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### Research Article

# Nutrient budgets in the Piratininga-Itaipu lagoon system (southeastern Brazil): effects of sea-exchange management

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ABSTRACT. The Piratininga-Itaipu Lagoon System and its drainage basin, located on the southeastern coast of Brazil, Niterói (RJ), has been the target of an intense process of urbanization over the last four decades. As a result of this process, both the lagoon and the adjacent sea area have shown signs of eutrophication due to the release of large quantities of domestic sewage semi (or not) treated. In an attempt to minimize these effects, in 2008 the government re-established a connection between the Piratininga lagoon and the sea. To evaluate changes and variations in the balance of dissolved inorganic nutrients, before and after interventions, the geochemical model of two stoichiometric mass balance boxes of the "LOICZ Program" (Land-Ocean Interactions in the Coastal Zone) was used. The salt and water balance showed different water residence times in the Piratininga lagoon for the two periods: 2005-2006 (before the opening of the connection between the Piratininga lagoon and the sea) and 2009-2010 (after the opening of the connection with the sea). The first period showed a value about two times higher than that obtained for 2009-2010,  $\tau = 83$  and 39 days respectively. The water residence time of the Itaipu lagoon did not show great variations between the two periods ( $\tau = 9$  and 8 days). For the period of 2005-2006, before the opening of the connection with the sea, both the lagoons were autotrophic ( $\Delta DIP > 0$ ) and nitrogen loss was predominant ( $\Delta DIN < 0$ ). The second period (2009-2010) was characterized by changes only in the trophic state of the Piratininga lagoon, which became heterotrophic ( $\Delta DIP > 0$ ).

Keywords: nutrient balance, DIP, DIN, LOICZ, Piratininga-Itaipu, Brazil.

# Balance de nutrientes del sistema lagunar Piratininga-Itaipu (sudeste de Brasil): efectos del manejo del sistema a través del intercambio con el agua de mar

**RESUMEN.** El Sistema Lagunar y su cuenca de drenaje, localizada en la costa sudeste de Brasil, Niterói (RJ), han sido objeto de un intenso proceso de urbanización en las últimas cuatro décadas. Como resultado, tanto el área lagunar como el área costera adyacente han mostrado signos de eutrofización debido a la liberación de aguas residuales domésticas tratadas y no tratadas. En un intento por minimizar estos efectos, el gobierno restableció en el 2008 la conección, que une la laguna de Piratininga con el mar. Para evaluar los cambios y las variaciones de los balances de nutrientes inorgánicos disueltos, antes y después de las intervenciones, se utilizó el modelo geoquímico LOICZ. El balance de agua y sal mostró tiempos de residencia de agua diferenciados para los dos períodos simulados. Para el periodo 2005-2006 en Piratininga, mostró un valor casi dos veces superior al obtenido después de la apertura de la conexión con el mar,  $\tau = 83$  y 39 días respectivamente, la laguna de Itaipu no reveló gran variación entre los dos períodos ( $\tau = 9$  y 8 días). Para el periodo 2005-2006, antes de la apertura de la conección con el mar, ambas lagunas fueron autotróficas ( $\Delta$ DIP > 0) y con procesos de pérdida de nitrógeno ( $\Delta$ DIN < 0). El segundo periodo (2009-2010) fue caracterizado por cambios en el estado trófico solo en la laguna de Piratininga que pasó a estado heterotrófico ( $\Delta$ DIP > 0).

Palabras clave: balance de nutrientes, DIP, DIN, LOICZ, Piratininga-Itaipu, Brasil.

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### INTRODUCTION

Coastal lagoons are among the most productive ecosystems in the world (Vollenweider et al., 1992; Bianchi, 2007). High levels of primary production, frequently observed in these systems, are directly associated with the large supply of dissolved inorganic nutrients from land, either of natural origin or anthropogenic sources or both (Zhang & Liu, 1994; Abreu et al., 1995; Souza et al., 2003, 2009). The input of nutrients in the lagoon systems can be from river discharge, streams, marshes, human activities and organic matter decomposition in water and sediments. Thus, knowledge about the nutrient flux from these sources is fundamental for understanding the functioning of lagoon systems, and improving management of such ecosystems (Bormann & Likens, 1967; Andrews et al., 1998; Micheli, 1999).

The Piratininga-Itaipu Lagoon System and its drainage basin, located on the southeastern coast of Brazil, Niterói (RJ), has been the target of an intense process of urbanization over the last four decades. In the 70s, urbanization was accelerated by the construction of the Rio-Niterói Bridge. At that time, the opening of a permanent channel between the Piratininga Lagoon and the sea was also performed and caused drastic changes in the lagoon system (Barroso et al., 2000). Urbanization processes followed by high human occupation in drainage basin area increased the organic load to the lagoons. In addition, fresh water from rivers carried large quantities of domestic sewage, which were stored in the form of macroalgal biomass in banks. In the 80's, macroalgal biomass reached 60-70% of the system surface area of the Piratininga Lagoon (Barroso et al., 2000). As a result, both the lagoon system and the adjacent sea area have shown signs of eutrophication due to the release of large quantities of semi-treated or raw domestic sewage. The eutrophication process was more intense in the Piratininga Lagoon, which had its old channel of communication with the sea closed during the 80's. This led to an increase in water residence time and organic matter accumulation in the lagoon, creating a hypertrophic environment.

In an attempt to minimize these effects, the local government re-established in 2008, the connection of the Piratininga Lagoon with the sea. Within the same period, a domestic wastewater treatment station for the region was constructed to reduce sewage loads into the lagoons. This study aimed to evaluate the effects of these interventions in the metabolism of the lagoon system by calculating the mass balance, considering conservative (salinity) and non-conservative elements (N, P). We performed calculations using the "LOICZ Program" (Land-Ocean Interactions in the Coastal Zone), by applying a two box geochemical model. The time series data was obtained from two years of the monitoring, 2005-2006 and 2009-2010. These periods were characterized by the absence and presence of the canal that linked the Piratininga Lagoon with the sea.

