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RESEARCH PAPER

Ecological Status Evaluation of Itaipu Lagoon (Niterói) Based on Biochemical Composition of Organic Matter

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Abstract

The variety of approaches for assessing the trophic environmental state indicates that there is a strong need for the identification of new and possibly integrated ecological descriptors in coastal marine areas. These approaches would be able to capture relevant variables associated with the eutrophication process, and would be reliable, applicable and valid worldwide. The main objective of this study was to provide evidence that the quantity of total organic carbon (TOC), total sulfur (TS) and biopolymeric carbon (BPC) is useful proxies to evaluate the benthic trophic status in transitional marine environments. Sediment samples collected in Itaipu Lagoon, a Brazilian coastal system of the State of Rio de Janeiro, were analyzed in this study. Geochemical data, such as TOC, TS and BPC concentrations, including proteins (PTN), carbohydrates (CHO) and lipids (LIP), are combined with additional environmental parameters of the bottom water measured in in Itaipu Lagoon. The analysis of quantity and quality of organic matter (OM) allowed the identification of three distinct regions in Itaipu Lagoon: an inner and impacted zone characterized by sediment particularly enriched in TOC, with lower quality of OM most probably provided by the contaminated effluents and rivers runoff; an outer-less impacted lagoonal area with relatively low TOC content where the highest values of BPC/TOC and PTN/TOC are indicative of the presence of OM with high nutritional quality; and an intermediate area characterized by transitional features between the two previously described. The organic matter accumulation depends on the hydrodynamic conditions mostly governed by tidal currents. The quality of organic matter seems to be mainly influenced by municipal effluents, rivers inputs and mangroves contributions as well as by the autochthonous lagoonal biological productivity. Results of this work indicate that the inner zone of Itaipu Lagoon is being affected by eutrophication.

Keywords: Organic matter. Biopolymers. Anthropic impact. Coastal lagoon.

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1. Introduction

Coastal lagoons are shallow water bodies separated from the ocean by a barrier. They are connected at least intermittently to the sea by one or more restricted inlets and are commonly oriented parallel to the coast line. These transitional environments occupy ca. 13% of coastal areas worldwide and are valuable littoral environments due to high biodiversity (Danovaro and Pusceddu, 2007a, b; Basset et al., 2008; Esteves et al., 2008). However, coastal lagoons are in general highly influenced by human activities (Kjerfve, 1994) and tend to accumulate several types of pollutants (Kemp and Boynton, 2012).

Due to the release of high amount of nutrients, which may lead to an excessive productivity, the long-lasting residence time and hydrodynamic characteristics, lagoons tend to become eutrophic, or in extreme conditions hyper-eutrophic ecosystems (Hearn et al., 1994; Knoppers, 1994). In such environments, sediments may record the processes taking place in the water column and represent the final storage of autochthonous and allochthonous organic matter (OM) input (Fabiano and Danovaro, 1994; Pusceddu and Danovaro, 2009).

Several studies have demonstrated that the sedimentary OM content and its composition, namely refractory and labile fractions, are important indicators of the trophic state and influence the ecosystem functioning (Pusceddu et al., 2011, Clemente et al., 2015; Martins et al., 2015a, 2016b).

A portion of labile OM consists mainly of simple and combined compounds (i.e. biopolymers), including carbohydrates, lipids and proteins, which are rapidly mineralized and transformed in refractory materials composed of complex substances such as humic and fulvic acids that are slowly degraded (Henrichs, 1992). Biopolymers represent from 10 to 70% of the carbon present in marine sediments (Pusceddu et al., 2004). Some labile organic compounds can be recalcitrant to degradation as a result of the complex interactions occurring in the sediment or sedimentary matrix and organic macromolecules (Keil et al., 1994).

High quality of OM is essential for maintaining a healthy ecosystem (Clemente et al., 2015; Martins et al., 2015a, 2016b). It contributes to a wide range of ecological functions such as supplying food to the microbes that are the base of the food chain. However, when the supply of OM exceeds its consumption, the decomposition process may give place to a marked depletion of the oxygen level that hampers the proliferation and viability of many organisms (Martins et al., 2010, 2013, 2014, 2015a, b, 2016a; Borja et al., 2012).

Despite the fact that biochemical quantification and composition of OM represent promising tools to evaluate the trophic state of a coastal system, most studies using these descriptors have been only carried out in the northern hemisphere (Fabiano et al., 1995; Danovaro et al., 1999; Dell'Anno et al., 2002; Manini et al., 2003; Pusceddu et al., 2003; Cotano and Villate, 2006).

Brazilian coastal lagoons are very important transitional ecosystems and most of them are concentrated in the states of Rio de Janeiro and Rio Grande do Sul (Esteves, 1998; Leipnitz et al., 2014). In these states, studies of these ecosystems are more developed due to the concern of the public authorities and scientific community about their environmental quality and conservation.

In addition to eutrophication, several Brazilian coastal lagoons are suffering of salinization by the permanent establishment and maintenance of bars/channels that connect these sensitive environments to the sea and due to climatic conditions. The change in the salinity pattern within these environments also greatly affect the natural biodiversity (Soriano-Sierra et al., 2014).

The aim of this work is to study the OM content and quality, in terms of biopolymers, in Itaipu Lagoon, a Brazilian transitional environment. The areas surrounding this coastal system have been the target of an intense process of urbanization and anthropic activities over the last decades. Moreover, this work also intends to test and evaluate the applicability of biochemical composition of the sediment OM as a proxy of the trophic state and environmental quality.

2. Study area

Itaipu Lagoon (22°57'23" - 22°57'41" S and 43°02'51" - 43°02'10" W) is part of one of the most important tourism and leisure center of the State of Rio de Janeiro. Covering an area of 1.2 km² and with a depth ranging between 0.2 m and 6.1 m, this lagoon is permanently connected to the sea (Fig. 1).

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Itaipu Lagoon is affected by a micro-tidal regime with a mean height recorded of 0.71 m, reaching up to 1.32 m during spring tide periods (Lavenère-Wanderley, 1999).

Due to the restricted connection with the sea through an artificial tidal channel, Itaipu Lagoon can be classified as a typical "Choked Lagoon" (Kjerfve, 1986). It is connected with Piratininga Lagoon (3 km²) through the Camboatá Channel. This channel receives large amounts of untreated organic waste and has no direct input of seawater (Lacerda et al., 1992).

Itaipu Lagoon also receives freshwater from three rivers: João Mendes, Vala and Colibris (Fig. 1).

