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RESEARCH PAPER

ASSESSMENT OF THE TROPHIC STATE OF SAQUAREMA LAGOONAL SYSTEM, RIO DE JANEIRO (BRAZIL)

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Abstract

This work intends to apply new ecological descriptors to a coastal marine area aiming to assess its environmental trophic status. This approach makes possible to identify relevant variables associated with eutrophication process applicable and valid worldwide. The aim of this work is to study the organic matter (OM) quality and quantity, in terms of biopolymers, in Saquarema Lagoonal System (SLS) located in Rio de Janeiro State (Brazil). Sediment samples collected in SLS were analyzed in this study for granulometric and geochemical data such as total organic carbon (TOC), total sulfur (TS) and biopolimeric carbon (BPC) concentrations, including proteins (PTN), carbohydrates (CHO) and lipids (LIP). These data were combined with additional environmental parameters measured in water of the four linked lagoons that compose SLS. Data analyses allowed the identification of four distinct regions in SLS: an inner and impacted zone characterized by sediment particularly enriched in TOC, with lowest quality of OM most probably provided by contaminated effluents and rivers runoff; an outer-less impacted lagoonal area with relatively low TOC content and submitted to high hydrodynamic forces; an intermediate area characterized by transitional features between the two previously mentioned and a zone that is influenced mainly by salinity. 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 the water renewal, rivers inputs and mangroves contributions as well as by the autochthonous lagoonal biological productivity. Results of this work indicate that the inner zone of SLS is being affected by eutrophication not necessarily caused by anthropic factors.

Keywords: Environmental impact. Organic matter compounds. Environmental quality.

1. Introduction

Coastal lagoons are defined as shallow inland marine waters, usually oriented parallel to the coastline, separated from the ocean by a barrier, and connected to the ocean by one or more restricted inlets (Kjerfve, 1994; McLusky and Elliott, 2007; Kennish and Paerl, 2010). The ocean entrance(s) can sometimes be closed off by sediment deposition due to wave action and littoral drift (Phleger, 1957; Kjerfve, 1994). These systems occupy 13% of coastal areas worldwide and are often impacted by both natural and anthropogenic factors (Sikora and Kjerfve, 1985; Kjerfve 1994; Laut et al. 2016 a). In Brazil, the formation of coastal lagoons was associated with eustatic oscillation processes during the Quaternary. This can be observed at all shorelines, but mainly in Rio de Janeiro and Rio Grande do Sul states (Esteves, 1998).

Excessive discharges of nutrients from domestic and industrial sewage, coupled with the runoff of urban and rural areas, lead to the enrichment of organic and inorganic nutrients of paralytic regions ecosystem (Ansari and Gill, 2014). These inputs result in intensification of the eutrophication process, which is currently considered the major stressor in coastal and marine environments (Meyer-Reil and Koster, 2000), especially in coastal lagoon systems of Rio de Janeiro state.

In aquatic ecosystems, the main components of available organic matter to biota are lipids, carbohydrates and proteins (Jones, 2001). These biopolymers are degraded by groups of bacteria with different metabolisms (Brock et al., 1994). In sheltered aquatic environment as coastal lagoons, there is a remineralization of organic components by esterase exoenzymes (Brock et al., 1994). However, the organic matter tends to accumulate in the system when its deposition rate is higher than the degradation capacity of the anaerobic microorganisms, which leads to the environment to eutrophic condition (Jones, 2001).

The bottom sediments of these environments work as a natural trap to organic matter and to different kind of pollutants (Ansari and Gill, 2014). Therefore, the sediment becomes a great source of nutrients and/or pollutants to the water column. It has influence on primary productivity connecting the group of benthic organisms to pelagic ones (Jørgensen and Richardson, 1996). The sediments are the final destiny of organic matter that is produced (*autochthone*) or introduced (*allochthonous*) to the lagoon depositional system. Thus, it represents the temporal record of all processes that occurs in the water column (Fabiano and Danovaro, 1994).

In the recent past new approaches relating the quality of the organic matter components (biopolymers) were developed in order to determine the trophic status of the coastal ecosystems (Meyers et al., 1987; Fabiano et al., 1995; Volkman et al., 1998). Dell'Anno et al. (2002) applied this new approach using the biochemical compounds in previously determined oligomesotrophic coastal regions and changed its classification to eutrophic environments.

In Brazil, these methodologies have been recently used in aquatic environments with intertropical climate aiming to evaluate the trophic status of the sediments. They allowed to identify the most impacted regions, as well as to understand the effects of the organic matter accumulation on the microbiota of coastal environments (Baptista Neto et al., 2005; Silva et al., 2008, 2010, 2011a, b; Clemente et al., 2015; Laut et al., 2016 a, b, c).

This study aimed to quantify and qualify the organic matter content of Saquarema Lagoonal System, correlating these results to sedimentological and physicochemical parameters in order to determine the trophic status and environmental quality of the ecosystem.

2 Study area

SLS is located in Rio de Janeiro State, southeast Brazil, between the latitudes of 22°55′S and 22°56′S and longitudes

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of 42°35′ W and 42°29′ W (Fig. 1). The lagoon system covers an area of ~21.2 km² and extends for ~11.8 km along the coast; it has an average depth not greater than 2.0 m. SLS consists of four large connected lagoons: Urussanga (12.6 km²), Jardim (2 km²), Boqueirão (0.6 km²) and Saquarema (6 km²). Urussanga Lagoon is bordered by swamps to the north and receives fresh water from Mato Grosso (or Roncador), Tingui and Jundiá rivers. Jardim Lagoon, which is surrounded by swamps, receives the fresh water input from Seco River. Saquarema Lagoon receives the discharge of Bacaxá River and has a mangrove fringe on the northern bank (Bruno, 2013). The Boqueirão Lagoon has no inflowing rivers (Moreira, 1989). The climate in the entire Rio de Janeiro State is warm and humid with a rainy summer season and a dry winter season. The average rainfall is between 1,000 and 1,500 mm/year (Barbieri and Coe-Neto, 1999). The climate in SLS is sub-humid, with prolonged periods of drought, and high temperatures (Carmouze and Vasconcelos, 1992). Climatic conditions are also influenced by Serra do Mato Grosso at the western side. The orographic processes of this mountain effect primarily the rivers that discharge into Urussanga Lagoon (Carmouze and Vasconcelos 1992). This lagoonal-coastal complex ecosystem is connected to the ocean through Barra Franca Channel. This channel is artificial with margins stabilized by stone blocks.