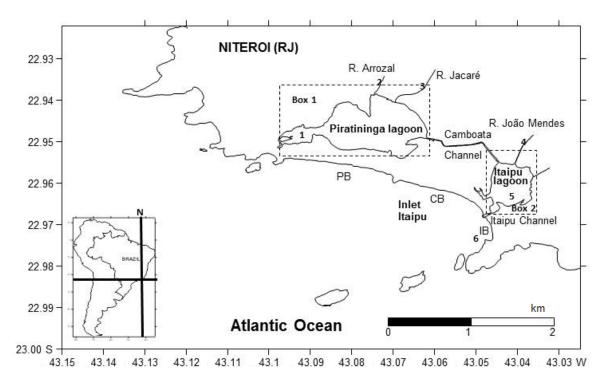
### MATERIALS AND METHODS

### Study area

The Piratininga-Itaipu Lagoon System and its adjacent coastal area are located in Niterói City (22°55'-22°58'S and 43°07'-43°03'W), Rio de Janeiro (Brazil), covering an area of 34.1 km<sup>2</sup>. The system is formed by two shallow lagoons communicating with each other through the Camboata Channel. Mean depth in the lagoons is about 1 m and freshwater input comes from the Arrozal, Jacaré and João Mendes rivers (Knoppers & Kjerfve, 1999). The drainage basin, with 45.5 km<sup>2</sup>, is limited by the peaks of surrounding hills (Viração, Proventório, Sapezal, Santos Ignacio) and mountains (Cantagalo and Jacaré). The lagoons are separated from the sea by a sand barrier system with three sandy beaches: Piratininga, Camboinhas and Itaipu (Fig.1). The area is subjected to a seasonal meteorological cycle characterized by a rainy summer and a dry winter. Tidal regime is semi-diurnal, with a short time-scale dynamics and 1.0 m tidal height (Knoppers & Kjerfve, 1999).

### **Sampling**

Water samples were collected during ten expeditions on the Piratininga-Itaipu Lagoon System and Itaipu Inlet, between June 2005 and November 2006 (before the opening of the channel connecting Piratininga Lagoon with the sea) and twenty three expeditions between April 2009 and March 2010 (after the opening). Sampling was carried out in six sites located downstream of the three rivers (sites 2, 3 and 4), in the two lagoons (sites 1 and 5) and in the Itaipu Inlet (site 6) (Fig. 1). Lagoons and inlet water samples were collected 0.5 m deep and river samples at the surface



**Figure 1.** The Piratininga-Itaipu Coastal Lagoons System and Itaipu Inlet (adjacent coastal area).\*1-\*2-\*3-\*4-\*5-\*6 = sampling points, Piratininga Beach (PB); Camboinhas Beach (CB) and Itaipu Beach (IB).

(0.1 m). The sampling periods included both high and low tides. Water samples and "in situ" data were collected using a 2 L Van Dorn Bottle. At each station, pH, temperature and salinity were measured using a WTW 330 pHmeter and an YSI 30 probe. Water sub samples were taken to analyze nutrients in laboratory. About 1 L of water was filtered through a pre-combusted GF/F Whattman glass fiber filter in order to separate the dissolved and the particulate fractions. Samples were stored in 1 L polyethylene bottles pre-washed with HCl 1:1, rinsed with distilled water and then with water from the sample. After collection, samples were kept on ice during transport and frozen until dissolved inorganic nutrients determination. Sampling period included both high and low tides.

## **Analytical methods**

Dissolved inorganic nitrogen species (DIN): ammonium (N-NH<sub>4</sub><sup>+</sup>), nitrite (N-NO<sub>2</sub><sup>-</sup>), nitrate (N-NO<sub>3</sub><sup>-</sup>), dissolved reactive phosphate (P-PO<sub>4</sub><sup>-3</sup>) (DIP), particulate organic nitrogen (PON) and particulate organic phosphorus (POP) of water samples were measured spectrophotometrically in the laboratory (Grasshoff *et al.*, 1983). Absorbance was measured using a Shimadzu mod. UV 1601 PC spectrophotometer. Detection limits (μM) were as follows (standard deviations of replicates in brackets): N-NO<sub>2</sub><sup>-</sup>.

0.01 (±3%); N-NO<sub>3</sub><sup>-</sup>, 0.05 (±3%); N-NH<sub>4</sub><sup>+</sup>, 0.1 (±5%); P-PO<sub>4</sub><sup>-3</sup>, 0.03 (±5%).

### Principles of the LOICZ approach

To understand the functioning of the Piratininga-Itaipu Lagoon System, before and after the opening of the connecting channel between the sea and Piratininga Lagoon, we adopted the simple mass balance modeling procedure described in the LOICZ guidelines (Gordon et al., 1996). The LOICZ is a budgeting procedure describing the rate material delivered to the system (inputs), the rate of material removed from de system (outputs) and the rate of changes of material within the system (internal sources or sink). In the LOICZ approach, four sequential budgets are established: (i) water balance, (ii) salt balance, (iii) balance of non-conservative materials N:P, and (iv) stoichiometric relationships among non-conservative balance. To construct the mass balance model, the system was divided into two boxes (Piratininga and Itaipu lagoons). Fresh water inflows precipitation  $(V_p)$ , and sewage discharge  $(V_o)$  into this lagoon system were considered equivalent to the outflow and their difference with evaporation (V<sub>e</sub>) represents the residual flow  $(V_r)$ . In this study, measured data for river discharge (V<sub>a</sub>), direct precipitation  $(V_p)$ , direct evaporation  $(V_e)$  and sewage  $(V_o)$ , are available in Tables 1 and 2.

**Table 1.** Summary of annual values, quantification of the parameters and data source, used for two-box models LOICZ, for the Piratininga-Itaipu Coastal Lagoons System. DIP: disolved inorganic phosphorus, DIN: disolved inorganic nitrogen.

