



Bulk, isotopic, petrographic organic matter and mineral distribution as proxies of environmental process in Guanabara Bay, SE, Brazil

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Abstract

Guanabara Bay is an estuarine environment of great socio-economic importance, where around 12 million people live in its drainage basin. We aim to characterize the sedimentary matter of Guanabara Bay, two mangrove systems therein (Suruí and Piedade mangroves), and the rivers, São João do Merití, Iguaçú, Sarapuí, Suruí, and Guapimirim, by performing sedimentological, mineralogical, elemental/isotopic organic matter composition (total organic carbon and total nitrogen, ¹³C and ¹⁵N) and organic matter petrography. Samples from the entrance of the bay present high values of quartz, low values of C/N ratio, and high percentages of diffuse amorphous organic matter indicating marine influence, whereas samples from rivers mouths present high percentages of translucent lignocellulosic, opaque lignocellulosic, gelified organic matter, and high C/N ratio probably due to the influence of terrestrial organic matter that comes from the drainage basin and the mangroves areas. Stations of the central sector of the bay were characterized by high percentages of TOC, intermediated values of δ¹³C, low C/N ratio, and also high diffuse amorphous organic matter indicating a predominant influence of organic matter from algae origin. High values of δ¹⁵N indicate large assimilation of nitrate or a high denitrification process in the highest productivity areas. In the river mouth regions, it is mainly influenced by terrestrial organic matter; however, in the northwestern and western sectors, organic matter is influenced both by terrestrial and domestic sewage influences which promote anaerobic decomposition of organic matter.

Introduction

The organic and mineral matter of sediments contains information to help reconstruct past histories of environmental conditions and climate variations and can assess human impacts on ecosystems. The elemental, isotopic, and molecular organic matter composition provides evidence of aquatic biota that lived in an environment and its drainage basin (Meyers 2003). Considering the sedimentary environment as an integrator of environmental conditions through

time, dependent on sedimentation rates, we can interpret the variations in the concentrations of elements in space as an indicator of the impact of human activities on the environment. Different sedimentation processes in Guanabara Bay as different sedimentation rates (Amador 1980; Godoy et al. 1999, Figueiredo et al. 2014) and organic and inorganic nature of the sediment can alter the dynamics of accumulation of different elements (Baptista Neto et al. 2000; Cordeiro et al. 2015, 2017) concentrating or diluting it. Multi-element geochemical analysis coupled with biological indicators and toxicity tests shows that there was no seasonal variation in sediment quality based on any methodology. All methods used showed that the NW sector and the harbor sectors were the most affected with indicators and that the NE sector had the best conditions (Abreu et al. 2016). A comparison between 10 estuaries systems in the world showed that the Guanabara Bay presents an overall magnitude of anthropogenic change (based on Median Enrichment Quotients, MEQ), with moderate values (3.0–5.0) comparing with high values observe for Derwent River, Santander, and Sydney estuary (> 5.0) (Birch et al. 2020). Guanabara Bay

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is still affected by multiple sources, causing risks to benthic organisms (Campos et al. 2019). Over the past 20 years, several Guanabara Bay recovery programs have been developed, but an integrated analysis of available data has indicated that these efforts have not achieved their objectives (Soares-Gomes et al. 2016).