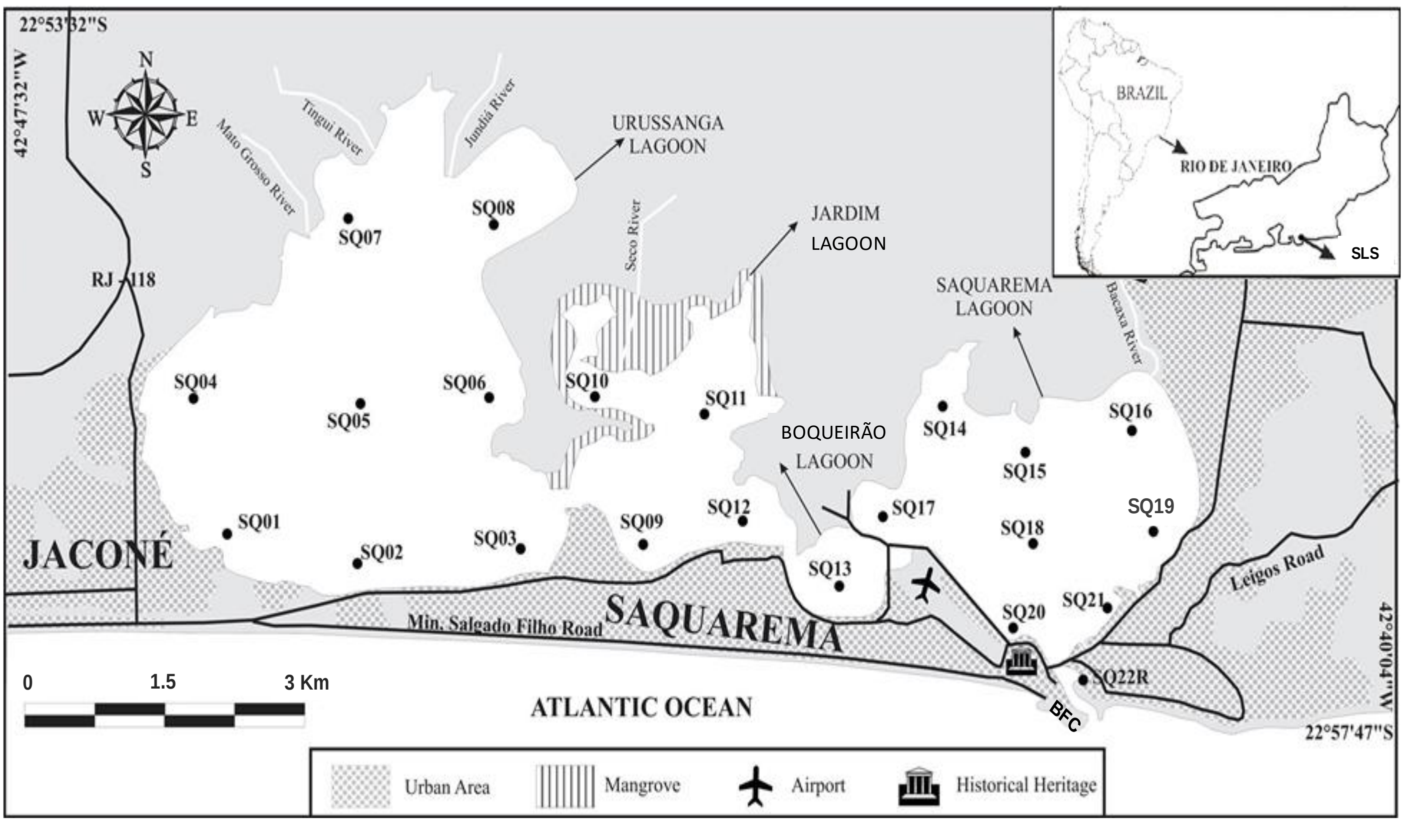

Fig. 1. Location of the study area and sampling stations in Saquarema Lagoonal System, Rio de Janeiro State, Brazil. Legend: SQ – Saquarema; SLS – Saquarema lagoon system; BFC - Barra Franca Channel.

According to Instituto Brasileiro de Geografia e Estatística (IBGE, 2004), the human population of Saquarema grew 72.2% between 1990 (37,888 inhabitants) and 2001 (59,938 inhabitants). Despite including 31,623 households, 47.97% of them are not occupied most part of the year. In 2007, population of Saquarema increased for 62,174 inhabitants (IBGE, 2004), indicating a growth of about 24.6% since 2012. This uncontrolled urbanization surrounding Saquarema, coupled with the natural effects of silting in Barra Franca Channel, have effectively increased domestic sewage in the lagoon and intensified the environmental disturbance (Bruno, 2013).

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3. Material and methods

3.1 Sampling Method

Twenty-two stations located through SLS were sampled in March of 2013 (Fig. 1). Each sampled station was georeferenced with a GPS (model GPSMAP® 78S). Physicochemical data such as salinity (Sal), temperature (T), dissolved oxygen (DO) and pH were obtained with a multi-parameter probe in water.

The sediment samples were collected with a van Veen Grab aboard of a small ship. The first upper centimeter of sediment was recovered and used in this study. Aiming to analyze total organic carbon (TOC), total sulfur (TS) and the biopolymers concentrations, sediment samples were placed in referenced plastic bags and cool preserved. Once in the laboratory, the sediment samples were lyophilized before the analyses.

3.2 Laboratory Analysis

3.2.1 Granulometric analysis

Sediment samples used in this study were dried at ambient temperature for 48 hours, homogenized and quartered for separating 50 grams of material for grain size analysis. These samples were: 1) washed with distilled water to remove soluble salts; 2) treated with hydrochloric acid (HCl) and hydrogen peroxide (H_2O_2) for removal of carbonate and organic particles; 3) dried in an oven at 60 °C and; 6) sieved using a Ro-tap system (sieve shaker) with sieves of 2.00 mm; 1.41 mm; 1.00 mm; 0.71 mm; 0.50 mm; 0.35 mm; 0.25 mm; 0.177 mm; 0.125 mm; 0,083 mm and 0,063 mm. Sediments smaller than 0,063mm (silt and clay) were analyzed by Pipette Sampling Method, based on Stokes' law.

3.2.2 Total Organic Carbon (TOC) and Total Sulfur (TS)

Parts of homogenized and lyophilized sediment samples (~2 g) were ground. Aliquots of ca. 0.26 g were weighed (0.1 mg precision) in porous porcelain crucibles previously weighed. 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 analyser (LECO SC 144) according to methodology described by Mendonça-Filho et al. (2003) and following the ASTM D 4239 Method (American Society for Testing and Materials, 2008).

3.2.3 Biopolymers concentrations analyses

Proteins (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 that widely used by Dubois et al. (1956), but was 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 were reported as tripalmitine equivalents.