Lagoons-Itaipu inlet	Parameters	Code	Quantity	Value	Data source
Piratininga-Itaipu lagoons	Evaporation	$\Lambda_e$	mm yr <sup>-1</sup>	1195.6	Average annual evaporation, 54-year time series (1935-1991) Climatological Atlas (Niteroi)
Piratininga-Itaipu Lagoons	Precipitation	$V_p$	mm yr <sup>-1</sup>	1224.1	Average annual evaporation, 54-year time series (1935-1991) Climatological Atlas (Niteroi)
Piratininga lagoon	Surface runoff (Rivers) Arrozal	$V_q$	$\mathrm{m}^3\mathrm{s}^{\text{-}1}$	0.03	Annual cycle (Knoppers et al., 1999)
Piratininga lagoon	Surface runoff (Rivers) Jacaré	$V_q$	$\mathrm{m}^3\mathrm{s}^{\text{-}1}$	90.0	Annual cycle (Knoppers et al., 1999)
Itaipu lagoon	Surface runoff (Rivers) Joao Mendes	$V_q$	$\mathrm{m}^3\mathrm{s}^{\text{-}1}$	0.1	Annual cycle (Knoppers et al., 1999)
Lagoon System	Sewage (DIN)	$V_{o}x(DIN)$	$10^3 \mathrm{mol~yr}^{-1}$	0.4	Annual cycle (Couto et al., 2000)
Lagoon System	Sewage (DIP)	$V_{o}x(DIP)$	$10^3 \mathrm{mol~yr}^{-1}$	3	Annual cycle (Couto et al., 2000)
Piratininga lagoon	Area		$\mathrm{km}^2$	8	Knopper et al (1999)
Itaipu lagoon	Area		$\mathrm{km}^2$	2	Knopper et al (1999)
Piratininga lagoon	Salt (2005-2006)	$\mathbf{S}_{sist}$		18.3	This study average annual (n=10)
Itaipu lagoon	Salt (2005-2006)	$\mathbf{S}_{sist}$		30.4	This study average annual (n=10)
Itaipu inlet	Salt (2005-2006)	$\mathbf{S}_{sea}$		33.2	This study average annual (n=10)
Piratininga lagoon	DIP (2005-2006)	$DIP_1$	mM	11.7	This study average annual (n=10)
Itaipu lagoon	DIP (2005-2006)	$DIP_2$	mM	2.1	This study average annual (n=10)
Itaipu inlet	DIP (2005-2006)	$\mathrm{DIP}_{\mathrm{ocn}}$	mM	0.97	This study average annual (n=10)
Piratininga lagoon	DIN (2005-2006)	$DIN_1$	mM	21.8	This study average annual (n=10)
Itaipu lagoon	DIN (2005-2006)	$DIN_2$	mM	12.1	This study average annual (n=10)
Itaipu inlet	DIN (2005-2006)	$\mathrm{DIN}_{\mathrm{ocn}}$	mM	4.3	This study average annual (n=10)
Piratininga lagoon	NOP:POP (2005-2006)	N:P		19	This study average annual (n=10)
Itaipu lagoon	NOP:POP (2005-2006)	N:P		∞	This study average annual (n=10)
Piratininga lagoon	Salt (2009-2010)	$\mathbf{S}_{sist}$		26	This study average annual (n=23)
Itaipu lagoon	Salt (2009-2010)	$\mathbf{S}_{sist}$		31.3	This study average annual (n=23)
Itaipu inlet	Salt (2009-2010)	$\mathbf{S}_{sea}$		34	This study average annual (n=23)
Piratininga lagoon	DIP (2009-2010)	$\mathrm{DIP}_1$	mM	2.4	This study average annual (n=23)
Itaipu lagoon	DIP (2009-2010)	$DIP_2$	mM	2.1	This study average annual (n=23)
Itaipu inlet	DIP (2009-2010)	DIPsea	mM	9.0	This study average annual (n=23)
Piratininga lagoon	DIN (2009-2010)	$DIN_1$	mM	17.7	This study average annual (n=23)
Itaipu lagoon	DIN (2009-2010)	$DIN_2$	mM	15	This study average annual (n=23)
Piratininga lagoon	NOP:POP (2005-2006)	N:P		18	This study average annual (n=23)
Itaipu lagoon	NOP:POP (2005-2006)	N:P		13	This study average annual (n=23)
Itaipu inlet	DIN (2009-2010)	$\mathrm{DIN}_{\mathrm{ocn}}$	mM	4.2	This study average annual (n=23)

Location	Sampling period	NO <sub>3</sub> -N (mM)	NO <sub>2</sub> -N (mM)	NH <sub>4</sub> -N (mM)	PO <sub>4</sub> -P (mM)
	2005 2006	$1.24 \pm 1.08$	0.44 (0.22)	$20.56 \pm 19.83$	$11.70 \pm 12.56$
Diagtinings I sees	2005-2006	0.09 - 2.95	0.17 - 0.82	2.97 - 51.68	0.95 - 34.53
Piratininga Lagoon	2000 2010	$3.49 \pm 3.02$	$0.69 \pm 0.84$	$13.54 \pm 24.27$	$2.44 \pm 4.64$
	2009-2010	0.01 - 10.91	0.04 - 3.96	0.01 - 79.98	0.05 - 14.96
	2005 2006	$1.84 \pm 1.47$	$0.74 \pm 0.67$	$9.88 \pm 15.56$	$2.08 \pm 5.71$
Itainu I annan	2005-2006	0.47 - 4.31	0.10 - 1.97	0.99 - 40.98	0.76 - 5.71
Itaipu Lagoon	2000 2010	$2.85 \pm 1.59$	$0.74 \pm 0.70$	$11.72 \pm 19.83$	$2.12 \pm 3.63$
	2009-2010	0.33 - 6.02	0.08 - 3.96	0.01 - 79.98	0.28 - 14.96
	2005 2006	$0.92 \pm 0.80$	$0.57 \pm 0.59$	$2.78 \pm 1.63$	$0.92 \pm 0.85$
Italian Inlat	2005-2006	0.01 - 1.95	0.10 - 1.72	5.32 - 0.73	2.61 - 0.34
Itaipu Inlet	2000 2010	$2.65 \pm 1.88$	$0.50 \pm 0.34$	$1.63 \pm 1.37$	$0.57 \pm 0.34$
	2009-2010	0.32 - 7.53	1.42 - 0.02	0.01 - 5.01	0.08 - 1.29

**Table 2.** Summary of dissolved inorganic nutrients in the Piratininga and Itaipu lagoons (mean ±SD, Minimum-Maximum).

We used the estimated sewage discharge presented by Couto *et al.* (2000), for the same lagoon system. Because of the difficulty to obtain data flow of groundwater, this input was not included in the model. Camboata Channel flow was not considered for the calculations done for LOICZ model since a "bidirectional" flow was deduced based on temporal series of salinity measured in a fixed sample station in the channel. Mean and standard deviation obtained were  $14.8 \pm 6.9$  and  $24.5 \pm 5.2$  for the 2005-2006 and 2009-2010 series, respectively. These results indicate an active water exchange between the two lagoons.

Based on this information, residual flow  $(V_r)$  was calculated according to the following equation (1):

$$Vr = (Vq + Vp + Vo + Ve) \tag{1}$$

In this equation the numerical value of  $V_e$  is negative, implying that water leaves the lagoons system by evaporation.  $V_q$ ,  $V_p$  and  $V_o$  are positive, implying that water enters the system by river discharge, precipitation and sewage flow. If  $V_r$  is negative, a net outflow from the lagoon system to the adjacent area takes place (export).

To conserve salt in the system, the amount of salt leaving the lagoon system with residual flow  $(V_r)$  is balanced by an amount of salt entering the system with mixing flow  $(V_x)$  caused by winds, tides or estuarine flow, leading to equation (2):

$$Vx = (-VrSr)/(S_{sea} - S_{syst})$$
 (2)

where  $S_{syst}$  and  $S_{sea}$  are salt concentrations of system and sea, respectively.