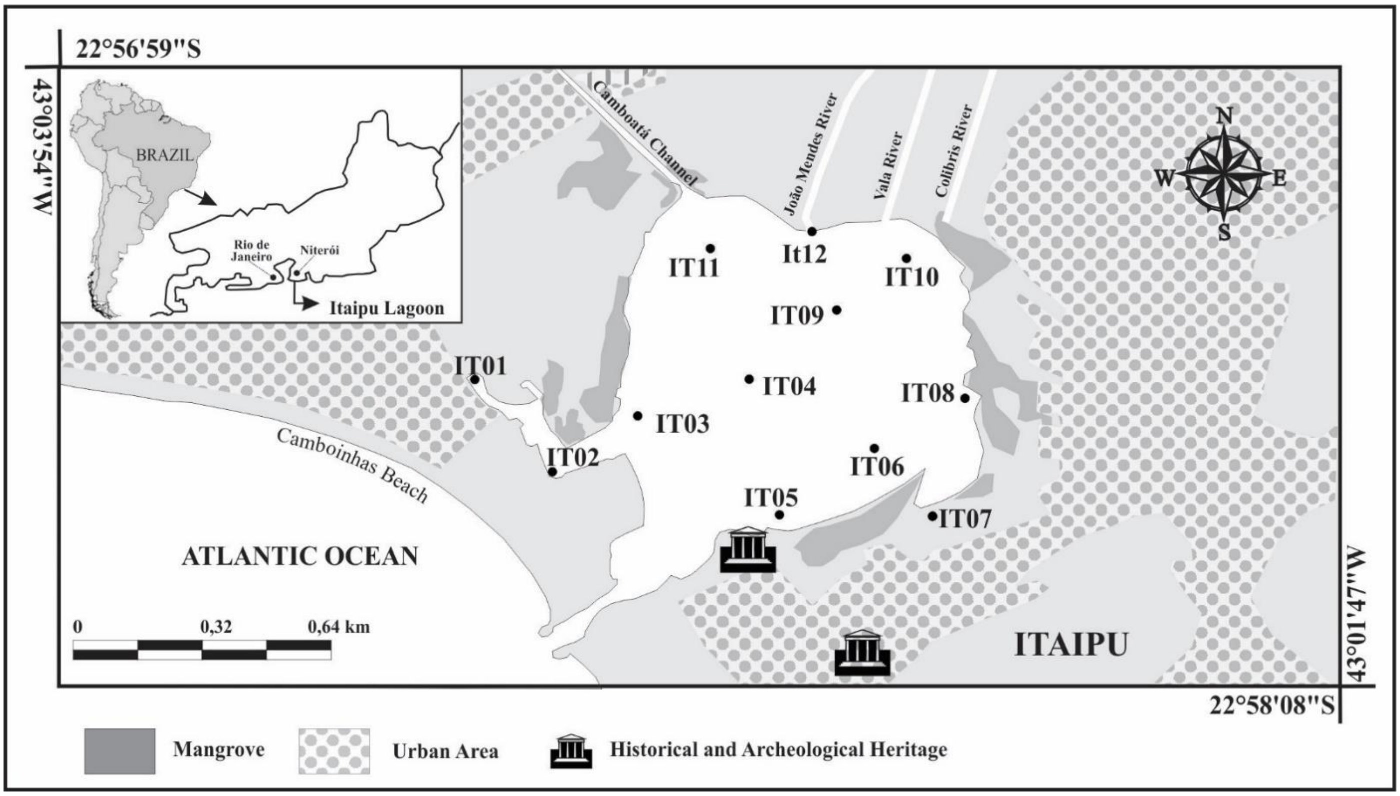

Fig. 1. Study area in Itaipu Lagoon, located in the State of Rio de Janeiro (Brazil). The sampled stations, the main cities and rivers that flow into this lagoon are indicated in this figure, as well as the urban areas, mangrove and the historical/archaeological heritage sites.

This complex ecosystem is composed of a mixture of lagoonal, swamp, mangrove, dunes and sandbanks areas that are affected by a warm-humid climate and heavy rains during summer and dry-mild winter season (Peel et al., 2007). This region falls in the climate zone of coastal plains and massifs with mean rainfall between 1,000 and 1,500 mm/year (Barbiére and Coe-Neto, 1999).

Over the last decades, the surroundings of Itaipu Lagoon have been the target of increasing urbanization processes (Cerda et al., 2013). An intense process of environmental degradation has been taking place, mainly driven by the occupation of slums and settlements on the lagoonal sand banks by poor infrastructure. Additionally, direct dumped sewage, riparian forest deforestation and slope erosion are also contributing to this lagoon deterioration.

The deposition of effluents into the lagoon promotes deleterious effect in this sensitive ecosystem. In the light of the growing interest in protecting this sensitive ecosystem and in monitoring its morphometric, physicochemical, and biological changes, some projects have been implemented to assess the water quality (Wasserman and Alves, 2004).

The present study, however, represents the first contribution aiming to understand the trophic conditions of Itaipu Lagoon, based on the analysis of the quantity and quality of sedimentary OM.

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3. Material and methods

Twelve stations located in Itaipu Lagoon were sampled in December 2012 during the summer rainy season (Fig. 1). Each sampled station was georeferenced with a GPS (model GPSMAP® 78S). Sediment samples were collected with a box-corer. Environmental parameters, such as salinity, temperature, dissolved oxygen and pH, were also measured in each station, in bottom water. These physicochemical variables were recorded with a refractometer ATC, a dissolved oxygen meter AKSO AK84 and a pH-meter TECNOPON μPA210P, respectively.

The first upper centimeter of sediment was recovered and used in this study. Three sediment samples collected in each station were placed in referenced plastic bags and freeze (-20ºC) for TOC, total sulphur (TS) and the biopolymer concentration analyses. Once in laboratory, sediment samples were lyophilized before the analysis.

3.1 TOC and TS analyses

Parts of homogenized and lyophilized sediment samples (~2 g) were ground. Aliquots of ca. 0.26 g were weighed (0.1 mg precision) in previously weighed porous porcelain crucibles. In order to eliminate the carbonate fraction, volumes of HCl (1:1 v/v) sufficient to cover the sample were added to the crucibles.

Samples were treated for 24 h before filtration of solid residue, which was then washed with distilled water until complete elimination of the HCl (to pH ~6). Sample residues were dried at 65ºC for 3 h and weighed for calculating the percentage of insoluble residue.

Measurements of TOC and TS were performed with a carbon and sulphur analyzer (LECO SC 144) according to a previously published method (Mendonça-Filho et al., 2003) and following the ASTM D 4239 (2008) method.

3.2 Biopolymers concentrations analysis

The protein (PTN) content determination was carried out after extractions with NaOH (0.5 M, 4 h) and was determined according to Hartree (1972) modified by Rice (1982). Concentrations are reported as albumin equivalents.

Carbohydrates (CHO) contents were analyzed according to Gerchacov and Hachter (1972) and expressed as glucose equivalents. The method is based on the same principle as the widely used method of Dubois et al. (1956), but it is specifically adapted for CHO determination in sediments.

Lipids (LIP) were extracted by direct elution with chloroform and methanol and analyzed according to Marsh and Weinstein (1966). Lipids concentrations are reported as tripalmitine equivalents.

For each biochemical analysis, blanks were performed with the same sediment samples after being treated in a muffle furnace (450°C, 2 h).

All analyses were carried out in 3-5 replicates. The sum of the carbohydrate, protein and lipid concentrations converted into carbon equivalents (by using the conversion factors of 0.40, 0.49 and 0.75 μg C μg-1, respectively) was defined as biopolymeric carbon (BPC) (Fabiano et al., 1995).

3.3 Statistical Analysis

Data were transformed by log (X+1) before the statistical analysis. The relationship among variables was assessed by Principal Components Analysis (PCA) and using Pearson correlations. A level of significance of $p<0.05$ was considered in this work.

In order to group the stations with similar characteristics in terms of quantity and quality of organic matter, a Q-mode Cluster Analysis (CA) based on the 1-Pearson r and Complete Linkage was applied. The groups of stations established by the Q-mode CA were then used to identify areas with different characteristics in Itaipu Lagoon.

Statistical analyses were carried out in Statistica 12.0. Maps were produced with Surfer 11.0.42®. The metric coordinates used are according to the WGS84 (UTM-23) datum.

4. Results

Samples location and water depth are reported in Table 1 and the values of the analyzed variables are presented in Table 2. Dissolved oxygen varied from 0.53 mg l^{-1} to 16.53 mg l^{-1} (mean 10.5 mg l^{-1}) and salinity from 9‰ to 40‰ (mean 28 ±8.8 ‰). Temperature ranged from 18.6°C to 30°C (mean 26.1±2.9 ºC) and pH values from 6.46 to 8.50 (mean 7.88±0.53).

