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ORGANIC POLLUTION IN THE NE SECTOR OF GUANABARA BAY (SE, BRAZIL)

Maria Virgínia Alves Martins[1, 2]*, René Rodrigues[1], Egberto Pereira[1], Paulo Miranda[2], Lazaro Laut[3], Pierre Belart[3], Hélio Heringer Villena[4], Mauro César Geraldes[1], Silvia Helena de Mello e Sousa[5], Wânia Duleba[6] and Sérgio Bergamashi[1]

1 Universidade do Estado do Rio de Janeiro, UERJ, Faculdade de Geologia, Departamento de Estratigrafia e Paleontologia, Rio de Janeiro, Brazil

2 Universidade de Aveiro, GeoBioTec, Departamento de Geociências, Portugal

3 Universidade Federal do Estado do Rio de Janeiro, UNIRIO, Laboratório de Micropaleontologia, Rio de Janeiro, Brazil

4 Universidade do Estado do Rio de Janeiro, UERJ, Faculdade de Oceanografia, Rio de Janeiro, Brazil

5 Universidade de São Paulo, USP, Instituto Oceanográfico, São Paulo, Brazil

6 Universidade de São Paulo, Escola de Artes Ciências e Humanidades, São Paulo, Brazil

* Corresponding author, virginia.martins@ua.pt

Abstract

This study characterizes the quantity and quality of organic matter present in surface sediments of the NE sector of Guanabara Bay (SE, Brazil), based on geochemical and statistical analysis. The geochemical analyses included stable isotopes in sedimentary bulk organic matter ($_{org}\delta^{13}C$), total organic carbon (TOC), total sulfur (TS) and Rock Eval pyrolysis parameters, such as free hydrocarbons (S1), generating source potential (S2), production index (PI), oxygen and hydrogen indices (OI, HI) and the maturation index of organic matter (Tmax). The analyzed data were statistically treated to find main factors that are influencing the sedimentary composition. The low activity of the bottom currents favors the deposition of fine-grained sediments, rich in organic matter, in most of the studied area. The organic matter present in the sediments is being supplied by local and allochthonous sources and can be considered a good source of type III kerogen, and therefore has the potential to generate gas, if the geological context is adequate. Considering the quantity, type of organic matter and potential of hydrocarbon generation four main groups of stations were identified. Stations in which the sediments: i) encompass a relatively high component of OM sourced mainly from the adjacent continental areas close to the Apa de Guapimirim (less contaminated by oil) and S. Gonçalo (Roncador River) regions; ii) contain some autochthonous contribution, located between the Paquetá and Governador Islands, where biogenic gas seeping should be predicted hereafter; iii) have higher contamination by oil, situated near Mauá and REDUC Oil Refinery, of Duque de Caxias; iv) present intermediate characteristics, located in the remaining study area.

Keywords: Rock-Eval pyrolysis. Stable isotopes. Oil generation potential. Depositional environment. Pollution. Coastal area.

1. Introduction

Many coastal environments are being heavily influenced by anthropogenic action that causes pollution and habitat loss around the world. Marine pollution comes mostly from land sources (World Summit on Sustainable Development, 2002). Domestic sewage and industrial effluents are released in the water courses in untreated or partially treated form. In

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many developing countries 90% of waste water and 70% of industrial wastes including, among others, certain toxic heavy metals, metalloids and organic pollutants, are discharged without treatment, representing a hazard for the coastal areas and the oceans (GESAMP, 2001; UNEP, 2005). At India, for instance, 25% of 5 million tons of fertilizers, 55,000 tons of pesticides and 125,000 tons of synthetic detergents are yearly ending up in the ocean (Sen Gupta et al., 1989; Qasim and Sen Gupta, 1983). These substances are more or less biodegradable while others are persistent. Their cumulative impact in the coastal marine environment, over a long period could be quite harmful (Sen Gupta et al., 1989).

In addition, coastal areas receive important detritus supply from allochthonous vegetation and autochthonous biological production (Rossi et al., 2010). The excessive input of nutrients in coastal areas from activities in the upstream hydrographical basins, atmospheric deposition and local effluents may cause eutrophication in coastal marine ecosystems with consequent algal blooms, increased growth of macroalgae, oxygen consumption and oxygen depletion in bottom water and sediments leading frequently to the mortality of benthic organisms and fish (Jørgensen and Richardson, 1996; Andersen and Conley, 2010).

Organic matter is a ubiquitous constituent in almost all modern sediments and sedimentary rocks. It can be found concentrated, for example in the form of coal, oil, hydrocarbons, or disseminated in the sediments, forming a minor constituent (Suárez-Ruiz, 2012). High organic matter sedimentation in estuaries and other coastal areas give place to methanogenesis and high methane (CH_4) concentrations in surface waters (Bange et al., 1994; Rehder et al., 1998; Upstill-Goddard et al., 2000). The oceanic areas with large bioproductivity, like near-coastal areas and estuaries, account for ≈75 % of the oceanic CH_4 emissions (Bange et al., 1998; Blumenberg et al., 2016). The current increase in the level of methane from both natural and anthropogenic sources, which is the second most important greenhouse gas after CO_2, accounting for 32% of the anthropogenic global radiative forcing (Stocker et al., 2013) is a cause for concern.

Oil is an important resource of the modern economy, as a font of energy and as a raw material in many applications. But it is also a source of pollution to marine environment, since it is a mixture of hydrocarbons and up to 25% of non-hydrocarbons such as sulphur, vanadium, and metals (Gorman, 1993; Garbuny Vogel, 2003). Environmental impacts occur at all stages of oil and gas production and use (Frankel, 1995; Clark, 2001). During the last decades, the concern for environmental risk of organic chemical

pollution is rising and lead to the regulation by national and international organisms (Gardes, 2003; Dachs and Méjanelle, 2010).

Pollution problems caused by organic matter affect coastal regions around the world. In Brazil, Guanabara Bay (GB) is one of the most polluted environments by anthropic activity. Several forms of anthropogenic impact threaten its environment since the beginning of the European colonization on 1500 (Soares-Gomes et al., 2016). However, the pollution problems largely began with oil refineries on the 1950s. Oil activity is the driving force of many alterations, involving hundreds of companies, especially related to the implementation of several projects for Petróleo Brasileiro S.A. (Petrobras), including the expansion of management and research structures in the Rio de Janeiro city, the gas terminal deployment in GB, increasing refining capacity in Duque de Caxias Refinery (REDUC), the implementation of the Petrochemical Complex of Rio de Janeiro in Itaboraí-São Gonçalo (COMPERJ) and ship building industry (Soares-Gomes et al., 2016). It is noted that on January 18, 2000, Brazil has experienced an oil spill incident. A pipeline spilled into a swamp adjacent to the waters of Guanabara Bay, 1.3 million liters of fuel oil.

Nowadays, the edge and surroundings of GB are heavily urbanized and the bay receives inputs of both industrial and domestic sewage, as well as residuals of agricultural crops from its green belt (Kjerfve et al., 1997; Xavier de Brito et al., 2002; Fistarol et al., 2015). On the other hand, sewage and water treatment is still very limited. Both industrial and urban contaminants are discharged into the bay or in the sea (Fistarol et al., 2015). For example, high concentration of metals (Fe, Mn, Zn, Cu, Pb, Cr and Ni) and high levels of organic matter in the near-shore sediments of GB were observed by Pereira et al. (2007), and a mercury contamination problem was detected by Barrocas and Wasserman (2005). Additionally, the presence of biogenic gas also was observed in areas of organic-rich mud deposits located at the inner region of the bay (Catanzaro et al., 2004; Delavy et al., 2016).

1.1 The main goals

The main objective of this study was to obtain basic information about the amount and type of organic matter in the NE Sector of Guanabara Bay (SE, Brazil). To achieve this goal an integrated assessment including indicators of organic matter content and quality using Rock–Eval pyrolysis parameters and $\delta^{13}C$ data was applied. The results presented in this research can help in decision-making on dredging, remediation or engineering works, providing

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information that may eventually reduce operational risks and environmental impacts.

2 Study Area

Guanabara Bay (GB) is located in Rio de Janeiro State, southeast of Brazil, between 22°40' S and 23°00' S of latitude and 43°00'–43°18' W longitude, and its area is 384 km² (Kjerfve et al., 1997; Figueiredo et al., 2014; Fistarol et al., 2015). A main channel from the entrance to the middle part of the bay connect GB with the Atlantic Ocean. Apart from the channel region, whose width is about 1.6 km, the bay has a semi-circular format, measuring 30 km and 28 km, in the N–S and E–W axes, respectively. About 84% of the bay water is shallower than 10 m deep but in the region of the central channel, the water depth can reach more than 40 m (Figueiredo et al., 2014).