Generally, the quality, quantity, and organic matter accumulation rate also highly variable and depend on the input of organic matter originated from the drainage basin, as well as the autochthonous primary production (Gorham et al. 1974; Meyers and Ishiwatari 1993). An increase of autochthonous organic matter is observed in environments with anthropogenic activities due to increased nutrients and consequently primary production. These processes can promote an increase in anoxic conditions, promoting decreasing in organic matter degradation (Demaison and Moore 1980). As a result, changes in the quality of organic and mineral matter of sediments can potentially be used as indicators of anthropogenic and natural processes. The quantity and quality of organic matter contained in sediments depend on the primary productivity, biochemical degradation, and depositional processes. Biodegradation acts more rapidly in the organic matter in marine than terrestrial organic matter due to the existence in the latter compounds more resistant to degradation, such as lignin and cellulose. The two most important pieces of information provided by the sedimentary organic matter are the source of organic matter and the abundance of biota that produced it (Meyers 2003). Generally, the organic matter in aquatic systems is more from microbial action than terrestrial plants (Meyers 2003). The plants can be divided into two groups geochemically significant from their biochemical composition: (1) algae and microalgae that contain little or no cellulose and lignin, which have a relatively high content of proteinaceous material rich in nitrogen, such as phytoplankton, and (2) higher plants that have high proportions of woody tissue, which may be rich in cellulose and lignin, such as grasses, shrubs, trees, and also macrophytes (Meyers 2003). From the information on elemental, isotopic compositions of carbon and nitrogen and microscopic analyses, these geochemical characteristics of organic matter make possible the study of their origins and characteristics.

The anthropogenic activity also affects the load on the input mineral in water bodies. The increased susceptibility of the drainage basins to weathering processes through deforestation of the watersheds, soil movement, as well as channels rectification is an example of how human activity can change the input of different types of minerals in the sediment–water bodies. The mineralogical characterization is of fundamental importance regarding the evaluation of the hydrodynamics of the sedimentary environment (e.g., the relationship between quartz and clay). Knowledge of the mineralogical distribution of sediments in Guanabara Bay

is still limited with few studies employing the X-ray diffraction technique. Baptista Neto et al. (2000) using the X-ray diffraction technique found, in the sandy and silty fraction of surface sediment, quartz with minor amounts of mica, feldspar, and heavy minerals, mainly ilmenite, magnetite, tourmaline, zircon, rutile, and garnet and lesser amounts of epidote, staurolite, kyanite, augite, and leucoxene amphibolites as a reflection of the regional geology of mainly metamorphic rocks. In the sediment fraction $< 5 \mu\text{m}$, the same author found clay, kaolinite, illite, smectite, and halloysite. Barbosa et al. (2004) studying sediments of the center channel identified the following minerals in the clay fraction $< 63 \mu\text{m}$, kaolinite, smectite, and biotite. However, the high activity (indicative of sediment contamination) measured at some stations was related to the presence of smectite indicating the role of the presence of smectite in the sorption capacity of metal contaminants. According to Faria and Sanchez (2001), the bottom sediments of the domestic sector of Guanabara Bay have to be rich in organic matter. The sediment is mostly terrigenous and its clay fraction consists mainly of kaolinite plus illite (mica) and vermiculite mixed layers, illite/vermiculite, and illite/smectite. In the bay, kaolinite tends to flocculate and accumulate near river mouths, whereas the content in illite/smectite increases toward the sea. Small amounts of illite in sediments were recorded, and the distribution of illite in the bay is homogeneous. The presence of clay fractions reflects the geological and pedological characteristics of the Guanabara Bay basin and the tropical climate conditions that lead to the transformation of mineral crystals. Quartz undergoes residual enrichment due to its greater resistance to weathering. Feldspars decrease in kaolinite and gibbsite. The plagioclases suffer decline becoming more pronounced in kaolinite and gibbsite. The biotite turns into vermiculite that can be transformed into kaolinite and gibbsite (Lima 2004). Since it is a receptacle of several drainage basins, one of the features that most attracts attention is the area with large sedimentation at the mouths of the various rivers. In another way, Amador (1997) extends the strip of sandy sediments from the entrance of the bay to the east of Ilha do Governador, while Quaresma et al. (2000) point out that these sands occur only about 3 km south of the Rio-Niterói bridge. The greater dynamics in this area promote the removal and prevent the deposition of very fine fractions. This distribution is certainly linked to the selection promoted by the tidal currents near the bottom, with maximums of 156 cm s^{-1} at flood tide, thus not allowing the deposition of fine-grained sediments (Quaresma et al. 2000). Several authors have demonstrated in recent times a great variability regarding muddy sediment accumulation rates in Guanabara Bay (Godoy et al. 2012, Figueiredo et al. 2014).