The distribution pattern of temperature, salinity, dissolved oxygen and pH show that the lowest values were recorded in the inner part of the lagoon. The lowest pH values were recorded in station IT07, located near residential buildings. The highest values of temperature, salinity, dissolved oxygen and pH were recorded near the connection with the ocean (Fig. 2).

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Tab. 1. Geographic coordinates, water depth and details of the studied stations in Itaipu Lagoon.

Stations	Latitude (S)	Longitude (W)	Water Depth(m)	Observations Station located:
IT01	-43.050411	-22.961294	2.0	Near residential buildings
IT02	-43.048294	-22.963923	2.3	At a navigation channel for boats, and jet skis
IT03	-43.046014	-22.962489	0.5	At a navigation channel for boats, and jet skis
IT04	-43.042976	-22.961464	1.8	At the center of Itaipu Lagoon
IT05	-43.042502	-22.965251	0.7	Close to the channel that connects the lagoon with sea
IT06	-43.039825	-22.963611	0.5	Near a mangrove vegetation area
IT07	-43.038619	-22.965447	0.5	Near residential buildings
IT08	-43.037163	-22.962214	0.8	Near a mangrove vegetation area
IT09	-43.040412	-22.959437	1.0	In the transition between the lagoon center and its inner areas
IT10	-43.038173	-22.957820	0.5	Near the mouths of Vala and Colibris rivers and a mangrove vegetation area
IT11	-43.043875	-22.957304	0.5	Near Camboatá Channel
IT12	-43.045542	-22.953911	0.7	Near João Mendes River mouth

The distribution of TOC and TS contents are presented in Figure 3. The lowest percentage of TOC was 0.22% (IT05) and the highest 6.00% (IT09). Mean and standard deviation of TOC content was 3.25 ± 1.85% (Tab. 2). The TS values varied from 0.03% (IT02) to 1.73% (IT10). The mean and standard deviation of TS was 1.00 ± 0.59%.

The ratio of TOC to TS contents (C/S) varied between 2.55 (IT10) and 8.95 (IT02). The mean and standard deviation of C/S was 3.99±1.67 (Tab. 2). The highest values of TOC and TS and the lowest values of C/S were recorded in the inner lagoonal area (Fig. 3).

4.1 Sedimentary organic matter composition

Carbohydrate (CHO), protein (PTN) and lipid (LIP) concentrations showed different spatial patterns (Fig. 4). Concentrations of these biopolymeric compounds were relatively high in the station IT04, located in the center of the lagoon.

The mean concentration of CHO in Itaipu lagoon was 0.85± 0.51 mg g^{-1}. The highest and lowest values of this variable were observed in IT04 (2.07 mg g^{-1}) and IT05 (0.17 mg g^{-1}) stations, respectively.

Protein concentrations (mean 0.95± 0.48 mg g^{-1}) reached the maximum value (2.12 mg g^{-1}) in the station IT04 and the lowest value (0.30 mg g^{-1}) in IT02.

Lipid concentrations ranged from 0.32 mg g^{-1} (in station IT05) and 2.52 mg g^{-1} (in station IT04) (mean 1.59± 0.63 mg g^{-1}). The highest concentrations of CHO and PTN were found in the center and at the eastern sector of the lagoon. LIP content exhibited a clear increasing trend from the lagoon mouth to its inner zone (Fig. 4).

The mean value of biopolymeric carbon (BPC) was 3.39±1.47 mg C g^{-1}. The BPC concentrations varied from 0.88 mg C g^{-1} (station IT2) to 6.71 mg C g^{-1} (station IT4). This BPC and LIP concentrations presented a similar trend of spatial distribution in Itaipu Lagoon.

The BPC/TOC values ranged from 0.48% (IT09) to 6.02% (IT03) (Tab. 2). The BPC/TOC values were significantly high near the lagoon mouth (IT03). The lowest values of this variable were recorded in the inner zone of Itaipu Lagoon. The PTN/CHO values varied between 0.68% (IT08) and 2.37 % (IT05) (Tab. 2). The lowest values of this ratio were recorded in the central and eastern sectors. Table 2 also presents data of PTN/TOC (ranging from 0.10-2.16 mg g^{-1}; mean 0.62± 0.66 mg g^{-1}) and LIP/CHO ratios (ranging from 1.21-3.75 mg g^{-1}; mean 2.16± 0.92 mg g^{-1})

4.2 Statistical analysis

Table 3 presents the matrix of Pearson correlations for the analyzed variables. This matrix evidences some interesting significant positive correlations, for instance: i) between TOC and TS, LIP, CHO and BPC; ii) between CHO and LIP and PTN; iii) between LIP and PTN; and iv) between O_2 and salinity. Significant negative correlations are also observed, for instance: i) between TS and PTN/TOC and BCP/TOC; and ii) between C/S and the biopolymers (CHO, PTN, LIP, and BPC).

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Tab. 2. The sedimentary content in total organic carbon (TOC), total sulphur (TS), carbohydrates (CHO), lipids (LIP) and proteins (PTN), total biopolymeric carbon (BPC), percentage of biopolymeric carbon (BPC) is presented. This table also shows the ratio values: C/S, BPC/TOC, PTN/CHO, PTN/TOC and CHO/LIP. Values of salinity (Sal), pH, dissolved oxygen (O_2) and temperature (Temp) measured in each site are also reported.

Variables/ Stations	TOC %	TS %	C/S	CHO mg g^{-1}	LIP mg g^{-1}	PTN mg g^{-1}	BPC mg C g^{-1}	BPC/ TOC	PTN/ CHO	PTN/ TOC	LIP/ CHO	Sal ‰	pH	O_2 mg l^{-1}	Temp ºC
IT01	5.16	1.35	3.83	0.79	1.62	0.64	3.05	0.59	0.81	0.12	2.04	19	8.50	13.40	27.8
IT02	0.29	0.03	8.95	0.22	0.36	0.30	0.88	3.06	1.32	1.02	1.63	29	8.25	8.63	26.4
IT03	0.58	0.14	4.21	0.90	1.35	1.26	3.51	6.02	1.40	2.16	1.50	21	8.25	8.70	26.7
IT04	4.20	1.33	3.16	2.07	2.52	2.12	6.71	1.60	1.02	0.50	1.22	30	8.20	13.14	27.5
IT05	0.22	0.04	5.28	0.17	0.32	0.40	0.89	3.97	2.37	1.78	1.92	40	8.14	10.13	25.9
IT06	3.99	1.21	3.30	0.91	1.87	0.69	3.47	0.87	0.76	0.17	2.06	30	8.08	14.25	26.3
IT07	3.81	1.08	3.54	1.48	1.79	1.39	4.66	1.22	0.94	0.37	1.21	40	6.46	8.46	30.0
IT08	3.51	1.37	2.56	1.12	1.88	0.76	3.76	1.07	0.68	0.22	1.68	37	7.84	13.53	27.5
IT09	6.00	1.43	4.19	0.88	1.37	0.61	2.86	0.48	0.70	0.10	1.56	30	7.87	14.50	18.6
IT10	4.42	1.73	2.55	0.52	1.86	0.92	3.29	0.74	1.78	0.21	3.60	9	7.32	0.53	22.0
IT11	4.30	1.55	2.77	0.51	1.92	1.12	3.55	0.83	2.20	0.26	3.75	30	7.54	16.53	27.6
IT12	2.56	0.73	3.49	0.59	2.19	1.22	4.00	1.56	2.06	0.48	3.70	21	8.06	4.40	27.4
Max.	**6.00**	**1.73**	**8.95**	**2.07**	**2.52**	**2.12**	**3.05**	**0.59**	**2.37**	**2.16**	**1.88**	**40**	**8.50**	**16.53**	**30.0**
Min.	**0.22**	**0.03**	**2.55**	**0.17**	**0.32**	**0.30**	**0.88**	**3.06**	**0.68**	**0.10**	**1.22**	**9**	**6.46**	**0.53**	**18.6**
Mean	**3.25**	**1.00**	**3.99**	**0.85**	**1.59**	**0.95**	**3.51**	**6.02**	**1.34**	**0.62**	**1.92**	**28**	**7.88**	**10.52**	**26.1**
St. Dev	**1.85**	**0.59**	**1.67**	**0.51**	**0.63**	**0.48**	**6.71**	**1.60**	**0.59**	**0.66**	**1.24**	**9**	**0.53**	**4.46**	**2.9**