For each biochemical analysis, blanks were performed with the same sediment samples after being treated in a muffle furnace (at 450°C, during 2 h). All analyses were carried out in 3-5 replicates. The sum of the concentrations of carbohydrates, proteins and lipids 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 Principal component analysis (PCA)

Principal component analysis is a standard tool in modern data exploration, since it is a simple, non-parametric method for extracting relevant information from confusing data sets. With minimal effort, PCA provides a roadmap that reduces a complex data set to a small dimension aiming to reveal sometimes hidden structures or to simplify complex relationships among the variables (Shlens, 2014). Through PCA, it is possible to identify which factors are impacting the stations and thus group them by similarity inside the lagoon. The parameters used were pH and DO, T, Sal, TS, CHO, LIP, PTN and BPC contents as well as percentages of sand, silt and clay fractions. PCA was performed using the PCORD 5 software.

3.4 Interpolation Maps

Interpolation uses vector points with known values to predict data at unknown locations in order to create a surface fulfilled with these values. As it is important to find a suitable

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interpolation method to optimally estimate values for the locations that lack sampled points. Spline with Barriers, Spline and IDW interpolation methods were tested. The method with the best spatial distribution was the IDW.

The IDW method gives each point such a weight that the influence of a sample on another one declines with the distance to a new point being estimated based on the principle of spatial autocorrelation. As a result, there is a spatial pattern that can be used to measure the similarity of samples or objects within an area and the interdependence level, nature and strength among variables.

The maps were shaped with ArcMap 10.2 and the IDW was configured with power 2 and 22 interpolation points for this study. The interpolation shows the spatial distribution of the parameters concentration inside the lagoon (Figs. 2-5).

4. Results

4.1. Physicochemical Parameters

Salinity varied between 31 (SQ11 station, Jardim Lagoon) and 33.8 in SQ09 station. In Saquarema Lagoon, the highest average salinity (35.3) among the lagoons was recorded. The highest value (43.3) was recorded in SQ18 station, in Saquarema Lagoon (Fig. 2).

The temperature presented few variations among the lagoon bodies with average of 29.7°C in Lagoon of Urussanga, 27°C in Jardim Lagoon, 26.7°C in Boqueirão Lagoon and 25.9°C in Saquarema Lagoon. The station SQ07, located near the mangrove fringe on the northern bank of Urussanga Lagoon, had the highest temperature value (47.9 °C) while the lowest temperature was recorded (24.9 °C) in SQ20 station that is close to the communication channel between Saquarema Lagoon and the Atlantic Ocean (Fig. 2).

The highest average dissolved oxygen value (7.4 mg/L) was found in Urussanga Lagoon and the lowest (6.3 mg/L) in Jardim Lagoon. However, the maximum value (8.3 mg/L) was recorded in SQ03 station and the minimum value of 5.5 mg/L) was measured in Jardim Lagoon (in SQ10 station; Fig. 2). Dissolved oxygen displayed the lowest value in SQ10 (5.5 mg/L) station, localized in Jardim Lagoon, and the highest in Urussanga Lagoon, at SQ03 station (8.3 mg/L).

The pH values are presented in Appendix 1. The highest pH value (8.7) was recorded in stations SQ02 and SQ03 in Urussanga Lagoon and SQ09 in Jardim Lagoon and the lowest (7.8) in SQ20 station from Saquarema Lagoon, in the most populated region (Fig. 2).

4.2. Sediment Grain Size

The predominant sediment grain size fraction in SLS was silt, but in the stations located near the Barra Franca Channel dominated sandy fractions. The same result was found in SQ03 station located on the south bank of Urussanga Lagoon. In Urussanga Lagoon the substrate is composed of mud sediments, with clay fraction ranging from 16.1% to 44.95% in SQ09 and SQ07 stations, respectively, and silt fraction reaching from 42.8% to 80.2% in SQ08 and SQ04 stations, respectively.

4.3. Total Organic Carbon (TOC) and Total Sulfur (TS)

The average values of TOC in Saquarema Lagoon system (SLS) decreased from the inner most confined region to the outermost (Urussanga - 8.6%; Jardim - 9.53%, Boqueirão – 5.88%; and Saquarema - 2.88%). The minimum recorded value was 0.09% in SQ22 station located in the communication channel with the Atlantic Ocean and maximum 21.5% in SQ10 station located on Jardim Lagoon (Fig. 4).

Saquarema Lagoon had the lowest (1.78%) average sulfur content and Urussanga Lagoon the highest (3.74%). However, the highest value (4.95%) of this variable was recorded in SQ08 station located at the northern bank of Urussanga Lagoon, situated near the Mato Grosso River mouth and the lowest in SQ20 and SQ21 stations (0.02%) from Saquarema Lagoon (Fig. 4). The C/S ratio (TOC/TS) varied between 16.2 and 0.43 in SQ20 and SQ22 stations, respectively. However, the average value per lagoon was 2.94 in Urussanga, 3.47 in Jardim Lagoon, 2.23 in Boqueirão and Saquarema Lagoons. The average for the entire SLS was 4.98 (Fig. 4).

4.4 Biopolymers

The average of total biopolymers concentrations (BPC) among the lagoons varied between 19.56-28.78 $mgCg^{-1}$ (Urussanga Lagoon - 23.24 $mgCg^{-1}$, Jardim Lagoon - 27.78 $mgCg^{-1}$, Boqueirão Lagoon - 28.78 $mgCg^{-1}$ and Saquarema Lagoon – 19.56 $mgCg^{-1}$). The highest BPC content (32.96 $mgCg^{-1}$) was found in SQ02 station located at the south bank of Urussanga Lagoon and the lowest value was found in SQ22 (1.78 $mgCg^{-1}$) (Fig. 5).

The maximum PTN value was recorded in SQ10 station (4.64 $mgCg^{-1}$) and the minimum in SQ22 station (0.45 $mgCg^{-1}$). Among the lagoons, the highest average value (3.16 $mgCg^{-1}$) was recorded in Jardim Lagoon (3.16 $mgCg^{-1}$) and the lowest (2.13 $mgCg^{-1}$) in Saquarema Lagoon (Fig. 5).

The highest and the lowest average CHO content was recorded in Boqueirão (21.7 $mgCg^{-1}$) and Saquarema lagoons (14.4 $mgCg^{-1}$), respectively (Fig. 5). In Jardim Lagoon (19.16 $mgCg^{-1}$), an average value relatively high of CHO was also found.