The characterization of sediments in Guanabara Bay as well as in mangrove areas and contributing rivers, concerning the quality of sediments, is of key importance for

an environmental diagnosis of these ecosystems since the physical and chemical characteristics of sediments (Catanzaro et al. 2004) have strong influences on the type of biota found (Abreu et al. 2016), as well as on the fixation of pollutants (heavy metals, oil, etc.) (Soares-Gomes et al. 2016). Thus, the present work aims at qualifying the origin of the sedimentary matrix through sedimentological, microscopic, mineralogical, and isotopic techniques.

Environmental setting

The Guanabara Bay drainage system and associated basin are inserted in the Guanabara rift (Ferrari 1990) which is part of the Tertiary series of depressions of the southeastern Brazilian coast, and its current configuration has linked to the Holocene variations in sea level (Suguio et al. 1985), which conditioned by flooding of an ancient Pleistocene river valley (Amador 1997). The Guanabara Bay is a eutrophic coastal bay, the bottom sediments are predominantly fine (silt and clay), which has about 384 km² and a drainage basin of approximately 4080 km² (Kjerfve et al. 1997). Cities, such as Rio de Janeiro, Duque de Caxias, São Gonçalo, and Niterói, have approximately 11.7 million inhabitants containing approximately 6000 industries surrounding the bay, and over 6000 other industries are in their bay drainage (Kjerfve et al. 1997). Despite the development of pollution control plans, the water and sediments quality of the bay is worrisome (JICA 1994). Large amounts of suspended solids, organic matter and hydrocarbons (Kjerfve et al. 1997), as well as heavy metals (Rebello et al. 1986; Perin et al. 1997), are released into the bay and accumulated in the sediments. Guanabara Bay has undergone an occupation process that is ruled by low investment in a non-existent sanitation and control process of industrial impact. With an area of 4600 km², the Guanabara Bay receives 18.8 m³/s of domestic wastewater, of which only 2.63 m³/s are treated. Fifty-five rivers drain into the bay. The net average discharge tributary to the bay is about 351 m³/s, ranging from a minimum of 167 m³/s in August to 551 m³/s in February (Amador 1997). The most polluted rivers are São João de Meriti, Sarapuí, and Iguaçu, as evidenced by high trace metal concentrations in sediments of these rivers mouths (Baptista Neto et al. 2006; Cordeiro et al. 2015).

Methodology

Sampling

Surface sediments were sampled using a van Veen sampler specially designed to avoid losses during the sampler

retrieval (Wagener et al. 2012). The upper 2-cm sediment layers were collected in 28 sampling stations shown in Fig. 1 in Guanabara Bay and 11 sampling stations in mangrove areas from Surui (5) and Piedade (6), besides 5 samples from São João do Meriti, Iguaçu, Sarapui, Suruí, and Macacu river sediments. Sediment collection was carried out in two sampling periods (29–02/02/2006 and 5–13/12/2006), being the datasets from each sampling statistically compared and average values for each station used to obtain a more representative and concise characterization.

Grain size analyses

A laser particle analyzer (CILAS 1064) was used to measure the grain-size distribution (particles between 0.04 and 500 µm) after the organic matter and carbonate destruction with H₂O₂ and HCl, respectively, and it dispersing in a Na₄P₂O₇ solution and sonification.

Mineralogical analyses

X-ray diffraction

The X-ray diffractogram of the sample, obtained by the powder method, was collected on a Bruker-AXS D5005 equipped with Goebel mirror for a parallel beam of X-rays. The following operating conditions were employed: Co K α by step with the counting time of 1.0 s per step and collected 50 to 80° 2 θ (35 kV/40 mA), goniometer speed of 0.02 to 2. The qualitative interpretation of the spectrum was performed by comparison with standards using database PDF02 (ICCD 1996) and DiffracPlus Bruker software.