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The PCA biplot, which explains most of data variability (72%), allows the recognition of four groups of variables (Fig. 5). Group I composed by TS, TOC, LIP, PTN, CHO and BPC. This group is in opposition to Group II, which includes PTN/TOC, BPC/TOC C/S and pH. Group III encompasses PTN/CHO and LIP/CHO and is negatively related to the Group IV, which contains salinity, CHO/LIP and oxygen content. These groups of variables agree with the results of Pearson correlations presented in Table 3.

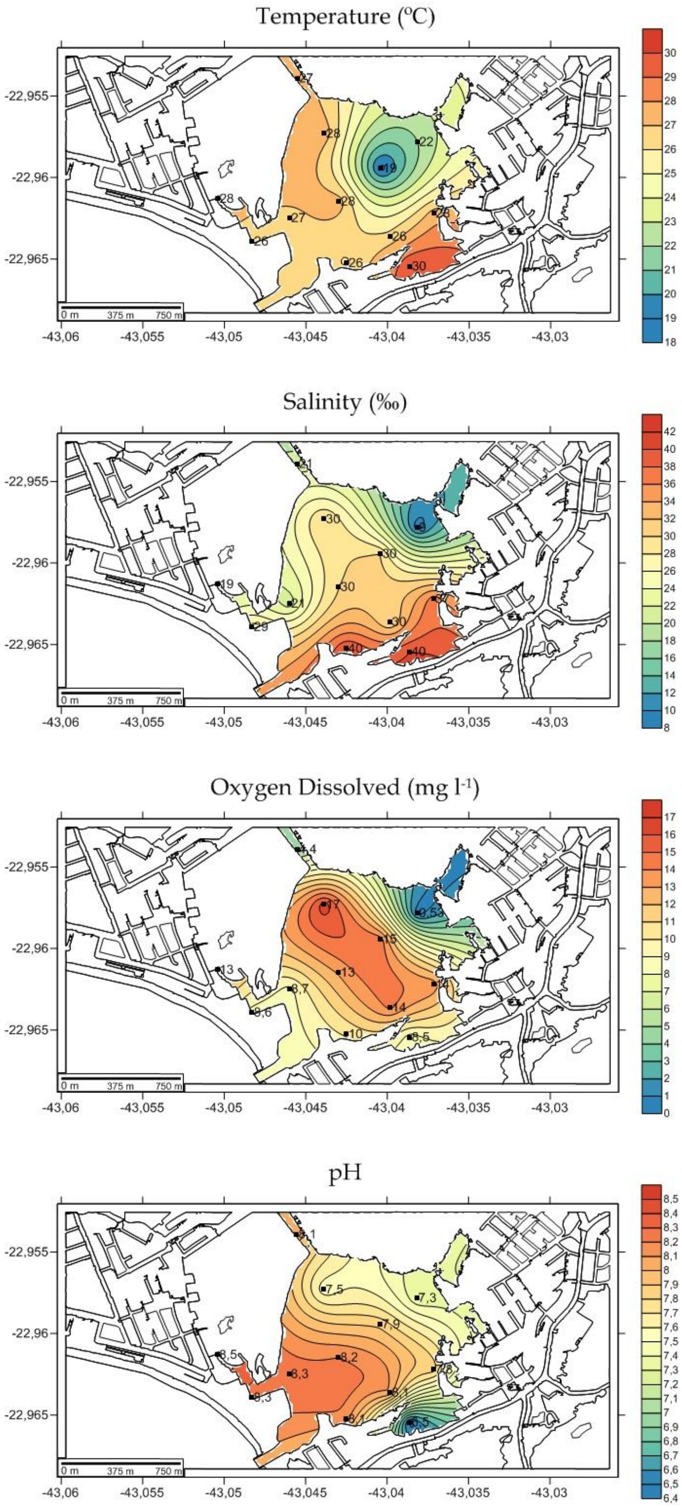

Fig. 2. Distribution patterns in Itaipu Lagoon of temperature (ºC), salinity (‰), dissolved oxygen (mg l^{-1}) and pH values.

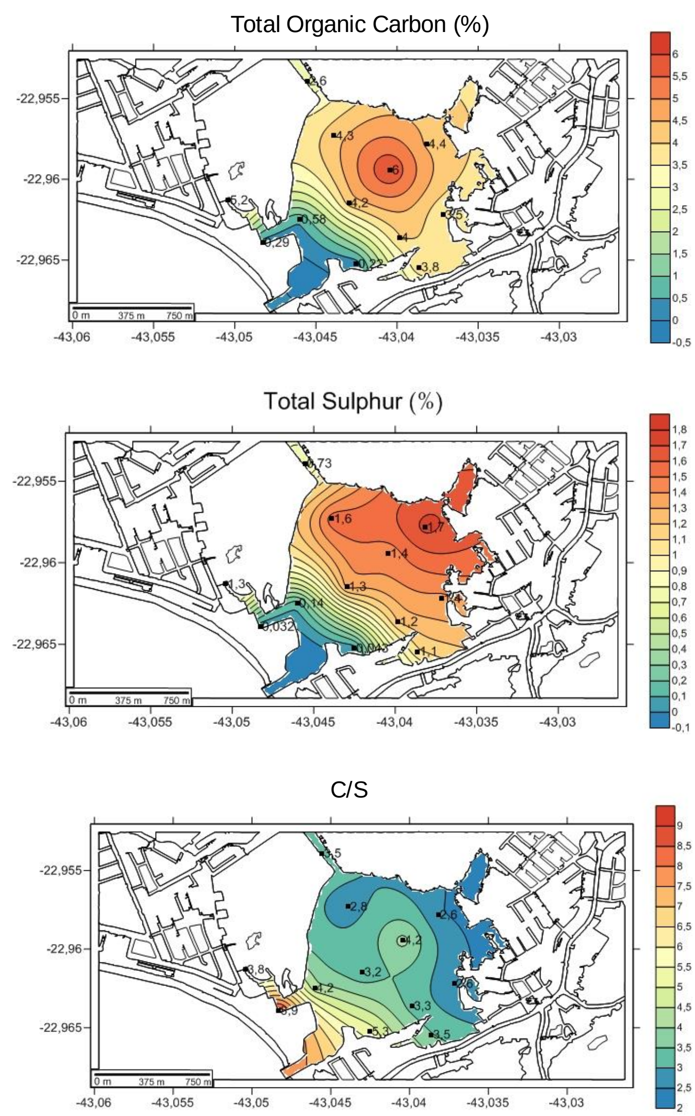

Fig. 3. Distribution patterns in Itaipu Lagoon of total organic carbon (%), total sulphur (%) and the C/S ratio values.