The tidal regime is an important component of Guanabara Bay water circulation (Paranhos et al., 1998). Tides are mainly semidiurnal in the bay. The currents are more intense at the entrance of the bay and between the mainland and the Governador Island because of a narrowing of the channel in these areas.

The replacement of 50% of water in the GB, takes 11.4 days (Kjerfve et al., 1997). This relatively short residence time is one of the main factors explaining why water quality is not worse, considering the amount of untreated sewage discharged into the bay. However, the renewal is not the same in all parts of the bay: the innermost regions, which are the ones receiving most urban sewage, have lower circulation and a longer residence time, causing accumulation of organic matter and other contaminants, making these the most polluted areas of the bay (Fistarol et al., 2015).

The drainage basin of Guanabara Bay has an area of 4,080 km², composed of 32 distinct fluvial sub-basins. Six rivers accounts for 85% of fluvial input into Guanabara Bay, which vary from 100 to 230 $m^3 s^{-1}$ per year, depending on weather conditions (Carreira et al., 2002). The freshwater discharge ranges from 33 $m^3 s^{-1}$, in the dry austral winter, to 186 $m^3 s^{-1}$ in the rainy austral summer (Kjerfve et al., 1997).

Even with the huge load of pollutants and their impact, the bay supports important regional fisheries (Jablonski et al., 2006) and still retains 40% of original mangrove forestry (Pires, 2010), half of which is relatively well preserved in environmental protection areas (e.g., Guapimirim Environmental Protected Area). Part of this area was transformed nowadays into the Guanabara Ecological Station (Cavalcanti et al., 2009).

Although Guanabara Bay is considered one of the most degraded coastal environments in Brazil (e.g., Kjerfve et al.,

1997; Baptista Neto et al., 2000; Machado et al., 2004; Aguiar et al., 2011) it has a rich biodiversity in its waters, containing species of fish, cetaceans, mollusks, as well as species of benthic organisms such as diatoms and foraminifera (Clemente et al., 2015; Soares-Gomes et al., 2016; Martins et al., 2016).

3. Material and methods

This work is based on the analysis of sediment collected, with a box-corer, in 2016/2017 at the NE sector of Guanabara Bay (SE, Brazil) on board a small boat, in 44 sites (Fig. 1; Appendix 1). Each sampled station was georeferenced with a GPS (model GPSMAP® 78S). During the sampling events physicochemical parameters also were measured, with multiparametric probes: water temperature and salinity and sedimentary pH and potential redox (Eh).

Delavy et al. (2016) signed the occurrence of high concentration of shallow gas in subsurface sediments of NE sector of Guanabara Bay (GB), by applying geophysical methodologies. Hunt (1996) defined a hydrocarbon source rock as "any rock that has the ability to generate and expel sufficient amounts of hydrocarbons to form an accumulation of oil or gas". To determine the potential of hydrocarbon production of sedimentary sequences, at least three factors must be considered: quantity, quality and degree of organic matter maturation (Tissot and Welte, 1984). The amount of organic matter present in sediments or sedimentary rocks can be determined geochemically and is usually presented as Total Organic Carbon (TOC) values. The values of TOC vary considerably with lithology. The highest TOC contents are found in black shales and the lowest in sandstones (Ferriday and Montenari, 2016). The TOC values, usually accepted as minimum for a silty - clayey rock to be considered as a hydrocarbon source rock ranges from 1% to 1.5% TOC (Peters and Cassa, 1994).

Considering that this work intends to identify the presence of organic pollution in the sediments of the NE sector of GB: textural, TOC (related to the amount of organic matter), total sulfur (TS), insoluble residue (IR), $\delta^{13}C$ values of organic matter ($_{org}\delta^{13}C$) and the Rock–Eval pyrolysis parameters were acquired. All the geochemical analyses were performed in the Laboratory of Chemostratigraphy and Organic Geochemistry of Universidade do Estado do Rio de Janeiro (LGQM-UERJ).

The methodology applied in textural and geochemical analyses was the same described by Delavy et al. (2016). Total organic carbon (TOC), total sulphur (TS), and insoluble residue (IR) analyses were performed with a LECO SC-632 equipment, after the elimination of carbonates with

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50% hydrochloric acid. The semiquantitative evaluation of the organic matter content in the analyzed sediments, was performed using Peters and Cassa (1994) criteria (Table 1).

The $\delta^{13}C$ values determined in sedimentary bulk organic matter ($_{org}\delta^{13}C$) are the sum of different carbon containing organic molecules (Hayes, 2001) and may trace changes in the source and overall composition of organic matter (Taipale et al., 2015). The analysis was performed using an elemental analyzer coupled to a Delta V Mass Spectrometer. The standard deviation of $\delta^{13}C$ data was ±0.15‰.

The insoluble organic matter present in sediments and rocks can be divided into two parts: kerogen and bitumen. According to Philp (2003), kerogen is the fraction of the sedimentary organic matter that is insoluble with the common organic solvents, while bitumen corresponds to the soluble one. Kerogen is not an organic substance with a well-defined chemical composition because it includes organic matter derived from continental areas and marine environments, which present different initial chemical compositions. The definition of kerogen also does not consider the state of biodegradation of organic matter nor its degree of maturation (Peters et al., 2005). Kerogen includes all the organic matter present in the rocks, modern sediments and soils whereas bitumen products are organic compounds derived from kerogen transformations related to changes in temperature and pressure that occur in the sedimentary basins by the processes of subsidence (Rahimi and Gentzis, 2007). Bitumen includes liquid hydrocarbons, such as oil, and other solid hydrocarbons (Rahimi and Gentzis, 2007).

Chemical and physical transformations of the remains of dead plants and animals, due to changes in temperature and pressure during the evolution of the sedimentary basins can give rise to fossil fuels (Peters et al., 2005). However, the formation of these fossil fuels is mainly dependent on the composition, quality and quantity of the initial or precursor organic matter present in the sediments (Tissot and Welte, 1984). These characteristics of precursor organic matter are closely related to the type of sedimentary environments where it accumulates.

The analysis by Rock Eval pyrolysis allows to evaluate the quality of organic matter, namely the kerogen and bitumen. In this work this analysis was performed with a Rock-Eval 6, Vinci Technologies. According to Espitalié et al. (1977), this technique simulates the thermal alteration process of sedimentary organic matter in the absence of oxygen. A flame ionization detector captures all hydrocarbons generated during pyrolysis, which are represented by two peaks, S1 and S2 (in mg of hydrocarbons/g of sediment or mg HC/g sediment), during the pyrolysis cycle below 350 °C

and between 300 °C and 550 °C, respectively, and an infrared detector indicates the S3 peak (mg of CO_2/g sediment). The temperature at which occurs the maximum peak height of S2 (Tmax; °C) also was recorded.

The type of organic matter present can be identified using Hydrogen Index [HI = (S2/TOC) x100, in mg HC/g TOC] and the oxygen index [OI = (S3/TOC) x100, in mg CO_2/g TOC], according to the procedures of Espitalié et al. (1977). These two indices roughly correspond, to the H/C and O/C ratios of the organic matter (Espitalié et al., 1977), and can be plotted in van Krevelen type diagrams (Krevelen, 1950), from which the organic matter is classified as being of type I, II, III or IV (Tissot and Welte, 1984). The hydrogen/carbon (H/C) and oxygen/carbon (O/C) ratios of organic matter in recent sediments are related to their geochemical composition and may indicate their hydrocarbon generation potential. However, the hydrocarbon production depends on organic matter maturation processes. Considering the variations in these ratios during the maturation process, it is possible to distinguish four different types of organic matter (OM): type I, II, III and IV. In view of this classification, the most important factor controlling the different hydrocarbons (oil, oil/gas condensate or gas), is the initial hydrogen content of the organic precursor. Type I OM is rich in hydrogen which is present in a substance rich in lipids, its origin being essentially seaweed material, from marine or lakes biological production. This type of OM has a high potential for oil generation, but is rare in the geological record. Type II has an intermediate composition and is derived from algae material (phytoplankton and zooplankton) as well as of continental origin rich in lipids, such as spores and pollens. This type of OM is present in the vast majority of the oil source rocks. Type III OM has mainly organic compounds derived from higher plants, and has potential to generate gas. The type IV OM has very low potential for generating hydrocarbons. This type of OM is essentially composed of remobilized or highly oxidized organic matter derived from marine or continental environments.