Infrared spectrometry

The mineralogical analysis was performed on the total fraction of the sediment, to determine the proportion of different mineral constituents using Fourier transform (Infrared Spectrometer, Perkin Elmer, mod. SPECTRUM 1000 CSI-L118-M100). This technique is based on the absorption of infrared radiation considering that the absorbance measured is proportional to the concentration of the minerals (Fröhlich 1989; Bertaux et al. 1998). The samples were macerated, weighed and mixed with KBr at a rate of 0.25%, and pressed (8 tons) to obtain the tablets. These tablets were analyzed in the infrared spectrometer with spectral scanning between wavelengths from 4000 to 400 cm⁻¹. The quantification of the minerals contained in the samples was performed from 50 spectra of mineralogical patterns.

Organic matter analyses

Total organic carbon, total nitrogen, and stable isotopes of C and N

To determine these parameters, the sample was treated with a 0.5 mol L⁻¹ HCl solution. The pre-treated sediment samples were analyzed for their elemental composition (carbon and nitrogen) and isotopic (¹³C and ¹⁵N) using an elemental analyzer PDZ Europa ANCA-GSL interfaced to a mass spectrometer PDZ Europa 20–20 isotope ratio (SERCON Ltd., Cheshire, UK). The samples were heated at 1020 °C in a reactor with a mixture of chromium oxide and cobalt oxide/cobalt coated with a thin film of silver. After combustion, the oxides were removed using a reducing reactor (reduced copper at 650 °C) where helium flows through a magnesium perchlorate trap to hold CO₂ (for the analysis of N). Nitrogen and CO₂ are separated in a column “Carbosieve GC” (65 °C, 65 mL/min) before entering into the isotope ratio mass spectrometer (IRMS). Two laboratory standards were analyzed for every 12 samples. We used standards laboratories including NIST 1547, NIST 1577b, acetanilide, cellulose, glycine, sucrose, and ammonium sulfate. δ¹³C and δ¹⁵N were obtained using the concentration ratio between stable isotopes of carbon (¹³C/¹²C) and nitrogen (¹⁵N/¹⁴N), where:

$$\delta^{13}\text{C}_{\text{sample}} = \left(\frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{reference}}}{(^{13}\text{C}/^{12}\text{C})_{\text{reference}}} \right) \times 1000$$

$$\delta^{15}\text{N}_{\text{sample}} = \left(\frac{(^{15}\text{N}/^{14}\text{N})_{\text{sample}} - (^{15}\text{N}/^{14}\text{N})_{\text{reference}}}{(^{15}\text{N}/^{14}\text{N})_{\text{reference}}} \right) \times 1000$$

Delta value is the difference between the sample and standards data, and naturally wide distributed and therefore, a value of delta = zero (i.e., atmospheric nitrogen to N with ¹⁵N = 0.3663033%; Pee Dee Belemnite for C, with ¹³C = 1.1112328%). The δ¹³C reference is the Chicago PDB Marine Carbonate Standard, obtained from the Cretaceous marine fossils, *Belemnitella* American from the PeeDee formation in South Carolina, North America. The absolute ratio (R) is measured for the sample and the standard, and therefore the relative measure of the delta is calculated. The determination of the relationship between the concentrations of carbon and other elements such as nitrogen and its isotopic composition allows the identification of the quality of the deposited organic material and production processes of the estuarine system of Guanabara Bay.

Petrography of organic matter (palynofacies)

For the analysis of organic matter petrography, samples were prepared according to the following protocol: samples were

dried and macerated, subjected to acid treatment (HCl 37% m/m) to remove any carbonate material, and treated with HF (10 ml, 40% m/m) to remove siliciclastic material and isolating the organic matter. Then, the mixture was centrifuged and washed 3 times with HCl (37% m/m) to dissolve the inorganic residue (Ercegovac and Kostić 2006); subsequently, the solid phase was washed with distilled water to remove residual acids. This procedure was accompanied by microscope observation. After preparation of the samples, a petrographic blade was produced as follows: a small amount of sample was placed on the center of a glass slide, dried on the slide, and added a thin layer of resin and its coverslip. Finally, after complete drying of the resin, the slides were observed under a microscope for reflected and transmitted light (Leitz Diaplan). For each slide, fifteen random fields were chosen and analyzed with the lens with a quadrant of 96 squares. Thus, the elements found were counted from the number of squares therein concerning the total number of squares. The values presented are semi-quantitative measures and were obtained by calculating the sum of occurrences of squares in each category, divided by the sum of all occurrences of all categories in the boxes multiplied by 100.