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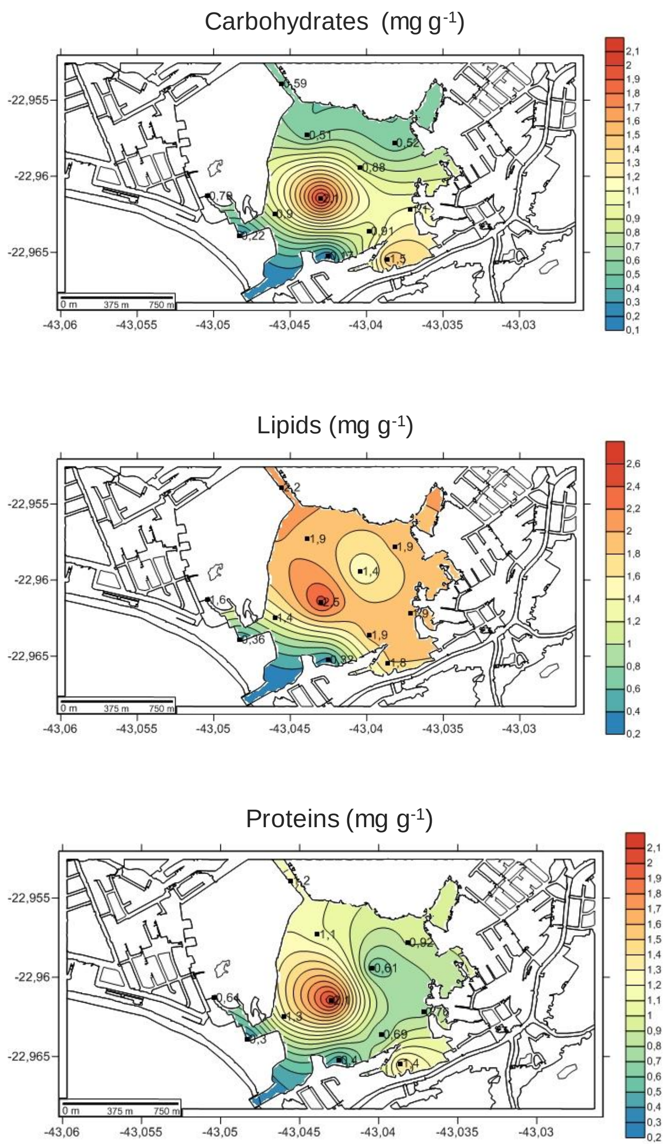

Fig. 4. Distribution patterns in Itaipu Lagoon of: Carbohydrates (mg g^{-1}); Lipids (mg g^{-1}); and Proteins (mg g^{-1}).

Results of Q-mode CA, based on TOC, TS, CHO, LIP, PTN and BPC, discriminate two main clusters of stations (Fig. 6). Cluster 1 can be further subdivided in two sub-groups of stations: Sub-group 1.1, including the stations IT01, IT06 and IT08-IT11, located in the inner part of the lagoon; and Sub-group 1.2, containing the stations IT04 (at the center of the lagoon), IT07 (positioned near residential buildings) and IT12 (situated next to São João River mouth). Cluster 2 contains the stations IT02, IT03 (located in a navigation channel for boats, and jet ski) and IT05 (set close to the channel that connects the lagoon with sea).

Results presented in Table 4 show that the stations of Sub-group 1.1 (IT1, IT6 and IT8-11, located in the inner lagoonal area) have, on average, the highest values of TOC, TS and LIP/CHO. Stations of Sub-group 1.2 (IT4, IT7, IT12, located in the central and lateral areas of the lagoon) display the highest concentrations of biopolymers and the highest values of C/S and CHO/LIP and the lowest values of pH and dissolved oxygen. On the other hand, stations of Cluster 2 are characterized by relatively low TOC and total biopolymer concentrations. Stations of this cluster also have low CHO/LIP values and the highest values of the ratios PTN/CHO, PTN/TOC, BPC/TOC and C/S. Cluster 2 contains the stations IT02, IT03 (located in a navigation channel for boats and jet skis) and IT05 (set close to the channel that connects the lagoon with sea).

5. Discussion

Salinity values recorded in Itaipu Lagoon evidence high variability (9-40‰) related to the influence of freshwater input by rivers, the seawater entrance through the inlet by tidal currents and strong evaporation.

In this lagoon, tidal mixing is significant (Kjerfve and Knoppers, 1999) along with the homogenization action played by wind. The estimated water residence time may vary from 14 days in summer to 289 days in winter (Carneiro et al., 1990). This variation is attributed to the worsening of the low circulation of this lagoon and mainly to the low effect of tidal waves energy (ranging between 0.8 m and 1.0 m) (Carneiro et al., 1990). The water high residence time may influence the oscillations of the physicochemical parameters, such as the salinity, temperature, pH and dissolved oxygen content as well as the production and accumulation of OM in the lagoon.

The evaluated TOC contents in Itaipu Lagoon were similar to those reported in other coastal and estuarine areas (Danovaro et al., 1994; Buscail et al., 1995; Danovaro and Fabiano, 1995).

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Tab. 3. Pearson Correlations based on the following variables: total organic carbon (TOC; %), total sulphur (TS; %), carbohydrates (CHO; mg g^{-1}), lipids (LIP; mg g^{-1}) and proteins (PTN; mg g^{-1}), total biopolymeric carbon (BPC; mg C g^{-1}), as well as the values of C/S, BPC/TOC, PTN/CHO, PTN/TOC, CHO/LIP, salinity (Sal; ‰), pH and dissolved oxygen (O_2; mg l^{-1}). Bold marked correlations are significant at $p<0.05$.

Variables	TOC	TS	CHO	LIP	PTN	BPC	C/S	BPC/TOC	PTN/CHO	PTN/TOC	LIP/CHO	CHO/LIP	Sal	pH	O_2
TOC	1.00	0.99	0.71	0.87	0.53	0.79	-0.77	-0.88	-0.48	-0.88	-0.2	0.2	-0.21	-0.33	-0.03
TS	0.99	1.00	0.72	0.91	0.59	0.83	-0.86	-0.84	-0.41	-0.84	-0.2	0.2	-0.23	-0.35	-0.07
CHO	0.71	0.72	1.00	0.83	0.76	0.91	-0.59	-0.36	-0.64	-0.41	0.4	-0.4	0.06	-0.25	0.20
LIP	0.87	0.91	0.83	1.00	0.81	0.97	-0.85	-0.56	-0.32	-0.57	-0.2	0.2	-0.27	-0.26	-0.08
PTN	0.53	0.59	0.76	0.81	1.00	0.91	-0.67	-0.09	0.01	-0.06	0.0	0.0	-0.13	-0.34	-0.08
BPC	0.79	0.83	0.91	0.97	0.91	1.00	-0.79	-0.42	-0.34	-0.43	0.0	0.0	-0.16	-0.30	-0.01
C/S	-0.77	-0.86	-0.59	-0.85	-0.67	-0.79	1.00	0.54	0.12	0.53	0.3	-0.3	0.25	0.36	0.20
BPC/TOC	-0.88	-0.84	-0.36	-0.56	-0.09	-0.42	0.54	1.00	0.46	0.99	0.3	-0.3	0.20	0.26	0.03
PTN/CHO	-0.48	-0.41	-0.64	-0.32	0.01	-0.34	0.12	0.46	1.00	0.56	-0.6	0.6	-0.24	-0.01	-0.41
PTN/TOC	-0.88	-0.84	-0.41	-0.57	-0.06	-0.43	0.53	0.99	0.56	1.00	0.2	-0.2	0.18	0.20	-0.01
LIP/CHO	-0.17	-0.22	0.40	-0.18	0.02	0.02	0.34	0.28	-0.61	0.21	1.0	-1.0	0.55	-0.01	0.48
CHO/LIP	0.17	0.22	-0.40	0.18	-0.02	-0.02	-0.34	-0.28	0.61	-0.21	-1.0	1.0	-0.55	0.01	-0.48
Sal	-0.21	-0.23	0.06	-0.27	-0.13	-0.16	0.25	0.20	-0.24	0.18	0.5	-0.5	1.00	-0.08	0.81
pH	-0.33	-0.35	-0.25	-0.26	-0.34	-0.30	0.36	0.26	-0.01	0.20	0.0	0.0	-0.08	1.00	0.30
O2	-0.03	-0.07	0.20	-0.08	-0.08	-0.01	0.20	0.03	-0.41	-0.01	0.5	-0.5	0.81	0.30	1.00