The types of organic matter (land derived and/or aquatic algae derived) found in a sediment or sedimentary rock are mostly influenced by the depositional environment. Heat and pressure convert organic matter into a substance called humin and then into kerogen. Time and temperature convert kerogen into oil. The assessment to the semi quantitative evaluations of the generation potential, type and stage of thermal evolution of organic matter was carried out using S2, HI and Tmax values, considering the scale (Table 1) established by Espitalié et al. (1985). The production index (PI) values also were determined through the formula:

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S1/S1+S2. PI was used to characterize the organic matter evolution degree, according to the range of values considered by Espitalié et al. (1985), presented in Table 1.

Variables were logarithmically transformed [log (x+1)] before to be submitted to statistical analysis. Variables with significant correlations with the two first factors of Principal Component Analysis (PCA) were submitted to this statistical method of data reduction. The PCA is based on the correlation matrix of the involved variables and was applied in order to identify the main influences that are broadly inducing the variables distribution in the study area. This analysis was conducted in Statistica 12 (Statsoft software). Some selected variables were compared by bi-plots and linear regression (in Microsoft Excel software). Maps were performed with ArcGis 9.2®, using metric coordinates according to the Córrego Alegre UTM Zone 23S.
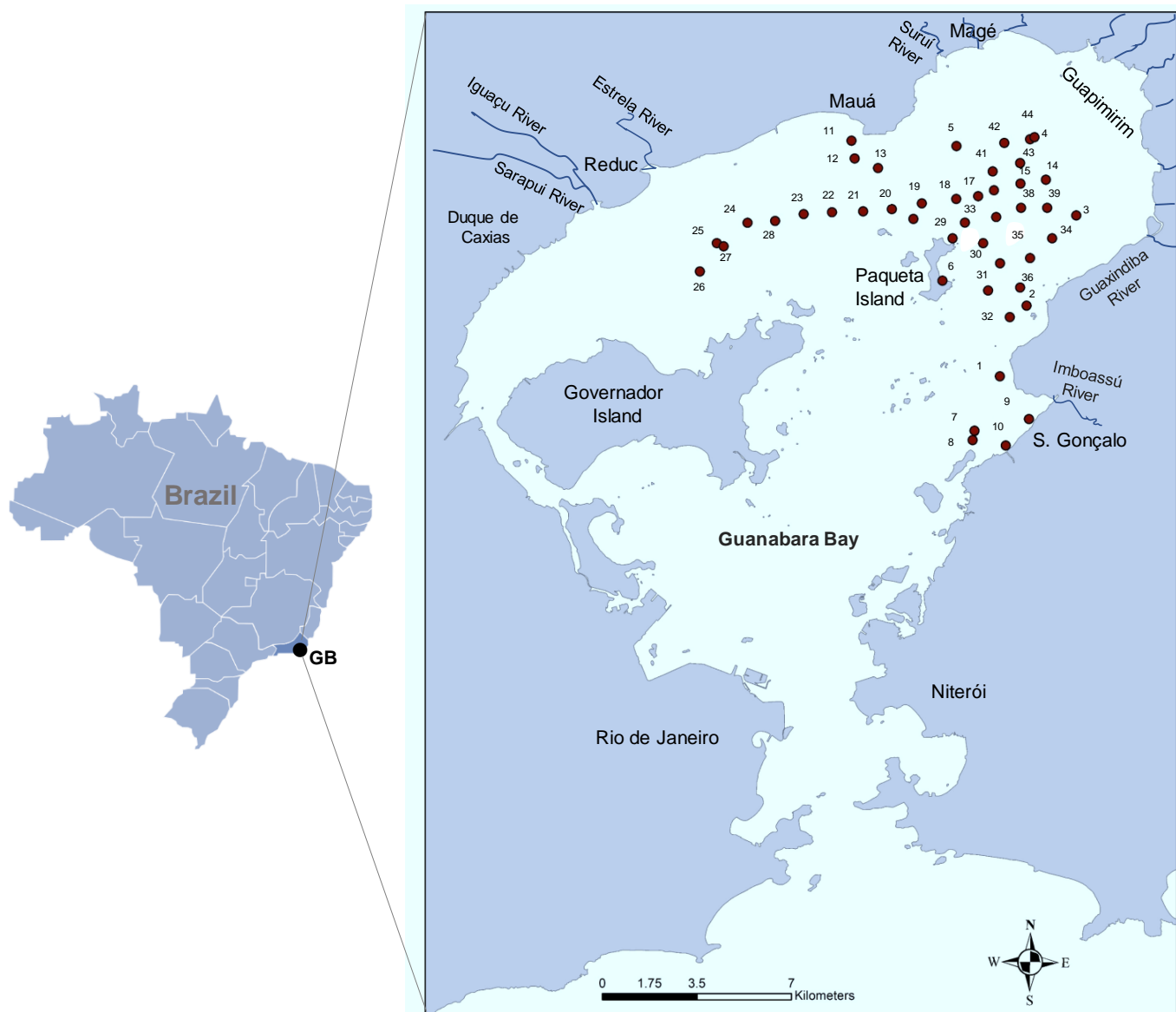

Fig. 1. Study area and samples location in the NE sector of Guanabara Bay (GB). Some of the rivers that flow into the study area are signed.

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Tab. 1. Scales for the semiquantitative evaluation of the organic matter content (according to Peters and Cassa, 1994), generation potential and thermal maturation of the organic matter (according to Espitalié et al., 1985).

Total Organic Carbon TOC (%)	
<0.5	Poor
0.5 – 1.0	Moderate
1.0 – 2.0	Good
2.0 – 4.0	Very Good
>4.0	Excellent
Hydrocarbon Generation Potential – S₂ (mg HC/g sediment)	
<2.0	Low generation potential
2.0 – 5.0	Moderate generation potential
5.0 - 10	Good generation potential
>10	Excellent generation potential
Hydrogen Index – HI (mg HC/g TOC)	
IH < 200	Gas Potential
200 < IH < 300	Gas and Condensate Potential
IH > 300	Oil Potential
Maturation – Tmax °C	
<440	Immature
440 – 470	Mature
>470	Senile
Production index	
< 0.10	Immature
0.10-0.30	Oil generation
> 0.30	Gas generation/oil cracking

4. Results

The physicochemical parameters of water and sediment varied for: temperature between 22.5 and 26.0 °C (mean 24.0±1 °C); salinity between 13.2-34.7 (mean 21.6±6.7); pH between 7.2-8.6 (mean 7.9±0.3); redox potential (Eh) between -130.8 and 50.8 mV (mean -69.7±29 mV).

The percentage of fine fraction varied between 19.8-99.6% (mean 91.0±19%). Most of the places have fine-grained sediments (Fig. 2A). Only locally, coarser grained sediments were found, such as near S. Gonçalo (at south of the study area), Paquetá island and close to the Suruí River outflow (at north).

The geochemical variables ranged for (Appendix 1): TOC between 1.0-6.1 % (mean 4.6±1 %); TS between 0.3-2.1 % (mean 1.5±0.3%); C/S between 1.9-4.2% (mean 3.1±0.5%) and; insoluble residue (IR) between 61.9-92.8% (mean 70.9±7.3%). The highest values of TOC were found in the inner northern sector of the study area (Fig. 2B).

The lowest values of TS were found near the Guapimirim Environmental Protected Area (known as Apa de Guapimirim) and in the southern sector of the study area (Fig. 2C). The highest TS values were found close to the Suruí River outflow, in the stations located behind the Governador Island and near the REDUC Oil Refinery (Fig. 2C). The lowest C/S ratio values were found in the southern region of the study area (Fig. 2D). The highest IR values were found in the southern region of the study area (Fig. 2E).

The Rock Eval pyrolysis parameters (Appendix 1) varied for: S1 between 0.5-2.5 mg HC/g (mean 1.5±0.5 mg HC/g; Fig. 2F); S2 between 2.0-17.0 mg HC/g (mean 9.9±3.3 mg HC/g, ; Fig. 2G); S3 between 2.1-8.0 mg CO_2/g (mean 5.9±1.2 mg CO_2/g; Fig. 2H); the hydrogen index (HI) between 128-280 mg HC/g TOC (mean 214±38.6 mg HC/g TOC; Fig. 2I); oxygen index (OI) between 102-204 mg CO_2/g TOC (mean 132±32.1 mg CO_2/g TOC). The Tmax values are <440 °C (400-420 °C; mean 411±4.4 °C). The production index (PI) values (S1/S1+S2) oscillated between 0.11-0.31 (mean 0.14±0.03). The PI values vary between 0.11 and 0.16 in most places (mean 0.13, without station 10), reaching 3.1 only in one location (station 10).

The $_{org}\delta^{13}C$ values vary between -24.6 ‰ and -20.3 ‰ (mean -22.4±1.3 ‰). The map of distribution of $_{org}\delta^{13}C$ values shows lower isotopic values near the Guapimirim environmental protect area and the highest in the northern area between Paquetá and Governador Islands (Fig. 3).