The ratio of the volume of the system  $(V_{syst})$  and the sum of volume of mixture  $(V_x)$  with the absolute value of residual volume  $(|V_r|)$ , is expressed in units of time, mean residence time of freshwater  $(\tau)$ , or hydraulic residence time of the system following equation (3).

$$\tau = (Vsyst)/(Vx + |Vr|) \tag{3}$$

The balance of non-conservative materials (N and P) is formulated as equation (4):

$$\sum [Source-Sink] = \sum inputs - \sum outputs = \Delta y$$
 (4)

Inputs and outputs are calculated as products of water input or output (V) and appropriate concentrations of nutriens (Y) following equation (5):

$$\Delta y = Vy \tag{5}$$

So,  $\Delta Y$  is given as equation (6):

$$\Delta Y = VqYq + VpYp + Vx(Y_{sea} - Y_{syst}) + VrYr \quad (6)$$

where  $Y_{sea}$  is the concentration of nutriens in the sea, and  $Y_{syst}$  the concentration in the system. In case of conservative behaviour,  $\Delta Y$  should be zero ( $\Delta Y = 0$ ). A positive  $\Delta Y$  indicates that the system is releasing material (r) and a negative  $\Delta Y$  indicates that it is uptaking.

## Stoichiometric relationships among non-conservative balance

The calculations are based on the stoichiometric model of the C:N:P ratio of 106:16:1 described by Redfield (1934), where the content of these elements in organic matter (OM) has a molar ratio similar to production of the phytoplankton (equation Whereas the basis of primary production processes phytoplankton, the production and mineralization of organic matter are described by equation (7):

$$106CO_2 + 16HNO_3 + H_3PO_4 + 122H_2O \leftrightarrow (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2 \tag{7}$$

where: the reaction, from the left to the right, is set to produce organic matter (p) and the reverse reaction shows mineralization (r). So, p-r is a measure of net metabolism ecosystem (NEM).

Therefore, to obtain the concentration of an element of the equation above and to define the stoichiometric relationship between these elements, the rest of the equation can be theoretically inferred. Whereas non-conservative flow of dissolved inorganic phosphorus (DIP) is an approximation of net metabolism of the ecosystem (photosynthesis and respiration) and the various reactions that occur with phosphorus are no less complex than those that occur with the nitrogen and carbon, the net metabolism of the system is defined by equation (8):

$$\Delta DIC = [p - r] = -\Delta DIP(C:P)_{part}$$
 (8)

A system that shows a positive  $\Delta DIP (\Delta DIP > 0)$  is interpreted as a DIC (dissolved inorganic carbon) producer mainly via respiration (P-r < 0; respiration > photosynthesis). If a system presents a negative  $\Delta DIP (\Delta DIP < 0)$ , it seems to be a primary producer of organic matter (P-r > 0; photosynthesis > respiration).

Assuming that the N:P ratio of particulate matter in a system is known,  $(N:P)_{part} = 16$  (Redfield ratio), the flux of DIN associated with the production and decomposition of the particulate matter from the flow of phosphorus dissolved ( $\Delta P = \Delta DIP$ ) can be estimated when multiplied by 16 (equation 9). In this study we used the N:P Redfield ratio and the N:P ratio obtained from our results for the suspended particulate matter (PON = particulate organic nitrogen, and POP = particulate organic phosphorus).

Thus, Nfixation-denitrification can be estimated as the difference between the measure of flow of DIN ( $\Delta$ DIN =  $\Delta$ NO<sub>2</sub>+ $\Delta$ NO<sub>3</sub>+ $\Delta$ NH<sub>4</sub>) and flow of DIN expected for the production and decomposition of organic matter ( $\Delta$ N<sub>exp</sub>) (equation 9). The difference

between the  $\Delta N_{observed}$  and the  $\Delta N_{expected}$  is indicative of other processes that can alter the concentration of N in the system, besides the production and mineralization of organic matter. When positive, the values obtained represent the fixed nitrogen in the system, whereas negative values represent nitrogen lost (equation 9).

$$(N_{fix} - N_{denit}) = \Delta DIN_{obs} - DIP \exp$$

$$(N_{fix} - N_{denit}) = \Delta DIN_{obs} - DIPx16$$
(9)

where: nitrogen fixation  $(N_{fix})$  and nitrogen denitrification  $(N_{denit})$ 

### **RESULTS**

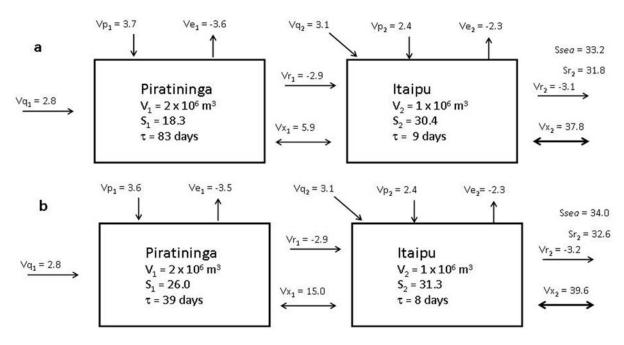
### Water and salt balance

To calculate the mass balance is important to quantify the input and output flows of conservative materials in the aquatic system. The water and salt balances for the Piratininga-Itaipu Lagoon System are represented by two compartments (box 1 = Piratininga, box 2 = Itaipu; Fig. 1 and Figs. 2a-2b) and by the adjacent Itaipu inlet, representing the coastal area.

The salinity obtained during the first period (2005-2006) for the Piratininga-Itaipu Lagoon System showed that the residual flow was negative  $(V_r)$ , indicating a water volume export of 2.9x10<sup>6</sup> m<sup>3</sup> yr<sup>-1</sup> from the Piratininga to the Itaipu lagoon, and of 3.1x10<sup>6</sup> m<sup>3</sup> yr<sup>-1</sup> from the Itaipu lagoon to the Itaipu inlet (Table 3). The values in the volume of mixture  $(V_{x1} = 5.9 \text{ and})$  $V_{x2} = 37.8$ ) were higher than the flow of fresh water and residual water, but enough to ensure that a salinity gradient could be observed (Table 3). The water residence time was 83 days for Piratininga and 9 days for Itaipu (Fig. 2a). The salinity observed for the second period (2009-2010) showed a similar pattern, with negative values for  $V_{r1} = 2.9$ ;  $V_{r2} = 3.2$  and greater positive values for  $V_{x1} = 15$ ;  $V_{x2} = 39.6$  (Table 3). For both periods the export volume was higher for fresh water inflow and small tributary streams, that support the Piratininga-Itaipu Lagoon System. The entry of groundwater probably also contributes to this balance. However, the water volume that enters the ecosystem from this source was not quantified for this study. In 2008, the opening of the channel connecting Piratininga lagoon to the sea increased salinity in 58% (Piratininga = 26.0), and decreased significantly the water residence time in the lagoon (31%; Piratininga = 39 days; Fig. 2b).