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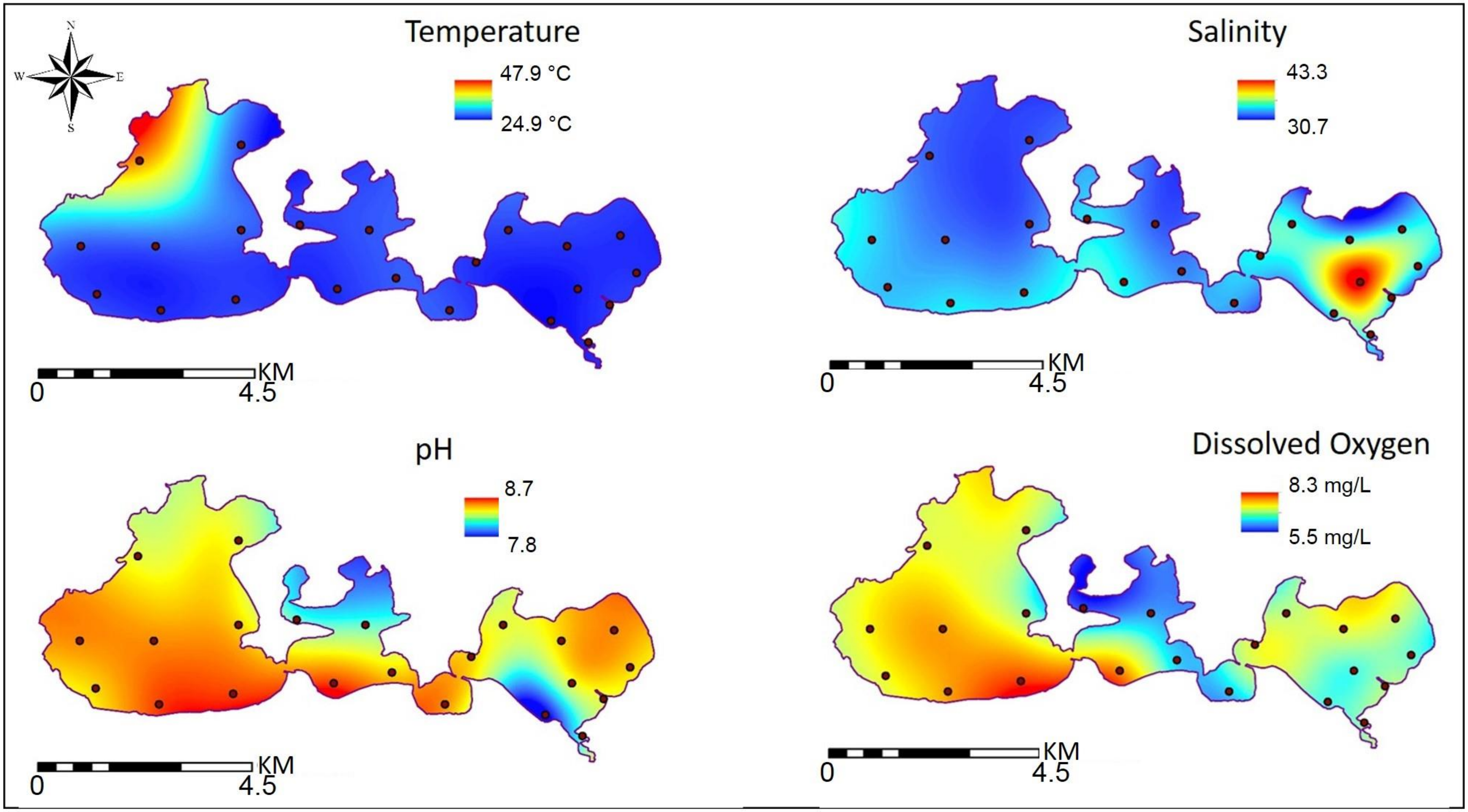

Fig. 2. Distribution map of physicochemical parameters from Saquarema Lagoonal System.

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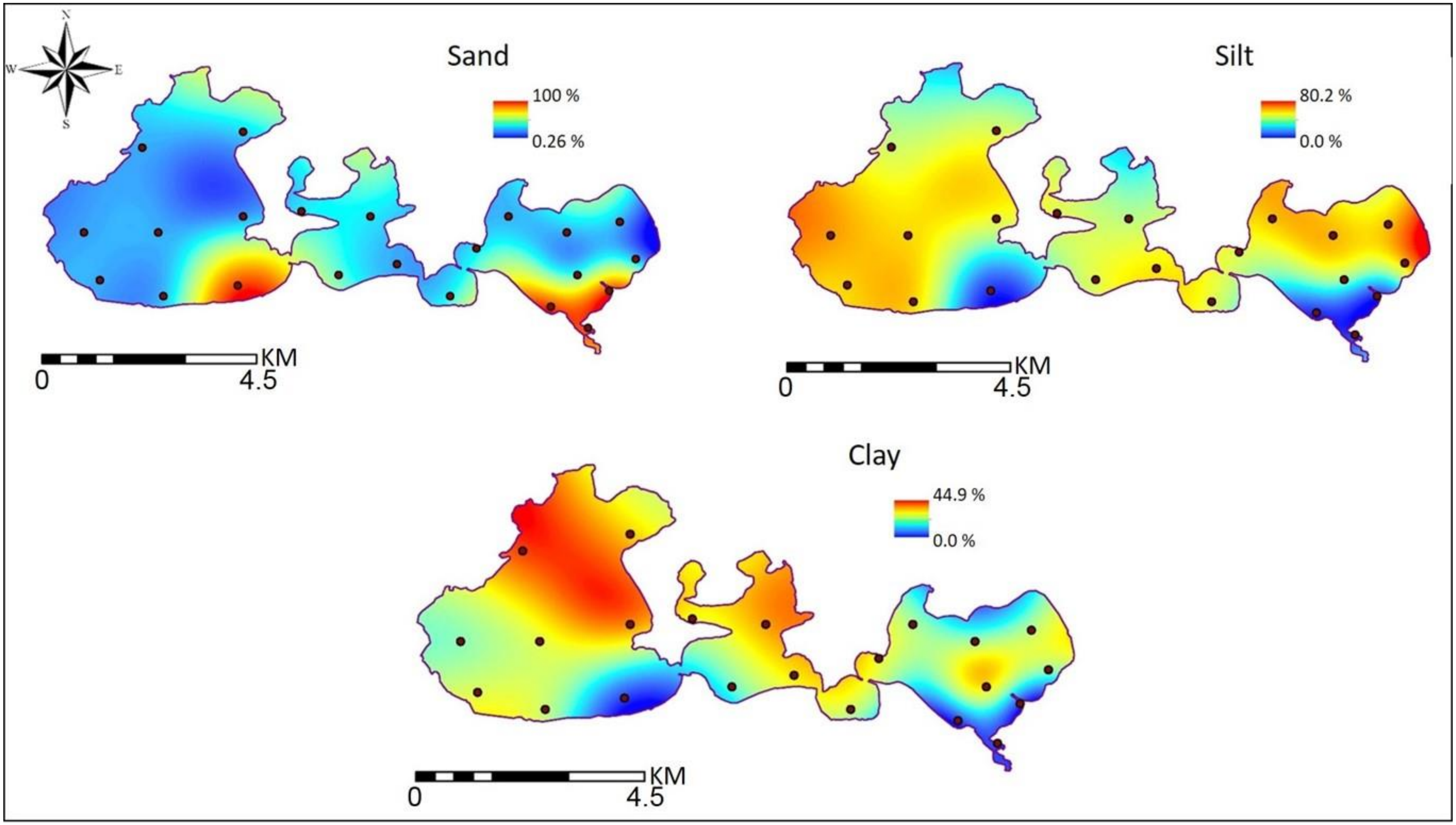

Fig. 3. Sedimentary grain size parameters distribution maps in studied stations in SLS.