In Figure 4 are presented biplots with regression lines and respective R^2 value of: A. TOC (%) versus TS (%); B. TOC (%) versus S1 (mg HC/g sediment); C. TOC (%) versus S2 (mg HC/g sediment) and; D. S1 (mg HC/g sediment) versus S2 (mg HC/g sediment). These results evidence strong positive correlations between these variables, indicating that the stations with higher TOC contents also have higher TS, S1 and S2 values. The S1 and S2 values tend to increase simultaneously.

The results of PCA are included in Figure 5. The two first factors of the PCA explain 77% of data variability since the Factor 1 and Factor 2 explain respectively 58% and 19% of data variability. Factor 1 is positively correlated with HI, PI, $_{org}\delta^{13}C$, C/S, S1, S2, S3, TOC, TS and fine fraction (Group I) and negatively with sand fraction, IR, OI, Eh, salinity (Group II). Factor 2 is positively correlated with S3, TOC, TS and fine fraction (Group III) and negatively with salinity, HI, PI and $_{org}\delta^{13}C$ (Group IV).

Table 2 presents the correlations of the analyzed variables with the two first factors of the PCA (Fig. 5). The variables of the groups I and II (Factor 1) are in some way linked to the sediment granulometry and the deposition of organic matter, whereas the Factor 2 has stronger correlations with PI and HI values. The correlations between the analyzed variables presented in Table 3, explain the PCA results.
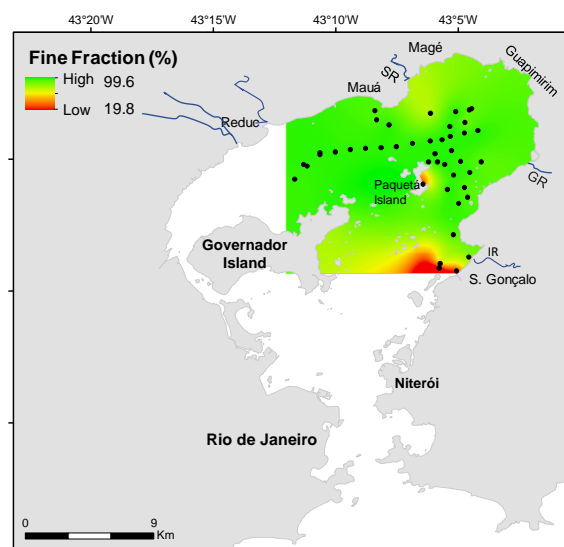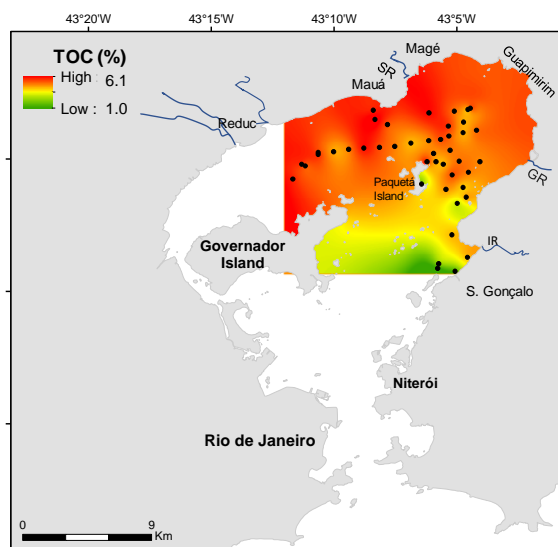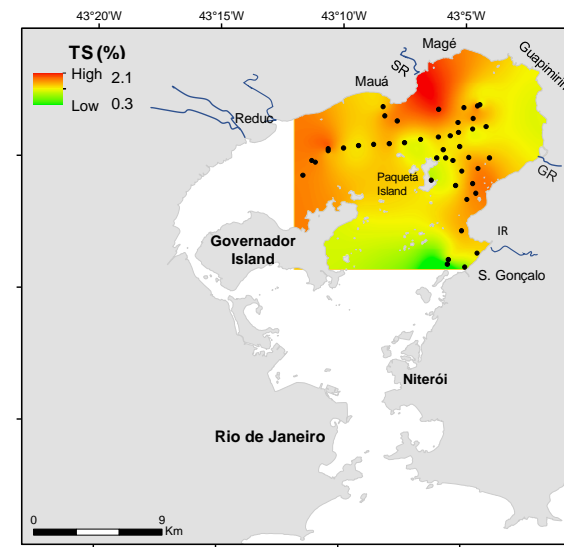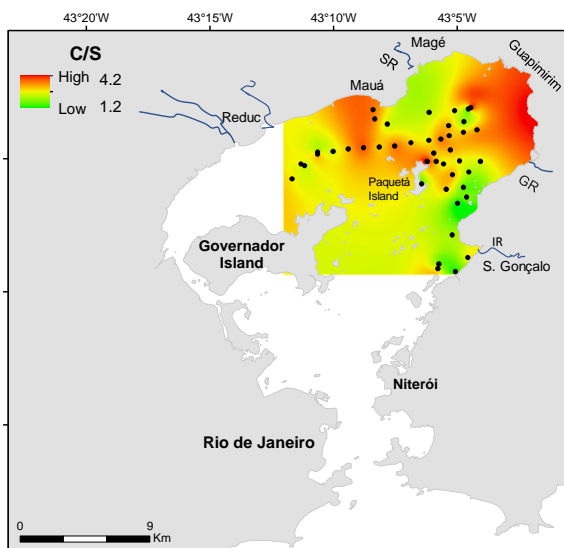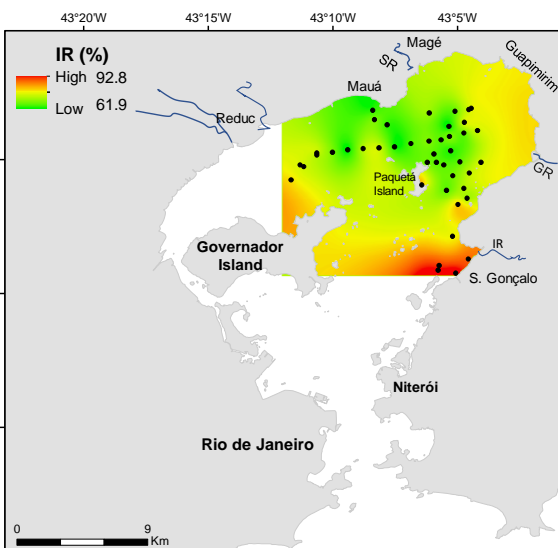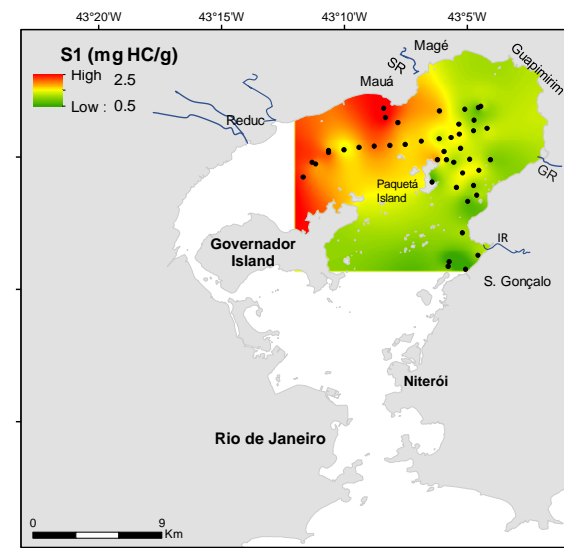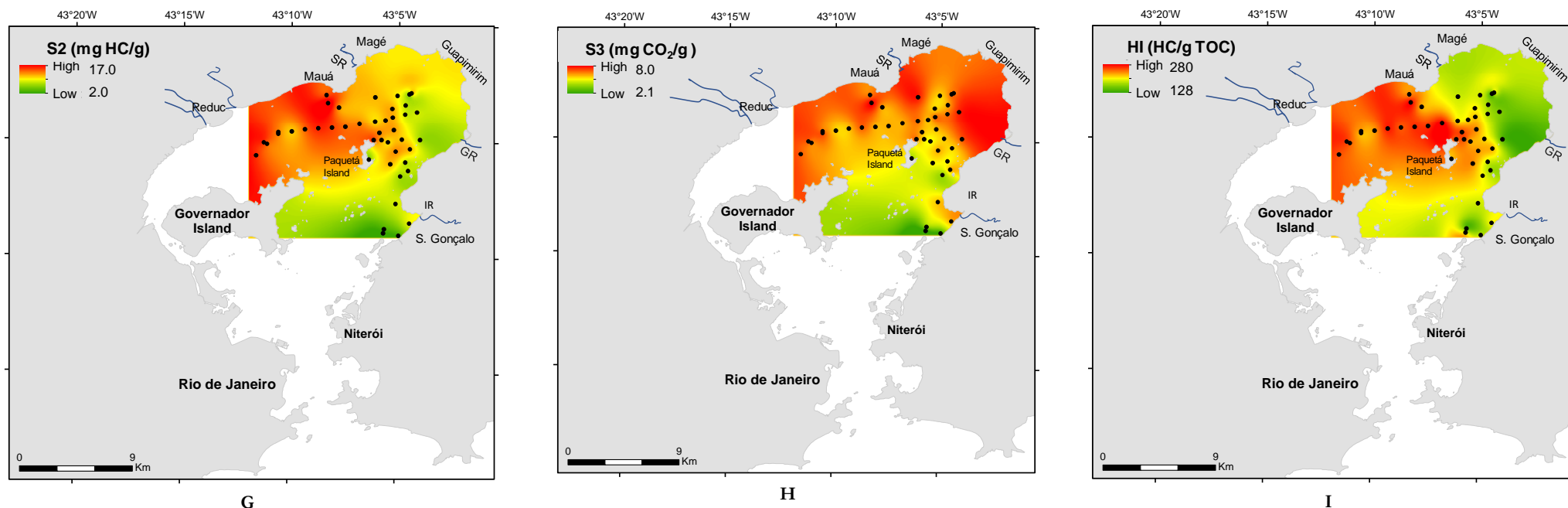
Fig. 2. Maps of distribution of: A. Fine Fraction (%); B. TOC (%); C. TS (%); D. C/S ratio; E. IR (%); F. S1 (mg HC/g sediment); G. S2 (mg HC/g sediment); H. S3 (mg CO_2/g sediment), I. IH - Hydrogen Index (mg HC/g TOC). Legend: SR – Surui River, GR – Guaxindiba River, IR – Imboassu River.
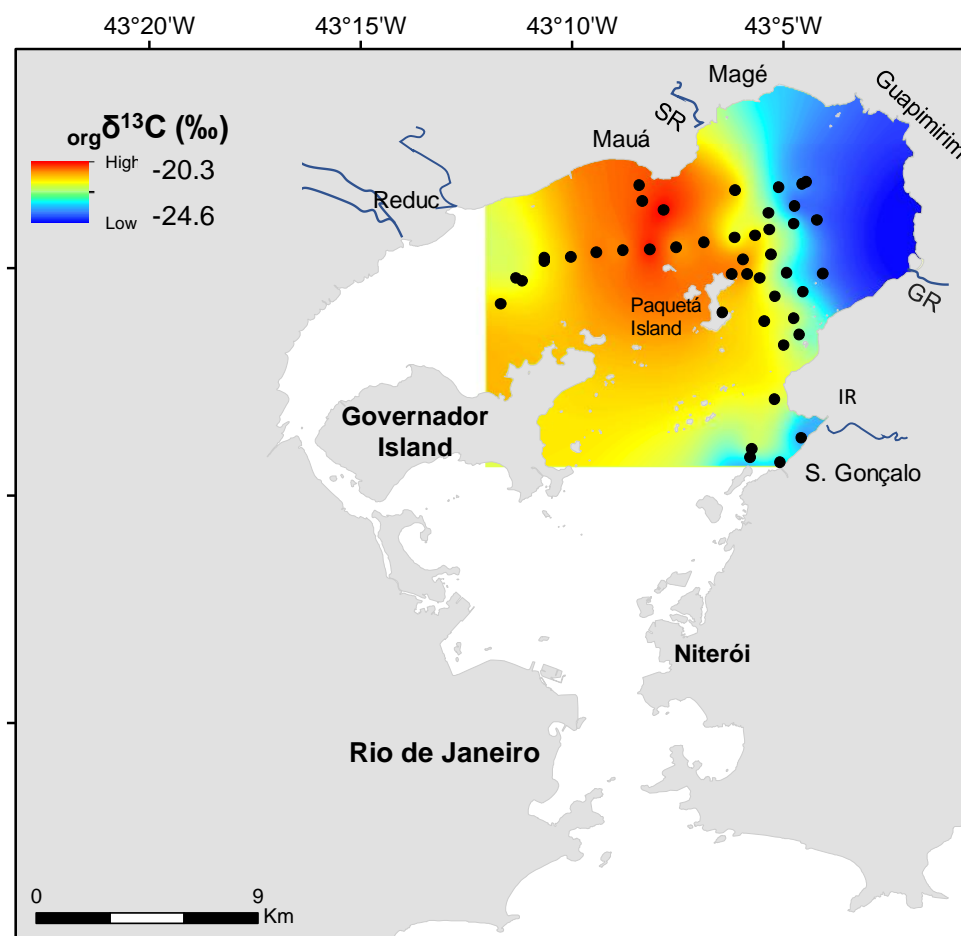
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Fig. 3. Map of distribution in the study area of bulk organic matter δ^{13}C (‰) values. Legend: SR – Surui River, GR – Guaxindiba River, IR – Imboassu River.