### **Nutrient balance**

The balance of dissolved inorganic nutrients, was obtained from the temporal variation of the



**Figure 2.** Water and salt budget for Piratininga-Itaipu Coastal Lagoons System = a) 2005-2006, and b) = 2009-2010. Water flux in  $10^6 \,\mathrm{m}^3 \,\mathrm{yr}^{-1}$ , salt flux in  $10^6 \,\mathrm{m}^3 \,\mathrm{yr}^{-1}$ .

**Table 3.** Summary of the results of the balance of salt and water of the conservative elements to the Piratininga-Itaipu Coastal Lagoon System.  $V_q$ : Volume of the rivers;  $V_p$ : precipitation volume;  $V_e$ : evaporation volume;  $V_r$ : residual volume;  $V_x$ : mixture volume;  $V_x$ : salinity system;  $V_x$ : alinity system;  $V_x$ : residual salinity.

Location	Year	Vq 10 <sup>6</sup> (m <sup>3</sup> yr <sup>-1</sup> )	Vp 10 <sup>6</sup> (m <sup>3</sup> yr <sup>-1</sup> )	Ve 10 <sup>6</sup> (m <sup>3</sup> yr <sup>-1</sup> )	Vr 10 <sup>6</sup> (m <sup>3</sup> yr <sup>-1</sup> )	$\frac{Vx}{10^6 (m^3 yr^{-1})}$	S <sub>sist</sub> salt	S <sub>sea</sub> salt	S <sub>r</sub> salt
Piratininga Lagoon	2005-2006	2.8	3.7	-3.6	-2.9	5.9	18.3		24.3
Itaipu Lagoon	2003-2006	3.1	2.4	-2.3	-3.1	37.8	30.4	33.2	31.8
Piratininga Lagoon	2000 2010	2.8	3.6	-3.5	-2.9	15	26	<u>-</u>	28.7
Itaipu Lagoon	2009-2010	3.1	2.4	-2.3	-3.2	39.6	31.3	34	32.6

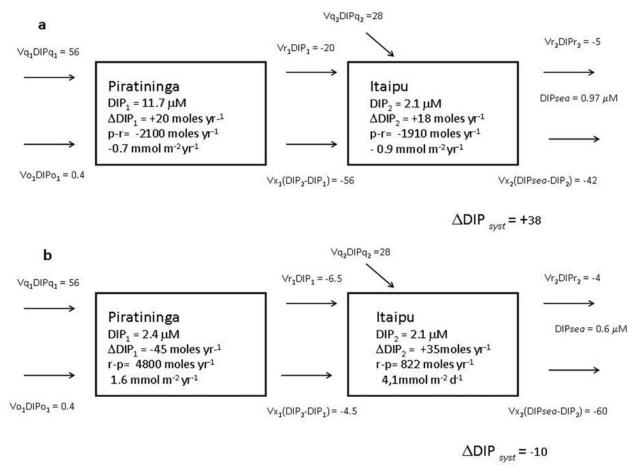
concentrations of these constituents in the water of the lagoons and the adjacent coastal waters (Table 2). As mentioned above, the model was composed by two boxes representing (1) the Piratininga lagoon, and (2) the Itaipu lagoon with adjacent coastal area. The exchange of nutrients between compartments (input and output) allows to identify if the system and the individual compartments act as retainers (sinks) or exporters (sources) of nutrients.

The balance of dissolved inorganic phosphorus during 2005-2006 showed a unidirectional flux between the compartments (Piratininga Lagoon → Itaipu Lagoon → Itaipu Inlet) in all conditions (Fig. 3a). Taking into account the annual flux for the whole system, the results suggest a net production of DIP (Piratininga +20x10³ mol yr⁻¹ and Itaipu +18x10³ mol

yr<sup>-1</sup>). Thus, the behaviour of Piratininga-Itaipu Lagoon System characterizes itself as an exporter ( $\Delta_{\text{syst}} = +38 \times 10^3 \text{ mol yr}^{-1}$ ) (Fig. 3a).

During the 2009-2010 period, after the opening of the channel, the phosphorus concentrations decreased in 65% (Piratininga = 2.4  $\mu M$ ), and the annual flow became negative of DIP (Piratininga = -45x10³ mol yr¹¹). On the other hand, the non-conservative flux in Itaipu lagoon was positive, with an increase of 32% on phosphorus concentration and an export of +35x10³ mol P yr¹¹ to the Itaipu Inlet. The behavior of the whole system revealed a net uptake of phosphorus  $(\Delta_{syst} = -10x10³ \text{ mol yr¹¹})$  (Fig. 3b; Table 4).

The balance for dissolved inorganic nitrogen forms in 2005-2006 showed a non-conservative DIN flux ( $\Delta$ DIN), with a negative value (Piratininga = -1200x10<sup>3</sup>



**Figure 3.** Dissolved inorganic phosphorus fluxes in the Piratininga-Itaipu System a) 2005-2006, and b) 2009-2010. Fluxes in 10<sup>3</sup>mol yr<sup>-1</sup>.

**Table 4.** Summary of the results of the balance of non-conservative material elements, phosphorus (DIP), dissolved inorganic nitrogen forms (NID), net ecosystem metabolism (p-r) and nitrogen fixation minus denitrification (nfix-denit) to the Piratininga-Itaipu Coastal Lagoon System.

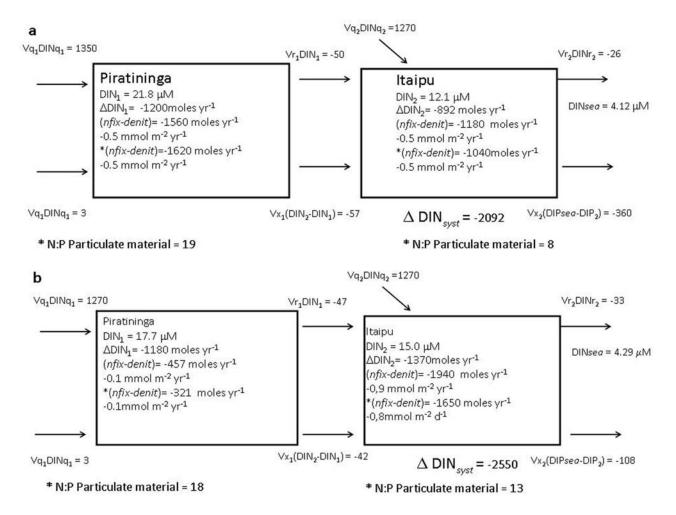
T	37	D DIP <sub>obs</sub>	D DIN <sub>obs</sub>	D DIN <sub>exp</sub>	(nfix-denit)	$(nfix-denit)^{*l}$	(p-r)
Location	Year	$10^3  (\text{mol yr}^{-1})$					
Piratininga Lagoon	2005-2006	+20	-1200	320	-1560	-1620	-2100
Itaipu Lagoon	2003-2000	+18	-892	288	-1180	-1040	-1920
Piratininga Lagoon	2000 2010	-45	-1180	-720	-457	-1321	4800
Itaipu Lagoon	2009-2010	+35	-1370	560	-1940	-1650	822