Results and discussions

Grain size variability

Grain-size distribution in the Guanabara Bay is according to hydrodynamics and point source. Higher average grain size predominates in the entrance of the bay, while large grain-size values are found in the main channel and at the mouth of major rivers. The average value for the Guanabara Bay sediment was 33.3 ± 47.4 μm, 23.3 ± 9.12 μm for the mangrove sediment and 19.8 ± 9.64 μm the average value for the river sediment being significantly lower than for the Guanabara Bay sediment (MW, p < 0.05). However, it should be emphasized that these values are higher than those observed in the sediments at the mouths of the respective rivers, which present lower hydrodynamics.

The sediments in the Guanabara Bay varied according to the classification of Folk and Ward (1957) have an average sorting value of 3.03 ± 0.55 for sediments in the bay, 3.19 ± 0.19 in mangrove and rivers is 3.77 ± 0.55. Sediments in mangrove areas tend to be poorly sorted with low variability. Sorting varied from well-sorted mainly at the mouth of the main rivers, São João de Meriti, Iguaçú, and Macacu

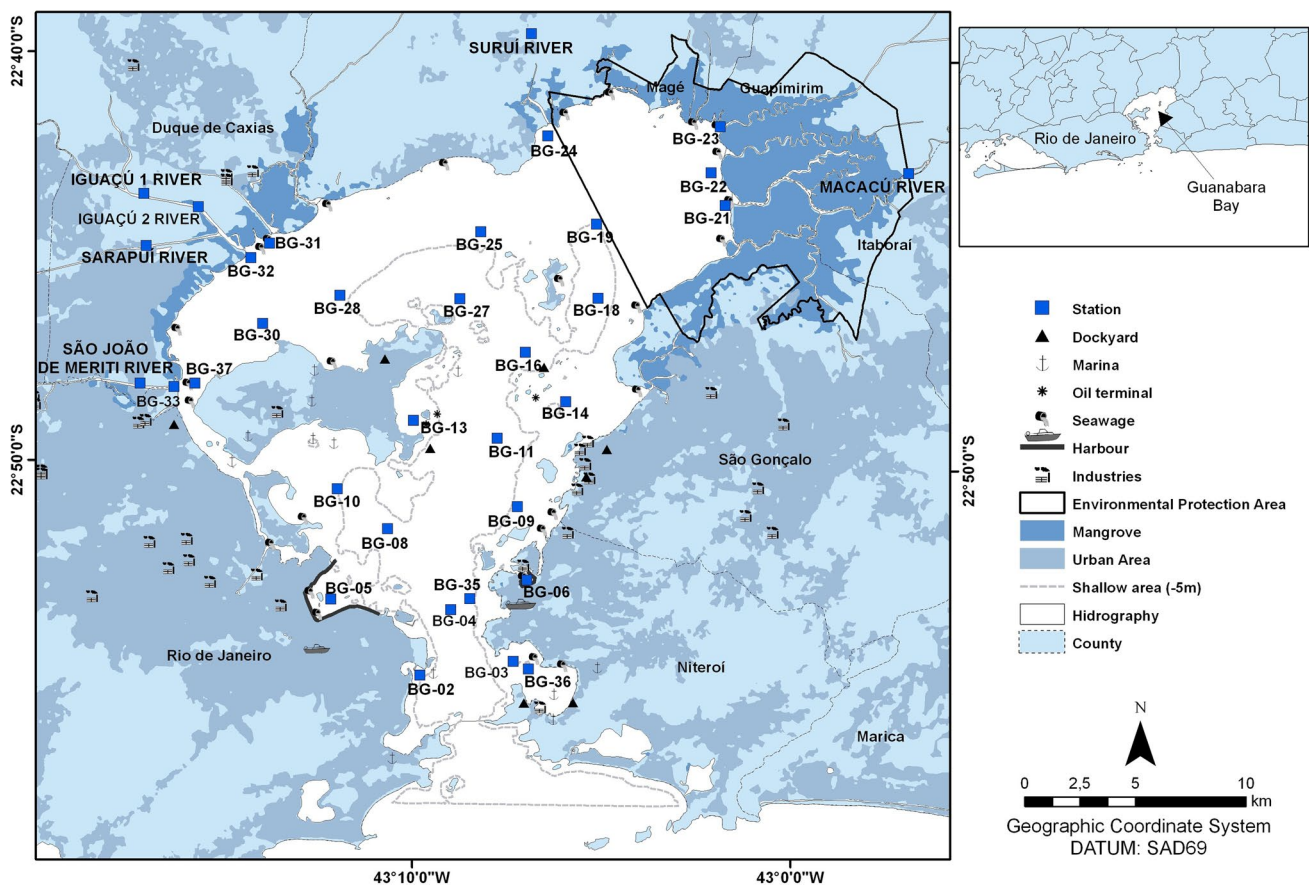


Fig. 1 Guanabara Bay and the sediment sampling points. The main rivers are shown on the map

ivers, to very poorly sorted at the entrance of the Guanabara Bay (Fig. 2). The sediments of the central sector tend to be less sorted probably because they receive continental and marine sources of sediments. Bay and rivers mouth sediments have an average skewness value of -0.27 , while mangrove areas have a -0.26 value, with a global trend of small deviation to fine particle size. The tendency to very fine skewed is observed in Botafogo sound (BG-02 and BG02b sampling station), Niteroi (BG-35), and São João de Meriti River mouth (BG-33). The south-west and northeast sectors of Guanabara Bay stations between BG-05 and BG19/BG-21 present fine skewness values with trends toward slightly symmetrical distribution.

Mineralogy

The mineralogical analysis allowed a quantitative characterization of the composition of the samples, as shown in Fig. 3. The main mineralogical constituents of the samples are muscovite, quartz, kaolinite, and microcline.

Among the most representative minerals, muscovite showed an average concentration of $27.3 \pm 11.7\%$ in Guanabara Bay sediments, $27.1 \pm 4.28\%$ and $21.4 \pm 8.13\%$ in

river sediments. The muscovite was generally abundant and had a higher incidence in northern and northeastern areas of the bay (Fig. 2), with a mean, considering the average of the four campaigns, 27.2% . Stations with the lowest value corresponding to the entrance of Guanabara Bay BG-02, BG-03, BG-09, and BG-36 stations (Fig. 3).

The average values of quartz between the bottom sedimentary compartments of Guanabara Bay, Surui and Piedade mangrove sediments as well as the sediments of São João do Meriti, Sarapuí Iguaçú, Surui, and Macacu rivers presented average values of $22.5 \pm 23.8\%$, $26.6 \pm 9.01\%$, and $25.6 \pm 7.25\%$, respectively. Some stations in Guanabara Bay showed values of quartz differentially higher than the other stations, namely, stations BG-02 (53.0%), BG-03 (91.9%), BG-09 (64.8%), BG-35 (77.7%), and BG-36 (59.8%). It is worth noting that the station BG-03 had the highest value found for grain size ($200 \mu\text{m}$), depending on the occurrence of the mineral quartz present in the sample.

