibited a lower concentration than in the Barra das Jangadas and Timbó systems. The balance between the residual and mixed volumes of the analyzed element fluxes showed continental influences on these systems with similar morphological characteristics (Fig. 1), while the Recife system, which exhibits different geomorphological characteristics of a complex estuarine area, showed a dominance of mixed materials over residual. The importance of this balance is associated with the controlling trend over the system autotrophy and heterotrophy (Swaney and Smith 2003). Thus, a negative ΔY would indicate a continental influence, and consequently, the system would be autotrophic, wherein the production is greater than the respiration and nutrients are consumed, thereby representing a sink of atmospheric CO_2. Meanwhile, a positive ΔY would indicate an influence of the mixing gradient, and consequently, the system would be heterotrophic, wherein the respiration is greater than the production and nutrients are exported, thereby representing an atmospheric CO_2 source. This metabolism was evident upon applying the equation of Gordon et al. (1996), showing that the Recife system was heterotrophic with respect to CO_2 and was thus a source of this greenhouse gas to the atmosphere. The heterotrophy rates were higher during the periods of low discharge, thereby allowing benthic processes such as heterotrophic respiration prevail. Other systems in Brazil have revealed similar results, such as those conducted in Paranaguá Bay by Marone et al. (2005), where the system changed from autotrophic to heterotrophic system over the course of a year, and in the Piauí estuary (Souza et al. 2009), where the results indicated heterotrophy within a system influenced by urban and mangrove characteristics. The rates reported by these authors ranged from 1.0 mmol C m^{-2} d^{-1} in Paranaguá to 19 mmol C m^{-2} d^{-1} in the Piauí system. Recently, Guenther et al. (2017) reported that the estuarine system of Recife is a hypereutrophic system and that the respiration and production rates therein range between 48-1080 and 4.8-6744 mmol C m^{-2} d^{-1}, respectively.

The rates reported here represent less than 10% of the primary productivity (128 mmol C m^{-2} d^{-1}), which is considered the upper confidence limit for this type of model (Swaney and Smith 2003).

The Recife system exhibited an eutrophic system under both types of discharge, indicating a poor environmental quality and high productivity with excess nutrients associated with high concentrations of chlorophyll-*a,* which was primarily observed during the summer months. The Barra das Jangadas and Timbó systems bear likely similarities to these results if we consider the work performed by Noriega and Araujo (2011) and Branco (2007) in the Barra das Jangadas Basin and by Grego et al. (2004) in the Timbó River.

CONCLUSIONS

This work represented an effort to help establish the rates of autotrophy and heterotrophy in urban estuarine systems in the RMR.

Within the estuaries, the nutrient dynamics were mainly controlled by spatial and temporal variability high and low fluvial discharges.

The work developed herein showed that tidal oscillations between low and high tide stages changed the trophic conditions of the systems; however, increases in the anthropogenic organic matter loads revealed the permanence of the eutrophic state. The Barra das Jangadas (BJ) and Timbo (TB) systems appeared to be dominated by river fluxes, where most of the loads were exported to adjacent coastal zones. However, the long residence times (1-2 weeks) produced internal transformations that changed the system to autotrophic. In the Recife system (RE), the opposite seemed to occur, with long residence times to change the metabolism to heterotrophic, which is characteristic of systems wherein mineralization prevails.

The variations in the non-conservative fluxes between the low and high river discharge periods among the study areas seemed to be related to residual fluxes associated with high concentrations of inorganic nutrients in the drainage basins.

The RE showed significant differences in the dimensions of fluvial discharge relative to the other systems studied. However, the nutrient concentrations in the Capibaribe Basin still influenced the weighted averages of the Beberibe and Tejipió systems, which were at critical levels of support relative to the nutrient concentrations. The use of the TRIX trophic state index revealed preliminary results indicating that the eutrophic state was permanent during the study period in the RE over the course of a year, thereby demonstrating that the levels of chlorophyll-*a* and inorganic nutrients therein were above the concentration levels for unpolluted estuarine regions. This index was also used by Alves et al. (2013) in the estuarine region of the Suape harbor in Pernambuco.

Using analyses of fluxes of dissolved inorganic nutrients and fluvial discharges, this work contributed to a better understanding of the spatial and seasonal variabilities in the hydrological structures of the tropical estuaries in northeastern Brazil. The estuarine dynamics therein are complex and require immense logistical efforts to obtain high resolution data set. However, the use of environmental modeling tools could contribute significantly to the knowledge of several processes that occur at the land-water and water-air interfaces and may help future investigations to study these areas, which are of great social interest.

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AUTHOR CONTRIBUTIONS

All authors (Carlos Noriega, Moacyr Araujo, Manuel Flores-Montes and Julia Araujo) reviewed the manuscript.

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SUPPLEMENTARY MATERIAL

Figure S1 - Generalized box diagram illustrating the salt budget for a coastal water body. The arrows show the net salt flux associated with each process. In general, residual flow (that is, VR×SR) is negative indicating flow from the system. Under such conditions, mixing (VX) is likely to transport salt into the system. Quantities which are generally measured are shown in light typeface, while quantities which are calculated within the budget are shown in bold typeface.

Figure S2 - Generalized box diagram illustrating the budget for a nonconservative material, Y, in a coastal water body. The arrows show the net flux of Y associated with each process. Mixing (VX) may be to or from the system. Quantities which are generally measured are shown in light typeface, while quantities which are calculated within the budget are shown in bold typeface. ΔY denotes the nonconservative flux of Y, and can be positive or negative with respect to the system.

Fluxes of the Salt Content and Mixture Composition Terrestrial and Oceanic Domains of Non-Conservative Fluxes