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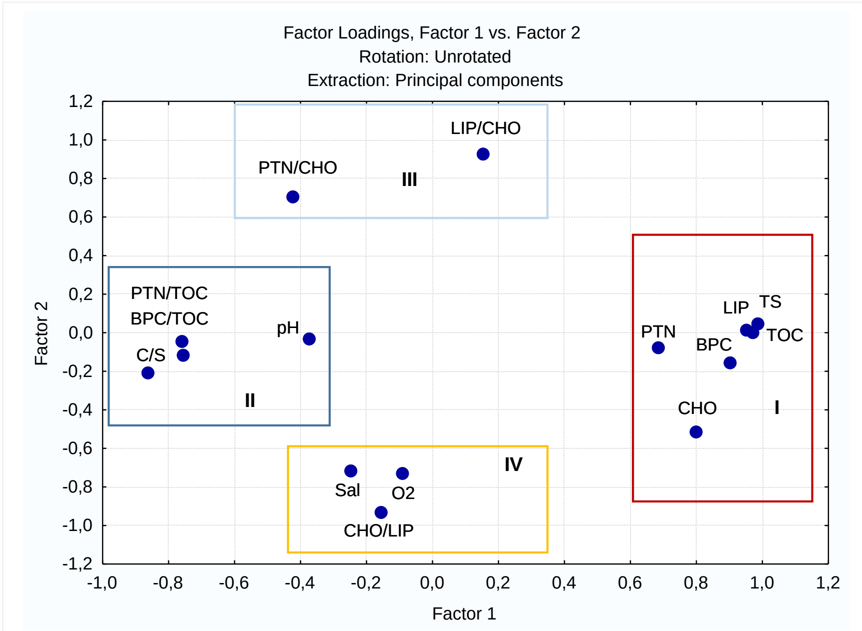

Fig. 5. Results of PCA based on the following variables: total organic carbon (TOC; %), total sulphur (TS; %), carbohydrates (CHO; mg g^{-1}), lipids (LIP; mg g^{-1}) and proteins (PTN; mg g^{-1}), total biopolymeric carbon (BPC; mg C g^{-1}), as well as the values of C/S, BPC/TOC, PTN/CHO, PTN/TOC, CHO/LIP, salinity (Sal; ‰), pH and dissolved oxygen (O_2; mg l^{-1}).

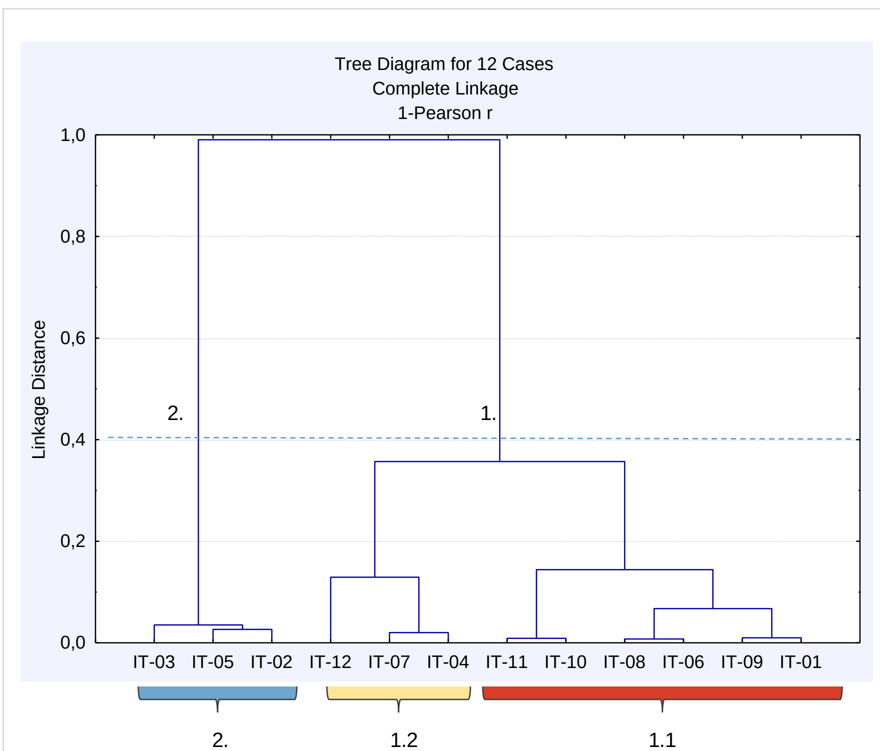

Fig. 6. Results of Q-mode CA, discriminating three groups of stations in Itaipu Lagoon.

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Tab. 4. - Maximum and mean values of TOC, TS, CHO, LIP, PTN, BPC, BPC/TOC, C/S, PTN/CHO, PTN/TOC, LIP/CHO, CHO/LIP, Salinity (Sal) , pH, O_2, Temperature (Temp.) in each group of stations identified by cluster analysis included in Figure 6.

Variables	Sub-Group 1.1 Stations 1, 6 8-11			Sub-Group 1.2 Stations 4, 7, 12			Cluster 2 Stations 2, 3, 5		
	Max.	Mean	St. Dev	Max.	Mean	St. Dev	Max.	Mean	St. Dev
TOC (%)	6.00	4.56	0.81	4.20	3.52	0.70	0.58	0.37	0.16
TS (%)	1.73	1.44	0.17	1.33	1.05	0.25	0.14	0.07	0.05
CHO (mg g^{-1})	1.12	0.79	0.22	2.07	1.38	0.61	0.90	0.43	0.33
LIP (mg g^{-1})	1.92	1.75	0.20	2.52	2.16	0.30	1.35	0.68	0.47
PTN(mg g^{-1})	1.12	0.79	0.18	2.12	1.58	0.39	1.26	0.65	0.43
BPC (mg C g^{-1})	3.76	3.33	0.30	6.71	5.12	1.15	3.51	1.76	1.24
BPC/TOC	1.07	0.76	0.19	1.60	1.46	0.17	6.02	4.35	1.24
C/S	4.19	3.20	0.63	3.54	3.40	0.17	8.95	6.15	2.03
PTN/CHO	2.20	1.15	0.60	2.06	1.34	0.51	2.37	1.70	0.48
PTN/TOC	0.26	0.18	0.05	0.50	0.45	0.06	2.16	1.65	0.47
LIP/CHO	3.75	2.45	0.89	3.70	2.04	1.17	1.92	1.69	0.18
CHO/LIP	0.64	0.46	0.14	0.83	0.64	0.26	0.67	0.60	0.06
Salinity	37.00	25.83	9.19	40.00	30.33	7.76	40.00	30.00	7.79
pH	8.50	7.86	0.38	8.20	7.57	0.79	8.25	8.21	0.05
O_2 (mg l^{-1})	16.53	12.12	5.29	13.14	8.67	3.57	10.13	9.15	0.69
Temp	27.80	24.97	3.48	30.00	28.30	1.20	26.70	26.33	0.33

C/S ratio is generally used as an indicator for evaluating the oxi-reduction conditions in sediments (Morse and Berner, 2000). Ratios >3 indicate oxidizing conditions, while lower values (<3) suggest reducing ones (Stein, 1991; Borrego et al., 1998). In the majority of the stations, C/S ratio points out to the presence of sediments with oxidizing conditions except in IT08, IT10 and IT11 located in the inner area of the lagoon, which exhibits more reductive conditions. The prevalence of low currents activity in this zone allows the accumulation of fine grained sediments and the settlement of organic materials, as observed in other coastal systems (Martins et al., 2013; 2014; 2015a; 2016b).