5. Discussion

5.1 General characteristics of the study area

The prevalence of fine-grained sediments (mean values of fine fraction content 90±19.1 %) enriched in organic matter (TOC 1.0-6.1 %; mean 4.6±1.1 %) suggest that the bottom currents are weak in most part of the study area. Similar observations were reported, for instance, by Baptista Neto et al. (2006).

According to the PCA results, presented in Fig. 5 (Group II), the RI, related to the mineralogical component of the sediments, has positive correlations with sand fraction, OI, salinity and Eh values (Table 3). These results indicate coarser grained sediments, composed mostly by a lithogenic component, with lower TOC contents and are oxic. This is verified in the southern area where the salinities tend to increase, due to stronger oceanic influence. In this zone, the organic matter is composed by higher oxygen contents.

The TOC content is high in most of the analyzed stations. Several authors have found similar values of TOC to that reported in this work, in Guanabara Bay (ranging from 0.02-8.55%), such as Eichler et al. (2003), Vilela et al. (2003),

Mendonça Filho et al. (2003), Carreira et al. (2004), Fernandez et al. (2005) and Sabadini-Santos et al. (2008).

In the present work, the highest TOC values were found near the Industrial Pole of Duque de Caxias, near the Sarapuí and Iguaçu rivers outflow, as well as was observed by Mendonça Filho et al. (2003), but also in front of Mauá and Magé City, close to the Suruí river outflow and at the Guapimirim area (Fig. 2B). According to Peters and Cassa (1994), amounts of TOC between 2% and 6%, which were found in most part of the study area, can be considered very good to excellent for hydrocarbons generation.