mol N yr<sup>-1</sup> and Itaipu= $-892x10^3$  mol N yr<sup>-1</sup>) indicating that the lagoon system acts as a non-conservative DIN exporter. During 2009-2010, it was observed that DIN concentrations decreased in 10% in Piratininga Lagoon, reaching 17.1  $\mu$ M. In opposite, DIN concentrations in the Itaipu lagoon increased approximately 10%, presenting concentrations up to 15.0  $\mu$ M. Negative flows were observed for the whole system (Piratininga =  $-1180x10^3$  mol N yr<sup>-1</sup> and Itaipu

-1370x10<sup>3</sup> mol N yr<sup>-1</sup>). For both cases, the Piratininga-Itaipu Lagoon System seems to be a nitrogen exporter showing a  $\Delta_{syst}$  = -2092x10<sup>3</sup> mol yr<sup>-1</sup> (Fig. 4a) during 2005-2006, and a  $\Delta_{sys}$ =-2550x10<sup>3</sup> mol yr<sup>-1</sup> (Fig. 4b, Table 4) during 2009-2010.

### Stoichiometric balance

Annual average values showed that the total liquid metabolism of the whole Piratininga-Itaipu Lagoon



**Figure 4.** Dissolved inorganic nitrogen fluxes in the Piratininga-Itaipu System a) 2005-2006, and b) 2009-2010. Fluxes in  $10^3$  mol yr<sup>-1</sup>.

System was heterotrophic during 2005-2006, presenting organic matter degradation. The production minus respiration (P-r) parameter was negative in both Piratininga and Itaipu lagoons  $(p-r_{\text{Piratininga}} = -2100; p-r_{\text{Itaipu}} = -1910)$  (Fig. 3a). In 2009-2010 the system changed from an heterotrophic to an autotrophic condition, showing positive values of (P-r) for Piratininga (+4800) and Itaipu (+822) (Fig. 3b).

Despite these differences in the (*p-r*) parameter, the stoichiometric balance results revealed that nitrogen loss exceeded nitrogen fixation in both periods, *i.e.*, before and after the opening of the connection of the Piratininga Lagoon with the sea in 2008. The nitrogen balances (*nfix-denit*) obtained for 2005-2006 and 2009-2010 ranged from -1560 to -1620 and -321 to -457 for the Piratininga Lagoon, and from -1040 to -1180 and -1650 to -1940 for the Itaipu lagoon in both periods, respectively (Table 4).

### DISCUSSION

Coastal lagoons are similar to lakes since they are naturally prone to eutrophication, but they are more dinamyc systems once they are also submitted to daily variations of water movement due to tides. Althoug the Piratininga-Itaipu Lagoon System is considered as a choking lagoon (Knoppers & Kjerfve, 1999), the water residence time differs between them. These characteristics were highlighted by the water and salt balance modeled with LOICZ (Fig. 2a). A higher water residence time was observed in Piratininga lagoon, but it was most evident during the first period (2005-2006). These considerable differences resulted from the low mixing and renewal of Piratininga waters due to the reduced capacity of the Camboata Channel (channel that connects the two lagoons) in transporting water. Couto et al. (2000) reported a similar pattern

for Piratininga and Itaipu lagoons (Piratininga = 46 days and Itaipu = 6 days) during 1980's, with a lower water residence time for Piratininga. Carneiro *et al.* (1990) estimated the water residence time for the two lagoons. For Piratininga the water residence time was 46 days in summer and 995 days in winter. For Itaipu, the water residence time was estimated to vary from 14 days in summer to 289 days in winter. This variation is attributed to the worsening of the low circulation of the system and mainly to the energy of tidal waves (ranging between 0.8 and 1.0 m) that regulates the circulation and dynamics of the system.

The opening of the connection between the Piratininga Lagoon and the sea in 2008 had a significant effect on water renewal of this lagoon. As expected, the great differences in the salt and water balances were observed in Piratininga, with a decrease of 31% in the water residence time in this lagoon (39 days). However, this intervention affected both Piratininga and Itaipu lagoons by increasing salinity in the whole system and improving the hydrodynamics (water and salt balances, as observed in 2009-2010). Therefore, the Piratininga-Itaipu Lagoon System changed from "choking" to "restricted" (Carneiro et al., 1990). The water residence time is a crucial factor associated to biological productivity in aquatic systems. Environments with high water residence time tend to produce more nutrients, while systems with higher water renewal tend to be conservative in relation to the variation of nutrients along a salinity gradient (Grelowski et al., 2000).

The highest DIP fluxes (ΔDIP) observed in the period before the opening of the channel (2005-2006) resulted from the high phosphate concentrations on waters in this period. Fluxes were positive between all compartments: Piratininga Lagoon→Itaipu Lagoon and Itaipu Lagoon→Itaipu Inlet (the adjacent coastal area). The system exported phosphorous and the water balance was positive. A similar pattern was observed for Paranaguá Bay estuary (Marone et al., 2005), Mhathuze and Mvoti estuary (Wepener, 2007) and for Piratininga-Itaipu Lagoon System in 1980's (Couto et al., 2000). After the opening of the channel (2009-2010), the water residence time and DIP concentrations decreased in Piratininga and  $\Delta DIP$  became negative. Therefore, the outputs became smaller than the inputs meaning that primary productivity prevailed over mineralization and/or respiration processes making the system autotrophic (Talaue-McManus et al., 2003). In contrast,  $\Delta DIP$  values increased after 2008 in the Itaipu Lagoon, making the lagoon more heteretrofic than before, as also observed in other study carried out in the Piratininga-Itaipu System (Couto et al., 2000) and in other lagoons

(Wattayakorn *et al.*, 2001). The phosphorus has a complex dynamics in lagoon systems (Lillebo *et al.*, 2004) and these results should be interpreted with caution since phosphorous concentrations are influenced both by its biological uptake and by physical adsorption-desorption processes in sediments.