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However, the lowest CHO content (1.09 $mgCg^{-1}$) was recorded in SQ22 station at the mouth of SLS and the highest value (25.9 $mgCg^{-1}$) in SQ02 in Urussanga Lagoon, the most confined region (Fig. 5). Lipids content ranged from 5.73 $mgCg^{-1}$ (in SQ11) to 0.24 $mgCg^{-1}$ in SQ22 (Appendix 1). The highest average LIP content was found in Jardim Lagoon (5.45 $mgCg^{-1}$) followed by Boqueirão Lagoon (4.48 $mgCg^{-1}$). The lowest average value (3.02 $mgCg^{-1}$) of LIP was found in Saquarema Lagoon (Fig. 5).

Values of PTN/CHO ratio varied from 0.53, recorded in SQ20 station located near the channel of communication with marine waters, and 0.07, found in SQ02 station located on the south bank of Urussanga Lagoon (Fig. 5). The average PTN/CHO ratio values were: 0.192 in Urussanga Lagoon; 0.167 in Jardim Lagoon; 0.100 in Boqueirão Lagoon and; 0.209 in Saquarema Lagoon.

4.5 Results of Statistical Analysis

The PCA results, with an accuracy of 91%, allowed to observe how the physical-chemical, biopolymers and granulometric parameters are distributed in the lagoon (Fig. 6). PCA shows the existence of four different groups in SLS (I, II, III and IV). The stations of group I (SQ03 and SQ20-SQ22), located near the Barra Franca Channel and on the southern margin of Urussanga Lagoon, were predominantly influenced by sandy fractions; the stations of group II (SQ01, SQ06-SQ08 and SQ10-SQ13) were mainly controlled by PTN, LIP and clay fractions; the stations of group III (SQ02, SQ04, SQ05, SQ09, SQ14-SQ17 and SQ19) were mostly related to BPC, CHO and pH; and the station of group IV (SQ18) was mainly associated with salinity.

5. Discussion

5.1 Environmental Characterization

The water physical-chemical parameters showed little variation throughout the lagoon system, but were quite different from those found by Lacerda and Gonçalves (2001).

The average value of salinity found on SLS was 33.3, which is close to the sea (35) (Li and Han, 2016). On the other hand, the lowest value was found in the lagoon body far from the Barra Franca Channel (SQ08) at the mouth of Jundiá River in Urussanga Lagoon. The highest value was found in SQ18 station, located in the middle of Saquarema Lagoon, under the influence of the Barra Franca Channel, wich suggests that the joint action of winds, tides and high evaporation rate contributes to the high concentration of salts in the center of the lagoon. The variation in salinity (30.7 to 43.3) as a whole characterizes SLS as euhaline coastal system, similarly to Venice Lagoon (Italy; Smayda, 1983).

The temperature has extreme value in SQ07 station which may be explained by the small depth of this station (<30 cm). In other stations this parameter ranged from 24.9 to 28.3°C. These values are similar to that found by Bruno (2013).

Dissolved oxygen is a very important factor for the maintenance of life in the aquatic environment, one of the main water quality indicators (Imhoff and Klaus, 1985).

Values of dissolved oxygen recorded in SLS were higher than that found in other Rio de Janeiro lagoons such as Maricá (Oliveira et al., 1955; Guerra et al., 2011; Silva et al., 2014), Araruama (Debenay et al., 2001) and Itaipu lagoons (Laut et al., 2016 a). The values obtained in SLS indicated a favorable environment to the establishment of aerobic organisms of several trophic levels, since they require oxygen for their functions.

The pH presented small variations in the entire SLS. In this system the sediment was basic, which does not agree with the pH values recorded by Lacerda and Goncalves (2001). The lowest values of pH were recorded in marginal areas of SLS, probably due to the highest accumulation of vegetation debris (Laut et al., 2011).

5.2 Sediment grain size in SLS and bottom hydrodynamics

The dominance of silt fractions indicates reduced bottom water hydrodynamic conditions (Teodoro et al., 2010). Low currents activity prevails in practically all lagoons of SLS, except in Saquarema Lagoon where the hydrodynamics seems to be more intense. Urussanga Lagoon is the most confined region of SLS, displaying the lowest hydrodynamics. On the northern bank of Jardim Lagoon, the presence of a peat bog area was observed during the sampling event, in low tide period.

According to Fernex et al. (1992), sandy sediments are more common in shallow areas with depth less than 0.5 m. In SLS it was possible to identify an increase of this sediment fraction in much of the southern SLS margin at depths greater than 1 m. These sandy sediments may be supplied by the wind, by removal, transportation and deposition from the dunes fields.

5.3 Organic enrichment in surface sediments of SLS

The organic enrichment in the study area was analyzed considering TOC, TS and biopolymers contents. The TOC values were considered moderate (<1%) only in some stations (SQ03 and SQ20-SQ22).