The surface sediments analyzed in this work have similar concentrations of TS (0.3-2.1%; mean 1.5±0.3%) to that previously recorded for instance by Fernandez et al. (2005). These authors recorded low TS concentrations (0.07%)in the region near the mangrove and higher contents (1.55%) in the port area of Guanabara Bay. The TS values recorded in this work are higher than that found in other Brazilian regions. For instance, Burone et al. (2003) recorded in the Ubatuba Bay, São Paulo State (Brazil), TS values varying between 0.01% and 0.48%.
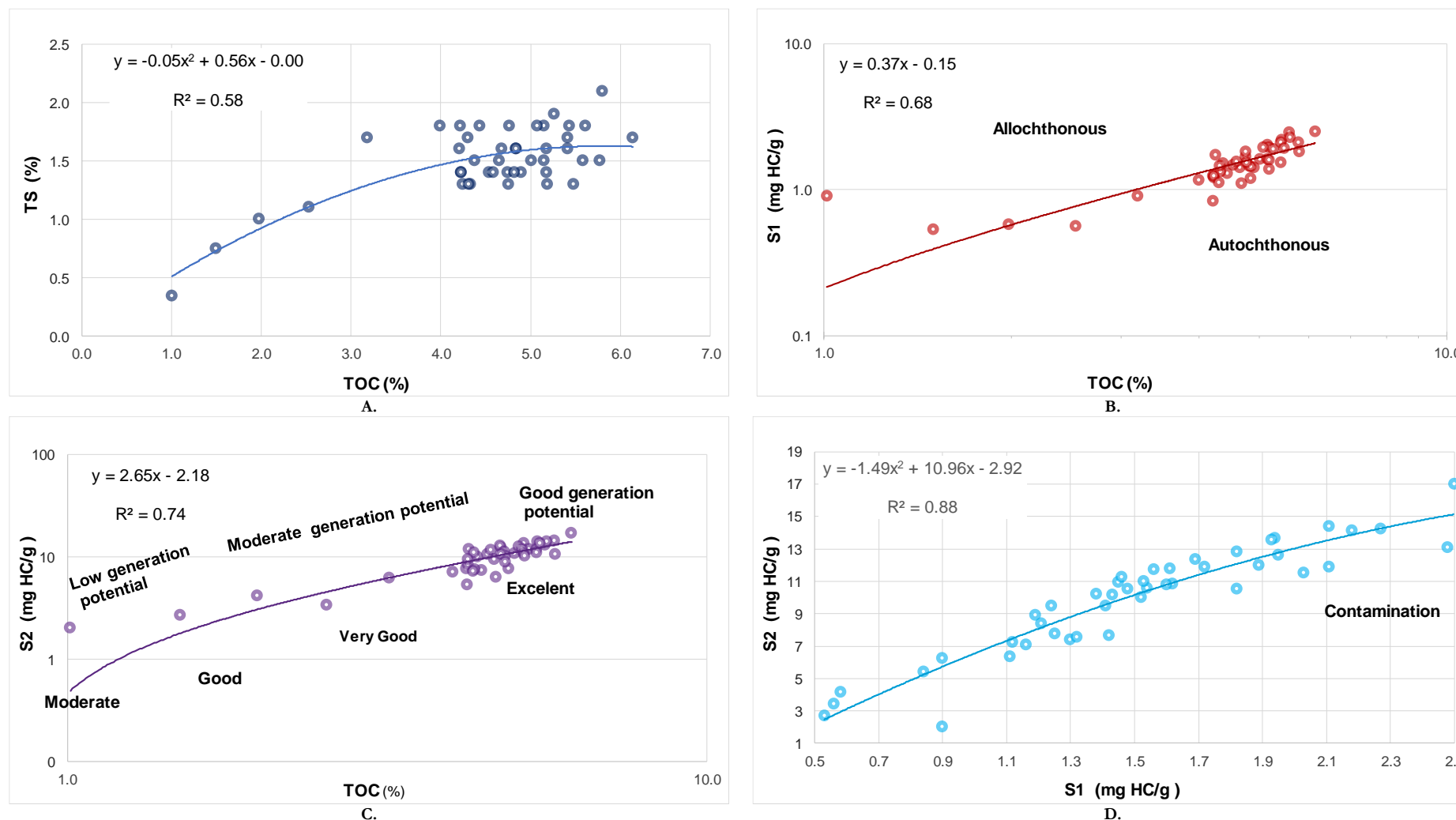
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Fig. 4. Biplots with regression lines and respective R^2 value of: A. TOC (%) versus TS (%); B. TOC (%) versus S1 (mg HC/g sediment); C. TOC (%) versus S2 (mg HC/g sediment) and; D. S1 (mg HC/g sediment) versus S2 (mg HC/g sediment).
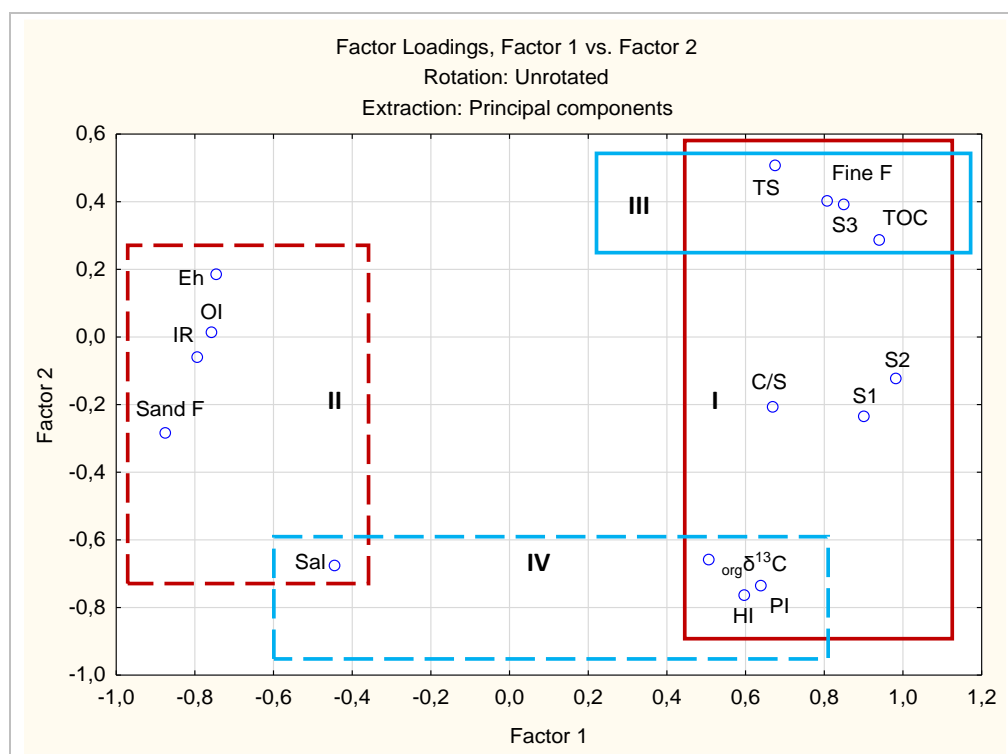
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Fig. 5. PCA associating the variables according to their correlation with Factor 1 and Factor 2. Legend: Sal – salinity; Eh - Redox Potential (mV); Fine F – Fine Fraction (%); Sand F – Sand Fraction (%); TOC -Total Organic Carbon (%); IR - Insoluble Residue (%); S1 (mg HC/g sediment) - quantity of hydrocarbons generated in nature; S2 (mg HC/g sediment) - quantity of hydrocarbons generated by pyrolysis; S3 (mg of CO_2/g sediment) - quantity of CO_2 generated by the organic matter of the rock; Tmax (°C) - temperature at which the maximum quantity of hydrocarbons is generated (maximum value of S2 peak); HI - Hydrogen Index [HI = (S2/TOC) x100, in mg HC/g TOC]; OI - Oxygen Index [OI = (S3/TOC) x100, in mg CO_2/g TOC]; PI - Production Index (S1/S1+S2), used to characterize the organic matter evolution degree.

The positive correlation evidenced in the biplot of TOC against TS of Fig. 4A indicates that the enrichment of sulphur is largely related to TOC content. Although there is a general tendency for the simultaneous increase of the TOC and TS values, as the results of the PCA also suggest (Fig. 5; Group I; Table 3), the higher values of both variables do not necessarily occur in the same stations (Fig. 2B, C), what indicate different sources for both variables. The highest values of TS were recorded close to the outflow of several rivers mainly in the northeast area (Fig. 2C), such as the Suruí, Estrela, Iguaçu, Sarapuí and Guaxindiba, which cross densely populated areas. These results suggest that anthropic activities are influencing the TS values. Thus, the highest TS values should be related to contamination. However, in the Guapimirim area, there are less sulphur anthropic pollution as shown by their lower TS values and higher C/S ratio values (Figs. 2C and 2D).

According to Berner (1995) and Borrego et al. (1998) the values of the C/S ratios above 3 indicate oxidant environments and values <3, indicate reducing environments. The C/S ratio values in most of the studied stations in the NE region of Guanabara Bay (1.9-4.2; mean

3.1±0.5) are similar to that found in other regions. For instance, Siqueira et al. (2006), found a C/S ratio varying between 0.09-3.90 (mean 1.86±1.26) in surface sediments of the Santos Estuary (SP, Brazil). Uehara et al. (2007), recorded C/S values between 1.75-5.03 in a sediment core collected in the estuarine-lagoon system of Cananéia (SP, Brazil), and concluded that in most part of the recorded period (with values >3) the sediments were deposited under low oxic conditions. Silva et al. (2011) recorded C/S values in Paraíba do Sul Delta (Rio de Janeiro State, Brazil), ranging from 1.80–4.3. These authors found C/S values >3 in most of the places and thus considered the Paraíba do Sul Delta as a potentially extremely oxidizing environment. In Spain, Borrego et al. (1998) found a variation of the C/S ratio in the estuary of the Odiel River of 2.6-7.03 within its main channel, marginal areas and saltmarshes. These authors associated the predominance of reducing processes to the presence of organic matter and the availability of sulfur. The C/S ratio values in most of the studied stations in the NE region of Guanabara Bay are >3, mostly near the Apa de Guapimirim region and in front of Mauá region, which means that surface sediments are yet oxic in most of the study area.