A DIN exportation was verified for both studied periods, like it was observed for other estuarine systems such as Mhathuze and Mvoti estuary (Wepener, 2007). The Piratininga-Itaipu Lagoon System has also shown a denitrification capacity (nitrogen loss) in comparison to N assimilation (fixation). This pattern was observed for the whole system during both periods (2005-2006 and 2009-2010) and for the two lagoons separately. Indeed, both systems presented a certain degree of anoxia (Couto et al., 2000) and denitrification was also observed for the upper Piauí Estuary (PI) during short periods of anoxia (Souza et al., 2003). In general, the majority of estuaries are considered denitrificators, and may cause a nitrogen loss from 10 to 20% to the atmosphere, and in extreme cases, up to 30% (Seitzinger, 1988; Knoppers & Kjerfve, 1999; Crossland et al., 2005; Capone et al., 2008). Of course other processes may also account for these losses of nitrogen, such as loss of ammonia to the atmosphere (Guimarães & Mello, 2006).

The LOICZ model results, carried out for Brazilian estuarine areas, revealed that these ecosystems work in autotrophic conditions and act as nitrogen-fixing and denitrifying systems, like Guaratuva Bay, Paranaguá Bay, Conceição Lagoon and Maricá Lagoon (Couto et al., 2000; Souza et al., 2003; Marone et al., 2005; Brandini, 2008). Some exceptions were the Piratininga-Itaipu Lagoon System during 2005-2006 (our data) and the upstream sector of Piaui River Estuary, with NEM heterotrophic denitrifying system (Souza et al., 2003) (Table 5). All systems have a different behavior compared to net ecosystem metabolism, depending on the different characteristics of each system. NEM Piratininga Lagoon behavior is similar to that presented by Paranaguá Bay in dry periods. On the other hand, Itaipu Lagoon behavior is similar to Guarapina Lagoon. Although the values of (p-r) in the Piratininga-Itaipu System are relatively low and, comparable to other systems, the Itaipu Lagoon increases its capacity of exporting DIP to adjacent coastal areas by increasing the exchange of this element. As results of the opening of the connection between Piratininga Lagoon and coastal waters, a decrease on the water residence time in the lagoon and an increase of the DIP loading to the Itaipu Lagoon were observed. Furthermore, the system in both

**Table 5.** Balance of NIP and DIN in some Brazilian coastal ecosystems.  $\tau$ : Residence time;  $\Delta DIP_{obs}$  and  $\Delta DIN_{obs}$ : observed; 1\*: (N:P) assuming particulate detritus from plankton to be 106; 2\*= (N:P) assuming particulate detritus from plankton to be 16.

Estuary	Periods	Section	t	$\frac{\text{DDIP}_{\text{obs}}}{(10^3 \text{molP yr}^{-1})}$	$\frac{(p-r)^l*}{(\mathrm{mmol cm}^2  \mathrm{yr}^{-1})}$	Process NEM	$\frac{\rm DDIN_{obs}}{(10^3 \rm molN~yr^{-1})}$	$nfix$ - $denit^2*$ (molNm <sup>2</sup> yr <sup>-1</sup> )	Process NEM
Baia de Guaratuva <sup>1</sup>	annual	Total	6	968-	1898	autotrophic	-12816	29.2	fixation
Baia de Paranagu $\hat{a}^2$	Dry	Total	30	-182.5	0-730	autotrophic	-19710	-36.5 to -36.5	denitrication
	Rainy	Total	14	4854	-1460 to -14600	heterotrophic	14235	-182.5 to -109.5	fixation
Estuary Piaui River <sup>3</sup>	annual	total	9	0.18	448.9	heterotrophic	0.002	0.001	fixation
Lagoa Conceicao <sup>4</sup>	June 1982	North	24	-56.5	233600	autotrophic	-345	21900	denitrication
		South	263	-127	1540	autotrophic	-1133	104025	denitrication
		Central	19	-94.5	536915	autotrophic	-1055	25915	denitrication
Maricá and Guarpina <sup>5</sup>		Maricá	115	-320	1200	autotrophic	229	171.5	fixation
		Guarapina	∞	290	5201	heterotrophic	-236	810.3	denitrication
Piratininga Lagoon <sup>6</sup>	annual (2005-2006)	Total	83	20	255	heterotrophic	-1200	182.5	denitrication
Itaipu Lagoon <sup>6</sup>	annual (2005-2006)	Total	6	18	328	heterotrophic	-892	182	denitrication
Piratininga Lagoon <sup>6</sup>	annual (2009-2010)	Total	39	-45	584	autotrophic	-1180	-36.5	denitrication
Itaipu Lagoon <sup>6</sup>	annual (2009-2010)	Total	∞	35	1496	heterotrophic	-1370	-328.5	denitrication
Source:	<sup>1</sup> Marone <i>et al.</i> (2005)	$^2$ Brandini (2008)	<sup>3</sup> Souza <i>et al.</i> (2009)		<sup>4</sup> Souza & Knoppers (2002)		<sup>6</sup> This study		

periods always showed an exportation of N, where denitrification is higher than N fixation (*nfix-denit* "negative") in contrast to the lower values observed in the Guarapina Lagoon System (Table 5). Lacerda *et al.* (1992) estimated for Piratininga that anoxia extends throughout the water column and reaches very low Eh values (-320 to +130 mV), whereas in Itaipu, anoxia is restricted to bottom waters (-66 to + 20 mV). This scenario is undergoing changes due to the positive effects generated by the construction of the channel that connects the system and coastal waters, decreasing the values of denitrification in Piratininga. Otherwise, as negative effects, an increasing on the denitrification values in Itaipu was observed.

One should bear in mind, however, that LOICZ model has limitations that may be important, especially when applied for shallow coastal ecosystems such as the Piratininga-Itaipu Lagoon System. These environments are affected by the high variability of physical phenomena such as change in weather conditions related to the entry of cold fronts (with frequency of 7-8 days) which end ups adding variability to the tidal waves force, directly influencing the sedimentary dynamics of the system.

### **CONCLUSIONS**

Based on the water and salt balances and dissolved nutrients (DIP-DIN), this study shows that, the engineering work for the Piratininga and Itaipu lagoons (the construction of the channel) has direct effects on the system, resulting in lower water residence times, specifically for Piratininga Lagoon, increasing and enhancing the system hydrodynamics. Associated to the lower water residence time, the whole system works like a producer of organic mater (autotrophic). Separately, Piratininga and Itaipu lagoons showed different patterns: Piratininga was autotrophic and Itaipu was heterotrophic, exporting material to the adjacent Itaipu Inlet System. The Piratininga-Itaipu System is a denitrifying system, despite the fact that the presence of benthic algae on the smaller mud flats could also account for nitrogen fixation. In general, despite of all mitigation measures and changes in the system, there are still sporadic dystrophic episodes and fish mortality induced by nutrient inputs, showing that measures are not yet sufficient.