The concentrations of the sedimentary labile organic compounds (*e.g.* carbohydrates, proteins and lipids) varied significantly in the lagoon due to the influence of the tidal currents, authochtounous biological production and the rivers inputs.

The highest concentrations of biopolymer compounds in this kind of coastal system can be manly related to the presence of large amount of OM: macroalgal coverage (*Ulva lactuca*), deposits of land-derived material (vascular plants and wood debris) and abundant polychaetes (Cividanes et al., 2002).

Pusceddu et al. (2014) comparing Tropical Marine Ecosystems observed that in the Caribbean Sea the highest phytopigment and biopolymeric carbon concentrations occurred in mangrove sediments; the highest phytopigment content in the Red Sea was found in reef areas, whereas, in the Celebes Sea, it was observed in bottoms with seagrass.

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The mangroves areas surrounding Itaipu Lagoon can provide large quantity of fine terrigenous and organic particles that are accumulated in the bottom where waters lose velocity and transportation capacity. High accumulation of OM in those areas and the processes related to their degradation lead to a decrease of oxygen availability. Under these conditions, the bacterial activity employs sulphate as an oxidizing agent with the consequent releasing of sulphide, a reduction product (Fontana et al., 2012). Otherwise, the formation of acids resulting from the OM degradation may lead to a decrease of pH (as it can be deduced from the composition of groups I and II of the PCA of Fig. 5).

In the sediments of Itaipu Lagoon, LIP (0.32-2.52 mg g^{-1}), PTN (0.30-2.12 mg g^{-1}) and CHO (0.17-2.07 mg g^{-1}) reach relatively high concentrations considering the biopolymers evaluation threshold values proposed by Dell'Anno et al. (2002).

Furthermore, the concentrations of these three biopolymer components of OM in Itaipu Lagoon were similar to those reported for other Brazilian environments (Tab. 5). These results indicate that the amount of OM in the sediments of Itaipu Lagoon is comparable with data from other Brazilian transitional environments.

The concentrations of PTN and CHO, in Itaipu Lagoon, are typical of eutrophic and hypertrophic environments, respectively. The relatively high concentrations of sedimentary PTN, CHO and LIP recorded in the study area (Tab. 5) are probably related to the morphodynamic, hydrological and physicochemical characteristics and climate regime of this lagoon that in turn influence the autochthonous biological productivity, the supply of allochthonous OM and the accumulation of organic materials in the sedimentary environment.

Concentrations of LIP reach relatively higher maximum and mean values than CHO and PTN (Tab. 4). Similar results were obtained in other estuarine areas (Ittekkot, 1988; Saliot et al., 1984). The concentration of LIP is lower than PTN only in the station IT05, which is under higher oceanic influence.

The LIP content and LIP/CHO ratio have been used as biochemical indexes to describe the quality of the organic content in the sediment (Grémare et al., 1997, 2002; Isla et al., 2006). Lipids in the sediments are probably associated with the refractory fraction of sedimentary organic matter (Grémare et al., 1997, 2002; Cartes et al., 2002; Isla et al. 2006). The highest lipids concentrations recorded in the inner lagoonal region of Itaipu Lagoon may be associated to the increase of recalcitrant substances originated by fluvial inputs.

High CHO content and very high LIP and LIP/CHO values were observed in Itaipu Lagoon. The LIP/CHO values range from 1.21 % to 3.75 %. This allows to infer that Itaipu Lagoon behaves as a detritus trap for organic matter accumulation with low nutritional values.

The PCA results (Fig. 5) suggest that LIP/CHO and PTN/CHO values (Group III) tend to increase in areas where dissolved oxygen concentrations and salinity are relatively low (Group IV). These characteristics were recorded in inner lagoonal areas.

Values of PTN/CHO ratio >1 have been attributed to the presence of fresh materials of recent origin, while values of PTN/CHO ratio <1 suggest the predominance of aged OM (Danovaro et al., 1993).

In Itaipu Lagoon, the PTN/CHO ratio remained >1 in the external sector (stations IT 02-05) and in some stations (IT 10-12) of the internal stations connected with the mouths of Vala, Colibris and João Mendes rivers and Camboatá Channel.

The PTN/CHO ratio remained <1 in the central and other inner zones of the lagoon, which is indicative of the accumulation of degraded OM in those area.

The lowest values of BPC/TOC ratio were recorded in the inner lagoonal area where the TOC values reached the highest values. These results indicate that, in spite of the fact that large amounts of detrital OM are accumulated in Itaipu Lagoon, the organic detritus is largely of low nutritional quality in its internal sector.

The supply of high amount of degraded organic matter may be a negative factor for the fauna that feeds on debris because it only has available poor quality of food and has to live in an environment where oxygen is scarce.

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Tab. 4. - Comparison of carbohydrate, protein and lipid concentrations from different regions and marine systems in Brazil.

Location	Materials	Carbohydrates (mg g^{-1})	Lipids (mg g^{-1})	Proteins (mg g^{-1})	Source
Itaipu Lagoon	Bottom sediments	0.17-2.07	0.32-2.52	0.30-2.12	Present study
Niterói Port			13.52-59.00	2.00-6.00	Baptista-Neto et al., 2005
Guanabara Bay		0.22-1.48	0.064-1.71	0.022-0.111	Silva et al., 2008
Jurujuba Sound	Cores	0.28-0.85	0.020-0.192	0.26-0.40	Silva et al., 2011
Suruí Mangrove		0.110-0.311	0.011-0.99	0.077-0.40	Fontana et al., 2010a
Suruí Mangrove	Bottom sediments	0.39-1.76	0.012-0.154	0.11-0.82	Fontana et al., 2010b
Guanabara Bay		0.219-1.483	0.064-1.711	0.22-0.111	Silva et al., 2011b
Paraíba do Sul River Delta		0.12-4.74	0.009-1.53	0.0013-0.056	Silva et al., 2011a
Funil Dam		0.005-0.010	0.015-0.092	0.004-0.0069	Chequer et al., 2011
Maricá Lagoon	Superficial water	9.8×10^3-1.4×10^3	8.6×10^3-4.2×10^3	0.00035-0.010	Guerra et al., 2011
Paraíba do Sul River Delta	Bottom sediments	0.22-7.74	0.01-1.58	0.05-6.14	Sarvegnini et al., 2013
São João River		0.15-8.89	0.12-3.92	0.17-6.70	
Rio das Ostras		0.68-35.65	0.02-7.63	0.41-13.00	
Guanabara Bay	Superficial and bottom water	0.25-16.23	0.46-3.68	0.61-3.85	Aguiar et al., 2013
Guanabara Bay	Bottom sediments	0.12-12.20	0.04-12.78	0.02-0.89	Sabadini et al., 2014
Guanabara Bay	Bottom sediments	0.0013- 0.0052	0.0004-0.0032	0.0007-0.0030	Clemente et al., 2014

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5.1 Organic matter origin in Itaipu Lagoon

The biochemical composition of sedimentary OM has recently been used to gather information on its origin, quality and food bioavailability (Fabiano et al., 1995; Danovaro, 1996). The spatial differences among several biochemical compounds suggest marked changes in the composition and/or in the origin of the OM inputs in Itaipu Lagoon.