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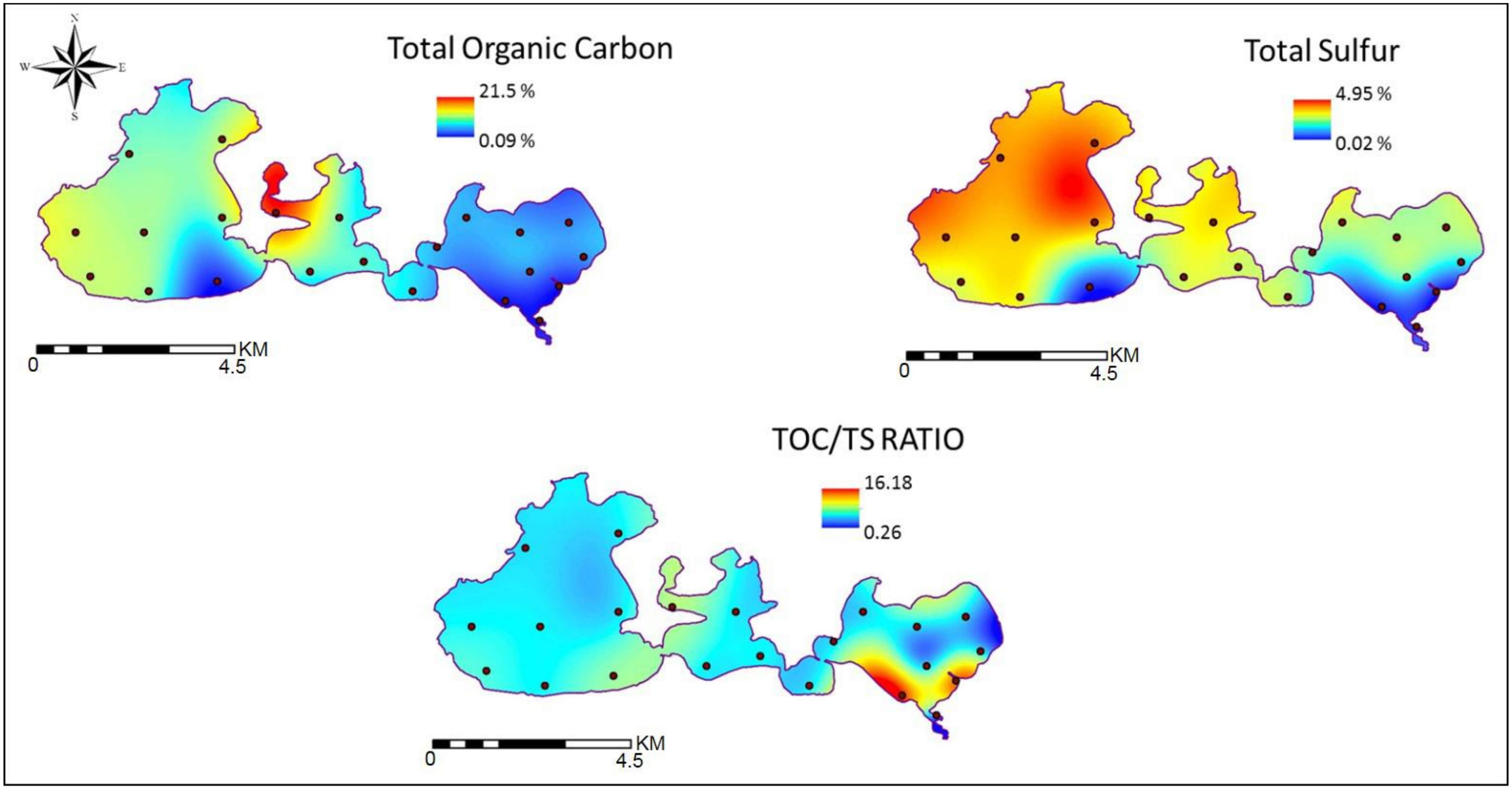

Fig.4. Distribution maps of values of total organic carbon (TOC) and total sulfur (TS) and TOC/TS rate in studied stations in SLS.

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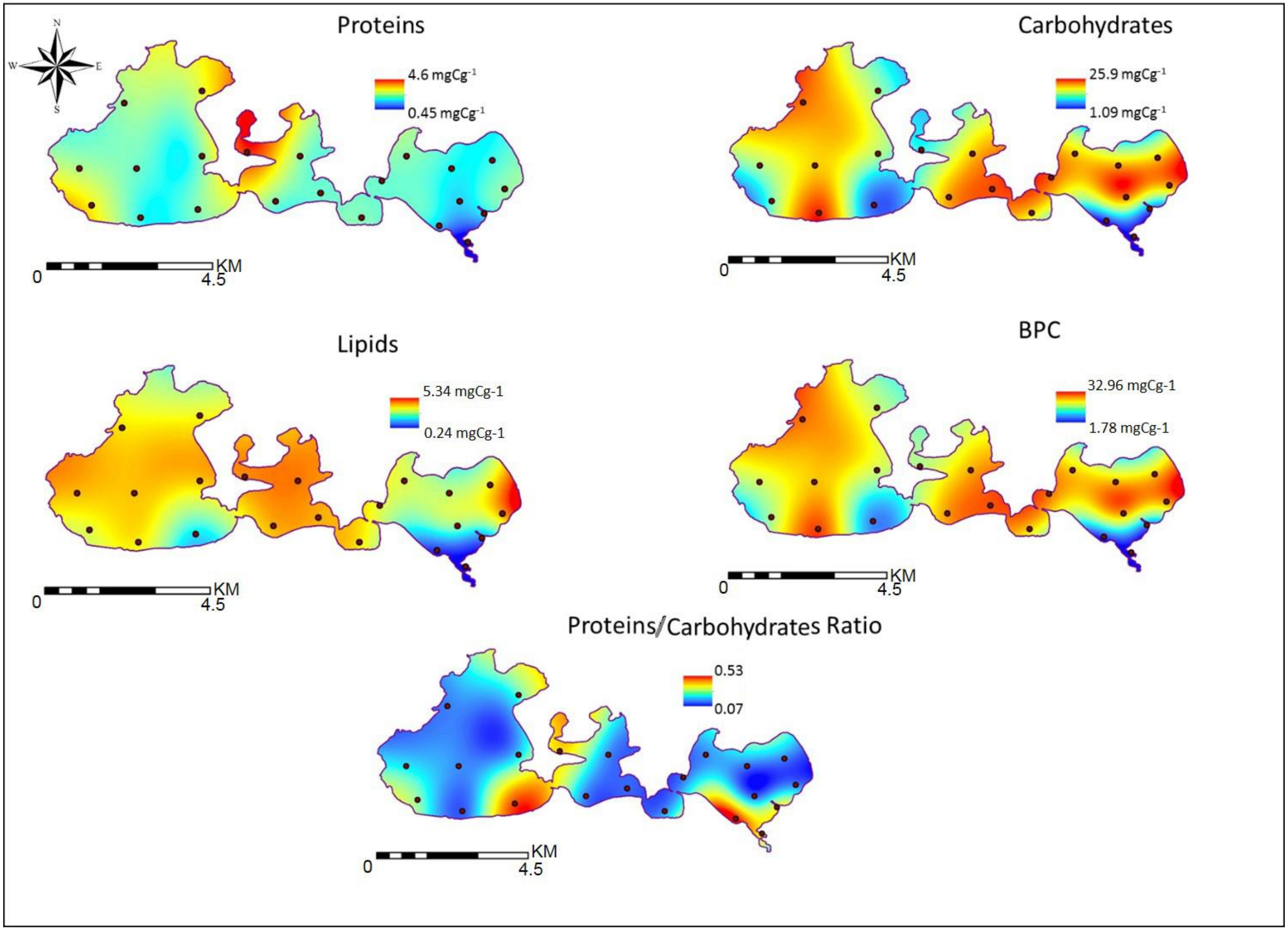

Fig. 5. Total of Biopolymers (BPC), protein, carbohydrates, lipid and the ratio PTN/CHO distribution maps in the studied stations in SLS.