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### **REFERENCES**

- Abreu, P.C., C. Hartmann & C. Odebrecht. 1995. Nutrient-rich saltwater and its influence on the phytoplankton of the patos lagoon estuary, southern Brazil. Estuar. Coast. Shelf Sci., 40: 219-229.
- Andrews, J.E., A.M. Greenaway & P.F. Dennis. 1998. Combined carbon isotope and C/N ratios as indicators of source and fate of organic matter in a poorly flushed, tropical estuary: HuntsBay, Kingston Harbour, Jamaica. Estuar. Coast. Shelf Sci., 46: 743-756.
- Barroso, L., R.S. Medina, P. Moreira-Turcq & M. Bernardes. 2000. A pesca nas lagoas costeiras fluminenses. IBAMA, Brasília, 50 pp.
- Bianchi, T.S. 2007. Biogeochemistry of estuaries. Oxford University Press, New York, 720 pp.
- Bormann, F.H. & G.E. Likens. 1967. Nutrient cycling. Science, 155: 424-429.
- Brandini, N. 2008. Biogeoquímica da Baía de Guaratuba, Paraná, Brasil: origem, metabolismo, balanço de massa e destino da matéria biogênica. Pós-Graduação em Geociências. Universidade Federal Fluminense, Niteroi, 274 pp.
- Capone, D.G., D.A. Bronk, M.R. Mulholland & E.J. Carpenter. 2008. Nitrogen in the marine environment. Elsevier, Amsterdam, 1705 pp.
- Carneiro, M.E.R., N.M. Ramalho, L.S. Valentim, C. Azevedo & B. Knoppers. 1990. Distribuição e comportamento dos nutrientes na bacia de drenagem do sistema lagunar de Piratininga-Itaipu, Niterói, RJ., Simpósio de Ecossistemas da Costa Sul e Sudeste Brasileira: estrutura, função e manejo aguas de Lindóia, pp. 108-115.
- Couto, C.G., A.C. Zyngier & M.F. Landim-de-Souza. 2000. Piratininga-Itaipú coastal lagoons, Rio de Janeiro State-and studies estuarine system of the South American regions carbon nitrogen and phosphorus fluxes. LOICZ Reports & Studies N°5. Institute for Sea Research, Texel, 87 pp.
- Crossland, C.J., H.H. Kremer, H.J. Lindeboom, J.I. Crossland-Marshall & M.D.A. Le Tissier. 2005. Coastal fluxes in the Anthropocene: the land-ocean interactions in the coastal zone project of the International Geosphere-Biosphere Programme. Springer-Verlag, Berlin Heidelberg, 231 pp.
- Gordon, D.C., P.R. Boudreau, K.H. Mann, J.-E. Ong, W.L. Silvert, S.V. Smith, G. Wattayakorn, F. Wulff

- & T. Yanagi. 1996. LOICZ Biogeochemical modelling guidelines. LOICZ Reports & Studies N°5. Institute for Sea Research, Texel, 96 pp.
- Grasshoff, K., V. Ehrhardt & K. Kremling. 1983. Methods of seawater analysis. Verlag Chemie, Weinheim, 419 pp.
- Grelowski, A., M. Pastuszak, S. Sitek & Z. Witek. 2000. Budget calculations of nitrogen, phosphorus and BOD5 passing through the Oder Estuary. J. Mar. Syst., 25: 221-237.
- Guimarães, G.P. & W.Z.D. Mello. 2006. Estimativa do fluxo de amônia na interface ar-mar na Baía de Guanabara: estudo preliminar. Quim. Nova, 29: 54-60.
- Knoppers, B. & B. Kjerfve. 1999. Coastal lagoons of Southeastern Brazil: Physical and biogechemical characteristics. In: G.M.E. Perillo, M.C. Piccolo & M. Pino-Quivira (eds.). Estuaries of South America. Springer Verlag, Berlin, pp. 35-66.
- Lacerda, L., M. Fernandez, C. Calazans & K. Tanizaki. 1992. Bioavailability of heavy metals in sediments of two coastal lagoons in Rio de Janeiro, Brazil. Hydrobiologia, 228: 65-70.
- Lillebo, A.I., J.M. Neto, M.R. Flindt, J.C. Marques & M.A. Pardal. 2004. Phosphorous dynamics in a temperate intertidal estuary. Estuar. Coast. Shelf Sci., 61: 101-109.
- Marone, E., E.C. Machado, R.M. Lopes & E.T. da Silva. 2005. Land-ocean fluxes in the Paranaguá Bay estuarine system, southern Brazil. Braz. J. Oceanogr., 53: 169-181.
- Micheli, F. 1999. Eutrophication, fisheries, and consumer -resource dynamics in marine pelagic ecosystems. Science, 285: 1396-1398.
- Redfield, A.C. 1934. On the proportions of organic derivatives in sea water and their relation to the composition of plankton. James Jones Memorial Volume, Liverpool University Press, Liverpool, pp. 176-192.

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- Seitzinger, S.P. 1988. Denitrification in freshwater and coastal marine ecosystems: ecological and geochemical significance. Limnol. Oceanogr., 33: 702-724.
- Souza, M., V. Gomes, S. Freitas, R. Andrade & B. Knoppers. 2009. Net ecosystem metabolism and nonconservative fluxes of organic matter in a tropical mangrove estuary, Piauí River (NE of Brazil). Estuar. Coast., 32: 111-122.
- Souza, M.F.L., B. Kjerfve, B. Knoppers, W.F. Landimde-Souza & R.N. Damasceno. 2003. Nutrient budgets and trophic state in a hypersaline coastal lagoon: Lagoa de Araruama, Brazil. Estuar. Coast. Shelf Sci., 57: 843-858.
- Talaue-McManus, L., S.V. Smith & R.W. Buddemeier. 2003. Biophysical and socio-economic assessments of the coastal zone: the LOICZ approach. Ocean Coast. Manage., 46: 323-333.
- Vollenweider, R.A., R. Marchetti & R. Viviani. 1992. Marine coastal eutrophication. The reponse of marine transitional systems to human impact: problems and perspectives for restoration. Elsevier, Bologna, 1310 pp.
- Wattayakorn, G., P. Prapong & D. Noichareon. 2001. Biogeochemical budgets and processes in Bandon Bay, Suratthani, Thailand. J. Sea Res., 46: 133-142.
- Wepener, V. 2007. Carbon, nitrogen and phosphorus fluxes in four sub-tropical estuaries of northern KwaZulu-Natal: case studies in the application of a mass balance approach. Water SA, 33: 203-214.
- Zhang, J. & M.G. Liu. 1994. Observations on nutrient elements and sulphate in atmospheric wet depositions over the northwest Pacific coastal oceans - Yellow Sea. Mar. Chem., 47: 173-189.