Biochemical composition of sedimentary OM in marine coastal areas is commonly characterized by small amounts of total LIP and large quantities of PTN, commonly exceeding CHO concentrations (Meyer-Reil, 1983; Sargent et al., 1983; Fabiano and Danovaro, 1994).

In Itaipu Lagoon, the relative abundance of the biopolymers LIP> PTN> CHO is different from other transitional environments (Pusceddu et al., 1999; Dell'Anno et al., 2002). As refereed, in most of the studied sites, LIP concentrations were higher than the other biopolymers. These results suggest a large supply of refractory OM from terrestrial sources is being discharged in Itaipu Lagoon with low consumption of these materials. Indeed, the values of the PTN/CHO ratio also support this inference.

Proteins concentrations were relatively low in most of the stations of Itaipu Lagoon. Bacteria more readily utilize these biopolymers than CHO (Newell and Field, 1983) and thus they are quickly degraded. The low abundance of labile PTN may be a potentially limiting factor for benthic consumers (Jumars and Wheatcroft, 1989; Fabiano et al., 1995).

5.2 Benthic trophic status of Itaipu Lagoon

The groups of stations established by the Q-mode CA allow to identify three main zones in Itaipu Lagoon that are plotted on the map of Fig. 7. The inner lagoonal zones (stations of the Sub-group 1.1: IT01, IT06 and IT08-IT11) are located near the river mouths and municipal effluents discharges, which have the lowest ratios of PTN/TOC and BPC/TOC and the highest concentrations of TOC and TS.

The highest TOC and TS contents suggest that the inner zone of Itaipu Lagoon is a detritus trap of OM. This region also exhibits the highest content of LIP. Accordingly, the results of this work allow to deduce that the sediments of the internal zone of Itaipu Lagoon have high content of OM but of poor quality.

The relatively low values PTN/TOC ratio (mean 0.18±0.05) also indicate the presence of large amount of aged OM in the sediments of the internal zone of Itaipu Lagoon. The C/S values (mean 3.20±0.63) also suggest that this area has been affected by diagenetic reactions associated with OM degradation. These characteristics reveal that internal zone can be considered a highly impacted sector of Itaipu Lagoon (Fig. 7).

On the other hand, the outer area of the lagoon (stations of the Cluster 2: T02, IT03, IT05) is characterized by relatively low values of TOC, biopolymers concentrations and LIP/CHO values. In this zone, the highest values of the PTN/CHO, PTN/TOC, BPC/TOC and C/S ratios were also recorded. The lowest concentrations of TOC and biopolymers should be related to hydrodynamic conditions in this sector, located at the passing channel (IT02 and IT03) near the inlet that connects the lagoon with the ocean. In this sector the currents activity prevents the accumulation of large amount of OM.

The BPC/TOC ratio reaches the high values in the stations of the outer area of the lagoon (T02, IT03, IT05) due to the high PTN content. The BPC/TOC ratio has been considered an indicator of the availability of OM with high quality for consumers (Danovaro and Fabiano, 1997). The relatively high values of PTN/CHO ratio recorded in these stations indicate the presence of newly produced OM. These features suggest that the OM contained in the sediments of the outer sector of Itaipu Lagoon is of relatively high quality. This sector can be considered a low impacted zone (Fig. 7).

Otherwise, the transitional area previously described (Sub-group 1.2, Stations 4, 7, 12; Fig. 6) is a medium-impacted sector as suggested by the intermediate values of the analyzed variables. In this area, the TOC values are yet relatively high (3-4%). However, the highest concentrations of BPC are indicative that the labile OM with high nutritional value is present in the center of Itaipu Lagoon (IT04). Despite its highest concentrations recorded in this region, LIP provides OM of good quality benthic fauna. This is also confirmed by the high values of PTN/TOC ratio.

Based on the biopolymers data and the scale of Vezulli and Fabiano (2006), Itaipu Lagoon should be considered an ecosystem impacted by OM.

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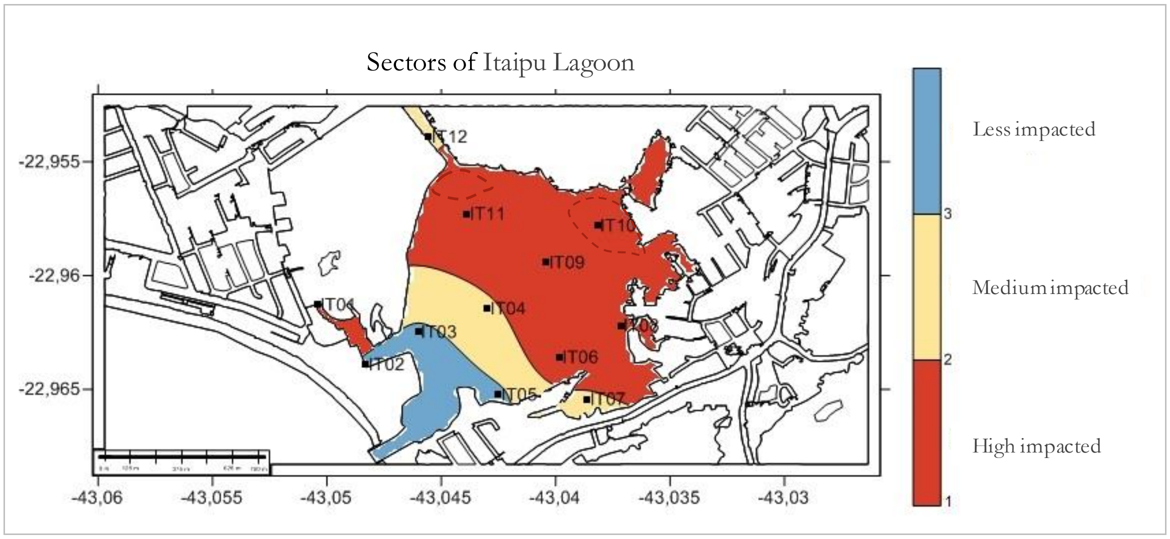

Fig. 7. Zones of Itaipu Lagoon with different degree of impact, considering organic matter quantity and quality.

6. Conclusion

Results of this study revealed significant spatial changes in the quantity and quality of the sedimentary OM in Itaipu Lagoon. The low BPC/TOC values observed in the most part of the studied stations indicate that large part of OM is impoverished in labile compounds. Such high amounts of sedimentary OM were therefore of low nutritional value and not directly available to benthic consumers, as they tend to be buried and accumulated into deeper sediment layers.

The inner sector of Itaipu Lagoon is a high impacted zone. This area has a minor tidal influence and consequently displays a less water renewal. It was characterized by sediments with high OM content. However, the OM of this sector has low quality and was probably provided by contaminated effluents and rivers runoff. The highest concentrations of lipids in the inner sector of Itaipu Lagoon also indicate the excessive presence of recalcitrant compounds that may not be used by the trophic chain.

The external sector of the lagoon, on the other hand, is less impacted. The highest values of BPC/TOC and PTN/TOC are indicative of the presence of OM with high nutritional value but in relatively low amount. The intermediate lagoonal area is a middle impacted region and shows transitional features between the two previously described zones.

Results of this work indicate that Itaipu Lagoon might be an environment where 'natural' variation in biochemical composition of the sedimentary OM is masked by significant allochthonous inputs. The high supply of organic matter to the bottom generates problems of eutrophication in most part of the benthic environment of Itaipu Lagoon. So this lagoon should be considered an ecosystem highly susceptible to environmental pollution by OM.

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