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At the majority of stations, high values (>4%) of TOC were found. Saquarema Lagoon presented the lower average TOC values (2.88%) than the other lagoons. This can be explained by relatively strong hydrodynamic conditions, which prevents the accumulation of organic matter. The highest average TOC content was found in Jardim Lagoon (9.53%), which can be explained by the presence of a peat bog in SQ10 station, with 21.5% of TOC.

Comparatively, TOC contents recorded in SLS were higher or similar to that observed in recognized impacted regions around the world. Aston and Hewitt (1977) found concentrations of TOC ranging from 0.07% to 1.97% in Walton Backwater (Essex, England). The region studied by Aston and Hewitt (1977) was impacted by organic matter due to the presence of commercial ports, drainage from agricultural fields and domestic sewage disposal.

In the Gulf of Izmir (Easter Aegean Sea), at an intensely industrialized area, Bergin et al. (2006) recorded TOC contents ranging from 0.40% to 3.12%.

Laut et al (2016a) registered the average TOC content of 3.25% in Itaipu Lagoon (Niteroi city), near Guanabara Bay, Rio de Janeiro state.

According to Mendonça Filho et al (2003), TOC contents >2.5% may be associated with dysoxic-anoxic environments and with a high rate of organic matter accumulation. High supply of organic matter and its break down can lead to a depletion of dissolved oxygen that ultimately might affect the proliferation and viability of marine organisms (Borja et al., 2012).

In SLS the surface sediment is oxygenated as suggested by our data but became low oxide or anoxic below the first centimeter beneath the sediment-water interface as indicated by the dark gray or black colors. As observed by Martins et al. (2015), in Bizerte Lagoon, a Mediterranean shallow coastal transitional system, in Tunisia, it is possible to find a low oxic water column and oxygenated surface bottom sediments and anoxic conditions some millimeters below the interface water-sediment. The development of benthic microalgae on the top of the sediment can provide the oxygen necessary for the surface sediment environment.

In SLS, TS values were variable and presented the lowest values concentrated in Saquarema Lagoon (0.02 - 2.98%). In coastal areas with low human impact as in the estuaries of the Guadiana and Arade rivers in the south of the Iberian Peninsula, the values ranged from 0.01% to 0.3% (Silva et al., 2013; Laut et al., 2016 b, c). In the Paraíba do Sul river delta, whose basin receives effluents from the most industrialized region of Brazil, the values ranged from 0.02% to 0.96% (Silva et al., 2011a).

The values found in SLS are comparable to regions with high human impact as in the port area of Rio de Janeiro where values from 1% and 55% of TOC content were registered (Fernandez et al., 2005), indicating the presence of waste water enriched in organic matter.

Siqueira et al. (2006) observed the TS mean value of 6.03% in Santos estuary (São Paulo State, Brazil). Using the same TS methodology of the present study, Clemente et al. (2015) recorded the mean value of 1.4% in Guanabara Bay; Laut et al (2016 a) recorded values varying from 0.03% (IT02) to 1.73% (IT10) in Itaipu Lagoon (both in Rio de Janeiro State); and Martins et al. (2016) found values of 0.04% in Bizerte Lagoon (Tunisia).

Thus, it is possible to assume that in SLS the sulfur content is lower than in Guanabara Bay and Santos Estuary, locations highly polluted by industrial and domestic sewage. The sulfur content is associated with import of organic matter, so SLS is not as impacted as Santos Estuary and Guanabara Bay.

The C/S ratio values >3 indicate oxidizing environments (Stein, 1991; Borrego et al., 1998). Accordingly, the surface sediments of Urussanga and Boqueirão lagoons, even with high sulfur values indicating, are not characterized by reduced surface sediments. However, Jardim Lagoon and Saquarema Lagoon seem to have the most reduced surface sediments in SLS with average C/S ratio values of 3.47 % and 4.98 %, respectively.

5.4 Organic matter quality in surface sediments of SLS

The biopolymer contents in marine and estuarine environments are used for the characterization and interpretation of the origin of accumulated organic matter in sediment (Silva et al., 2011 a, b).

Excessive amount of PTN and LIP may be associated with anthropogenic organic matter, while CHO are more related to phytoplankton origin and vegetal detritus (Cotano and Villate, 2006). Still on the functional role of proteins, Dell'Anno et al. (2002) relate their high concentrations to primary productivity.

The lowest values of LIP, CHO and PTN were found in SQ22 station, located in the channel of communication with the Atlantic Ocean and can be explained by increased hydrodynamic in this region.

The highest CHO value was found in SQ02 station (25.9 mg C g^{-1}), near the southern margin of Urussanga Lagoon which has domestic effluent discharge ducts and is an environment similar to that described by Cotano and Villate (2006).