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Tab. 2. Correlations of the analyzed variables with the two first factors of the PCA (Fig. 5). Legend: Eh - Redox Potential (mV); Fine Fraction (%); Sand Fraction (%); TOC -Total Organic Carbon (%); IR - Insoluble Residue (%); S1 (mg HC/g sediment); S2 (mg HC/g sediment); S3 (mg of CO_2/g sediment); HI - Hydrogen Index (HC/g TOC); OI - Oxygen Index [mg CO_2/g TOC); PI - Production Index (S1/S1+S2); $_{org}\delta^{13}C$ – stable carbon isotopes of sedimentary bulk organic matter (‰). Significant positive correlations are signed with black bold and negative one with blue.

Variables	Factor 1	Factor 2
Fine Fration	**0.85**	0.39
Sand Fration	**-0.88**	-0.28
TOC	**0.94**	0.29
TS	**0.67**	**0.51**
C/S	**0.67**	-0.20
IR	**-0.79**	-0.06
S1	**0.90**	-0.23
S2	**0.98**	-0.12
S3	**0.81**	0.41
HI	**0.60**	**-0.76**
OI	**-0.76**	0.01
PI	**0.64**	**-0.73**
Salinity	-0.45	**-0.67**
Eh	**-0.75**	0.19
$_{org}\delta^{13}C$	**0.51**	**-0.66**
Percent of variance	0.58	0.19

5.2 Quality of organic matter

The results presented in this work show that the accumulation of organic matter is high in the northeast internal area of GB. The range of OI between 102-204 mg CO2/g TOC (mean 132±21.3 mg CO2/g TOC) is lower than that reported by Mendonça-Filho et al. (2003), from 114-425 CO_2/g TOC. However, in both cases the highest OI values were recorded in the southern region of Guanabara Bay, indicating a changing in the composition of organic matter and the presence of organic materials composed by higher oxygen content.

The HI (128-280 mg HC/g TOC; mean 214±38.6 mg HC/g TOC) of organic matter in recent sediments are related to their geochemical composition and may indicate their hydrocarbon generation potential. According to the information presented in Table 1 (based on Espitalié et al., 1985), the sedimentary organic matter of the NE sector of Guanabara Bay have potential to produce gas and condensate.

Plotting the HI against the OI of the analyzed samples on a diagram of van Krevelen type (van Krevelen, 1950; Fig. 6), it is observed that organic matter content of Type III prevails in the study area. This kind of organic matter, when subjected to anaerobic bacterial degradation and/or to high temperatures, can give place to gas and condensate production, as mentioned. In fact, Delavy et al. (2016), observed the presence of gassy sediments and evidences of gas seeping in the NE sector of GB, in front of the Apa de Guapimirim.

Tab. 3. Correlations between the analyzed data. The bold numbers are significant at $p < 0.05$

|	Fine F	Sand F	TOC	TS	C/S	IR	S1	S2	S3	HI	OI	PI	Sal	Eh	$_{org}\delta^{13}C$
Fine F	1.00														
Sand F	**-0.96**	1.00													
TOC	**0.90**	**-0.86**	1.00												
TS	**0.79**	**-0.69**	**0.80**	1.00											
C/S	**0.43**	**-0.53**	**0.58**	-0.01	1.00										
IR	**-0.70**	**0.75**	**-0.70**	**-0.44**	**-0.58**	1.00									
S1	**0.60**	**-0.67**	**0.79**	**0.50**	**0.68**	**-0.59**	1.00								
S2	**0.78**	**-0.80**	**0.91**	**0.63**	**0.66**	**-0.72**	**0.91**	1.00							
S3	**0.81**	**-0.75**	**0.92**	**0.77**	**0.51**	**-0.57**	**0.69**	**0.77**	1.00						
HI	0.21	**-0.32**	**0.32**	0.04	**0.49**	**-0.41**	**0.69**	**0.69**	0.15	1.00					
OI	**-0.71**	**0.70**	**-0.70**	**-0.55**	**-0.42**	**0.63**	**-0.60**	**-0.75**	**-0.38**	**-0.48**	1.00				
PI	0.26	**-0.36**	**0.38**	0.09	**0.50**	**-0.44**	**0.72**	**0.73**	0.20	**1.00**	**-0.50**	1.00			
Sal	**-0.50**	**0.50**	**-0.56**	**-0.53**	-0.24	**0.48**	-0.26	**-0.33**	**-0.58**	0.20	0.28	0.18	1.00		
Eh	**-0.43**	**0.55**	**-0.63**	**-0.38**	**-0.56**	**0.47**	**-0.81**	**-0.73**	**-0.59**	**-0.57**	0.38	**-0.60**	0.33	1.00	
$_{org}\delta^{13}C$	0.20	-0.22	0.29	0.15	0.28	**-0.44**	**0.58**	**0.56**	0.17	**0.74**	-0.37	**0.76**	0.26	**-0.41**	1.00

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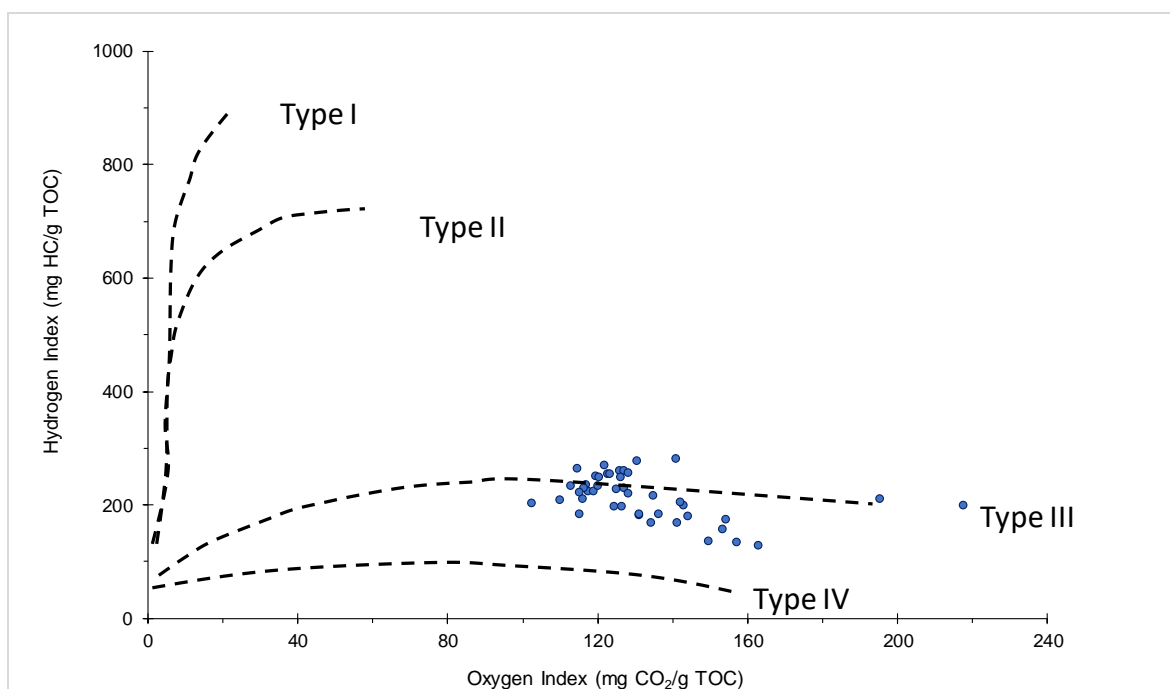
Fig. 6. Diagram of van Krevelen type (van Krevelen, 1950), based on results obtained in the NE region of Guanabara Bay.

The Tmax values, which specifies the temperature at which the maximum quantity of hydrocarbons is generated (maximum value of S2 peak), are <440 °C (400-420 °C; mean 411±4 °C) indicate that the organic matter is immature in the study area, what would be expected from surface sediments.

The S1 values, which represent the free hydrocarbons in the sediment, or the quantity of hydrocarbons generated in nature (0.5-2.5 mg HC/g; mean 1.5±0.5 mg HC/g) are in most of the places similar to that reported by Mendonça-Filho et al. (2003), ranging from 0.01-2.5 mg HC/g. However, these authors found higher values, behind the Governador Island (3.5 mg HC/g) and in a harbor area of Rio de Janeiro City (5.6 mg HC/g) and attributed these higher S1 values to pollution. In this study, the highest values of S1 were found near Mauá, where there is a harbor area for small boats, and near the REDUC Oil Refinery, of Duque de Caxias. According to the biplot presented in Fig. 4B, the higher S1 values should be related to allochthonous materials and probably to contamination by oil mostly close to Mauá and the REDUC Oil Refinery.

The source of organic matter may also be accessed for the results of $_{OM}\delta^{13}C$. According to Meyers (1994) marine organic matter has $\delta^{13}C$ values ranging between -20 ‰ and -22 ‰. The $\delta^{13}C$ values of organic matter produced from atmospheric CO_2 by C3 terrestrial plants range from -23 ‰ to -34 ‰, while C4 plants have $\delta^{13}C$ values between -9 ‰ and -17% (Schubert and Calvert, 2001). Thus, the $_{org}\delta^{13}C$ values varying between -24.6 ‰ and -20.6 ‰ (mean -22.4 ‰; Fig. 3), may be related to mixed sources. The map of

distribution of $_{org}\delta^{13}C$ values in the study area show the occurrence of lowest values near the Apa de Guapimirim, influenced by the outflow of several rivers and near the Imboassú River, suggesting a higher contribution of organic matter from C3 terrestrial plant remains, what is also shown by the lower hydrogen index (HI) values in this area (Fig. 2I). Otherwise the highest values of $_{org}\delta^{13}C$ values recorded in the northern region, between the Paquetá and Governador Island, suggest an increased contribution of autochthonous biological productivity induced by an excessive supply of nutrients to GB water, corresponding to the area with higher values of $_{org}\delta^{13}C$ and hydrogen index (HI).

According to the PCA results presented in Fig. 5 the $_{org}\delta^{13}C$ values are positively correlated with salinity, and HI values. These highest HI values may be influenced by the quality of organic matter associated to local biological production but also to the presence of contamination by oil.

The S3 values (2.1-8.0 mg CO_2/g; mean 5.9±1.5 mg CO_2/g), which represent the quantity of CO_2 generated by the sedimentary organic matter, are also similar to that reported by Mendonça-Filho et al. (2003), except for values <2 mg CO_2/g. These values would be expected to be opposite to those of S1 and S2, because they are related to other type of organic matter. However, the higher S3 values in all the northern area where several rivers flow also trace the presence of terrestrial OM. The highest S3 values associated to the lowest values of HI near the Apa de Guapimirim also indicate that this region receives OM mainly of terrestrial sources.

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The S2 values are the quantity of hydrocarbons produced by pyrolysis; this variable is related to the generation potential of the sediments if they were submitted to ideal temperature conditions for the generation of hydrocarbons. The S2 values recorded in this study are also similar to that observed by Mendonça-Filho et al. (2003); but lower values than 2.0 mg HC/g were not recorded in our study area.

According to the biplot presented in Fig. 4C, the highest S2 values are related to excellent (high) amount of organic matter and indicate a good generation potential if these organic materials are submitted to ideal temperature and

pressure conditions for the generation of hydrocarbons. The presence of contamination by oil released by vessels and effluents from the refinery also influence the S2. Thus, the highest values of S2 and S1 found in the north region of GB (Figs. 2G and 2F, respectively) also should be related to the presence of contaminants, as noted in the biplot of Fig. 4D.

Thus, based on the results of this work it was possible to identify four main groups of stations (Fig. 7): 1) with OM sourced mainly from adjacent continental areas; 2) with some autochthonous contribution; 3) strongly polluted by oil and; 4) an intermediate situation among those mentioned.
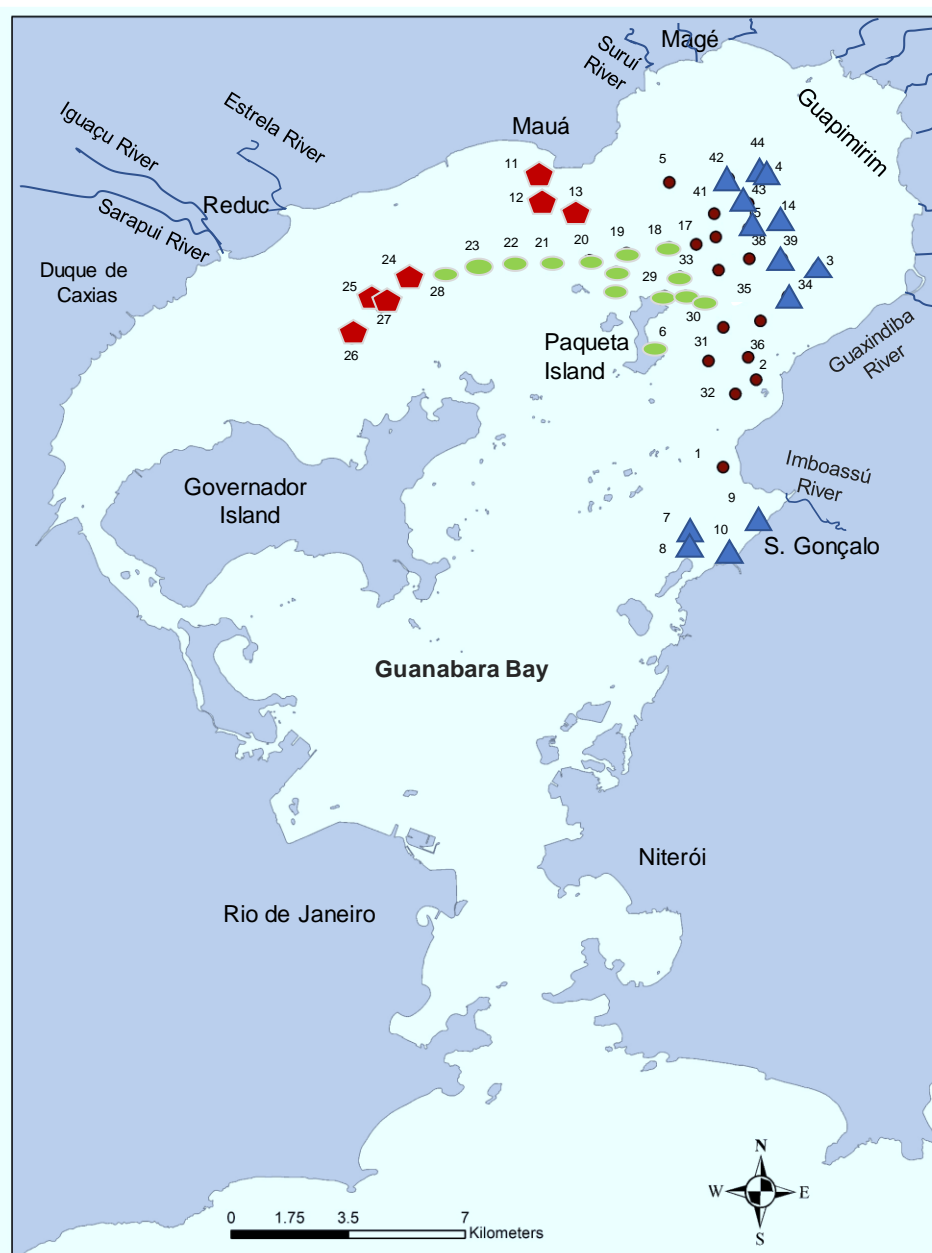

Fig. 7. Characteristics of organic matter in the study area. Legend. 1. Blue triangles – stations that receive mostly terrestrial organic matter contribution; 2. Green ovals – stations that receive a relatively high contribution of authoctone organic matter; 3. Red hexagons - stations polluted by oil; 4. Brown points – transition region among those mentioned.

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Delavy et al. (2016) observed the presence of gas seeping and accumulation of gas at a depth of about 9 m below the sediment surface, near the Apa de Guapimirim, the NE sector of GB. Our results also indicate that the organic matter amount and quality from surface sediments between the Paquetá and Governador Islands is also suitable for gas production. Our results also evidence that the sediments close to Mauá and the REDUC Oil Refinery are contaminated by hydrocarbons but near the Apa de Guapimirim they are less contaminated by oil.

6. Conclusion

Most of the study area of the NE sector of Guanabara Bay is composed by fine grained sediments with high TOC content. The results of the Rock Eval pyrolysis parameters and $_{org}\delta^{13}C$ values allowed to identify areas with different types of organic matter: under the influence of the rivers outflow of the Apa de Guapimirim and the region of S. Gonçalo (Roncador River) the sediments contain a relatively high component of OM sourced mainly from the adjacent continental areas; in the northern area between the Paquetá and Governador Islands some autochthonous contribution was found; near Mauá and REDUC Oil Refinery the sediments are polluted by oil; the sediments near the Apa de Guapimirim are less contaminated by oil.

Previous research has identified the presence of gas seeping and gas accumulation in subsurface sedimentary strata, near the Apa de Guapimirim, the NE sector of GB. The results of this work also indicate that the amount and quality of organic matter present in surface sediments between the Paquetá and Governador islands are also suitable for gas production. So, we should predict the occurrence of biogenic gas seeping in this area, in the near future.

Appendix 1 is attached as supplementary material (SM1) in
http://www.e-publicacoes.uerj.br/index.php/jse/article/view/37826

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