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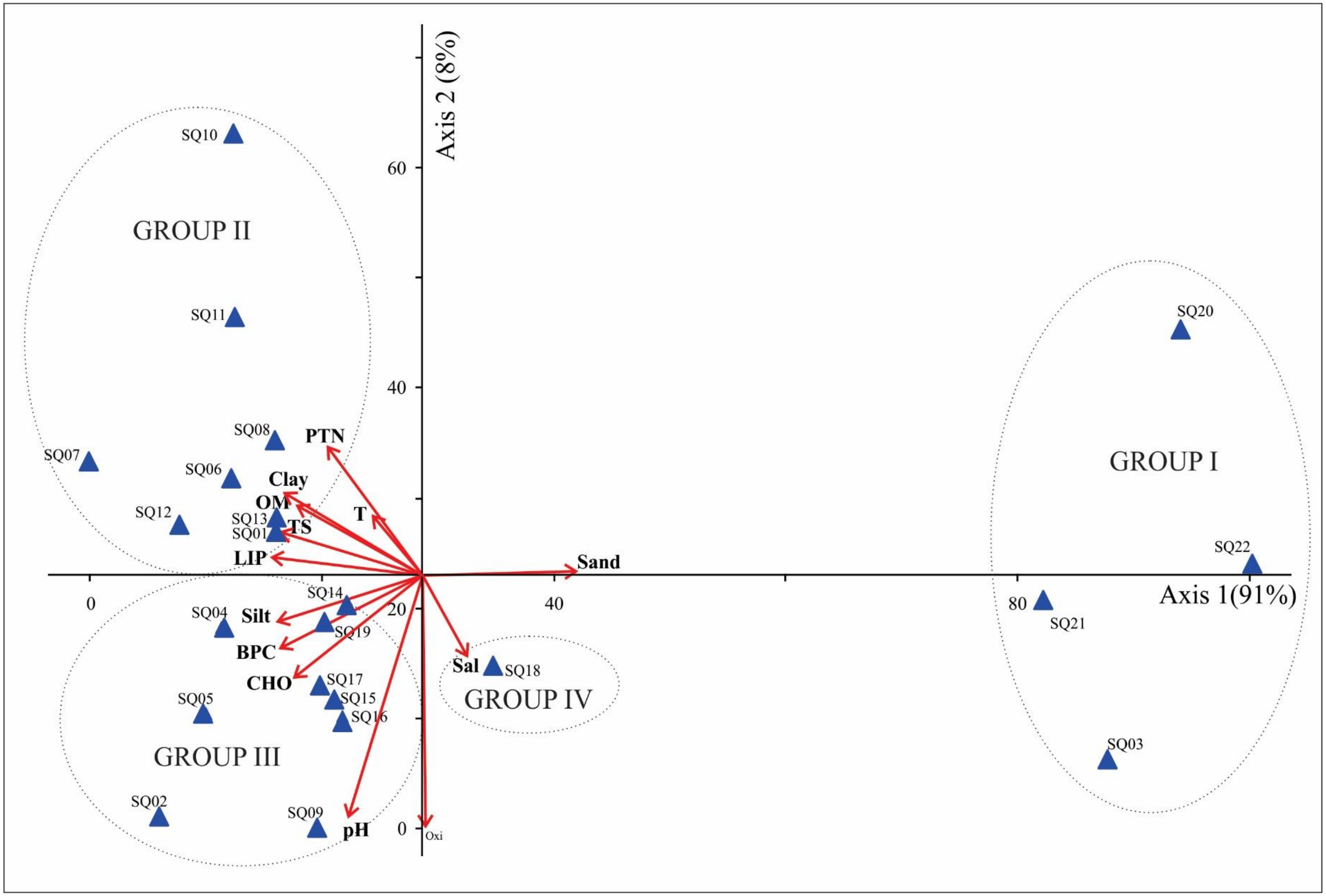

Fig. 6. Principal Components Analysis of Saquarema Lagoonal System (BPC = Biopolymers Concentration; CHO = Carbohydrates; LIP = Lipids; PTN = Proteins; TS= Total Sulfur; OM = Organic Matter; T = Temperature).

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In SLS, BPC values ranged from 1.78 $mgCg^{-1}$ to 32.96 $mgCg^{-1}$ and had the average 23.23 $mgCg^{-1}$. When compared to other polluted locations, such as Itaipu Lagoon (0.88 $mgCg^{-1}$ to 6.71 $mgCg^{-1}$; Laut et al, 2016a), Marsala Lagoon (9.3 $mgCg^{-1}$ to 11.9 $mgCg^{-1}$; Pusceddu et al., 1997), and Aegean Sea (3.48 $mgCg^{-1}$ to 3.74 $mgCg^{-1}$ in the southern and 4.06 to 5.17 $mgCg^{-1}$ in the northern regions; Danovaro et al., 1999), Saquarema system seems to be the most impacted coastal system by this parameter. The average value of BCP found in SLS indicates that the region is highly impacted.

The PTN/CHO ratio has been used to indicate the age of the organic matter present in the sediment (Danovaro et al., 1993). Danovaro et al. (1993) suggested that PTN/CHO >1 should be linked to the presence of fresh organic matter, since protein degradation is faster than the other biopolymers. In SLS all the values found were <1, which might evidence a predominance of aged organic matter in the sediments.

5.5 Environmental characterization of surface sediments of SLS

Based on the PCA results, four groups of stations characterized by different trophic levels found on surface sediment were identified in SLS. Group I includes stations (with coarse grained sediments) located at and close to the Barra Franca Channel (SQ20, SQ21 and SQ22) and in the southern margin of Urussanga Lagoon (SQ03) characterized by active hydrodynamism and highest marine influence.

Group II is influenced by relatively high temperature, sulfur, proteins, lipids and clay fraction contents. This group represents the transitional region in SLS where the hydrodynamic is lower than in the Barra Franca Channel, but still allows a good renovation of the water body.

Group III is related to silt fraction, CHO and BPC concentrations. Stations of this group can be considered the most confined; they are located in protected areas, under the prevalence of calm hydrodynamic conditions where fine grained sediments can be accumulated.

Group IV is composed only of the station SQ18 located in the center of Saquarema Lagoon, in front of the Barra Franca Channel (the lagoon mouth), which is mainly ruled by salinity and relatively strong hydrodynamic conditions. This region receives laterally the influence of tides, the movement of entrance and output of water. The sediment tends to deposit in this central zone contributing to depth reduction.

The outermost stations (of Group I and IV) of SLS are the less impacted by organic matter and BPC, and the inner most and confined stations are the strongly impacted zones.

6. Conclusion

Results of this study revealed significant spatial changes in the quantity and quality of the sedimentary OM in Saquarema Lagoonal System. The TOC content indicates that the surface sediment is oxygenated but became low oxide or anoxic some millimeters below the sediment-water interface as indicated by the dark gray or black colors. The most reduced sediments in SLS were found in Jardim Lagoon and Saquarema Lagoon.

The average values of BPC in SLS indicate that the region is highly impacted, being the inner sector the highest impacted zone. This inner sector has small tidal influence and consequently displays a minimum water renovation. It was characterized by sediments with high OM content. The highest concentrations of lipids in the inner sector of the SLS also indicate the excessive presence of recalcitrant compounds that may be not used by the trophic chain.

The lowest values of PTN/CHO in SLS related to a predominance of aged organic matter in the sediments and high residence time of water. The intermediate lagoonal area is a middle-impacted region and shows transitional features between the two previously described zones.

The applied methodology in this work allowed to characterize the trophic state of SLS, which might be defined as an environment where 'natural' variation in biochemical composition of the sedimentary OM is caused mostly by significant autochthonous inputs. The high supply of organic matter to the bottom generates problems of eutrophication in most part of the benthic environment of the Lagoonal System; however, the surface sediment remains oxic in most part of SLS. Saquarema Lagoonal System should be considered an ecosystem highly susceptible to environmental pollution by organic matter contents.

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Appendix 1 is attached as supplementary material (SM1) in http://www.e-publicacoes.uerj.br/index.php/jse/article/view/28194

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