Quartz often showed an average abundance of less than or close to 20% in the Guanabara Bay (Fig. 3), with a higher concentration in Jurujuba Sound (station BG-03). Minimum values of 3.1% and 3.9% were recorded for this mineral in stations BG-19 and BG-28, respectively. The southern sector

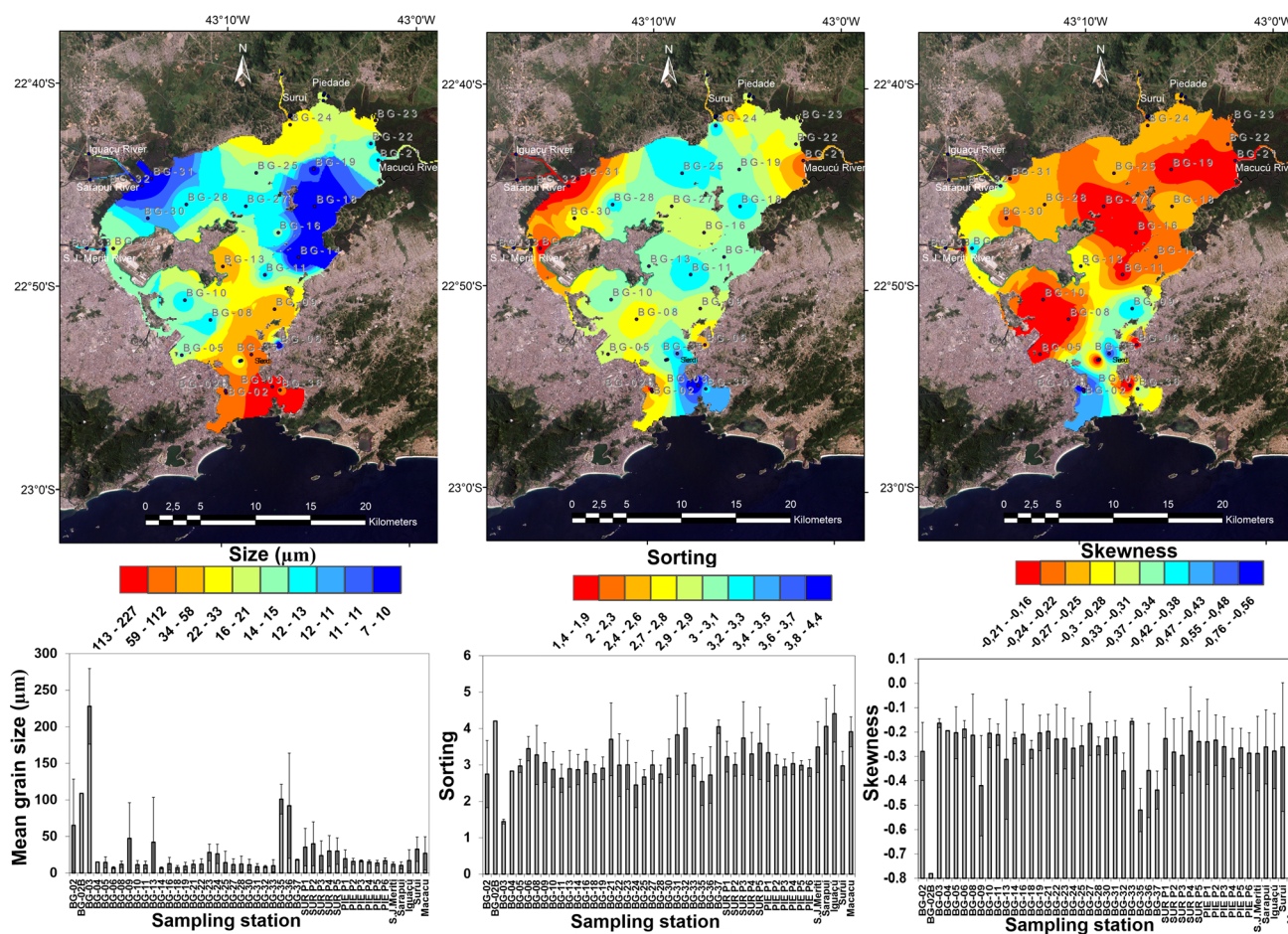


Fig. 2 Average grain-size sorting and skewness of sediment distribution on maps and for each sampling point at Guanabara Bay (BG), Surui (SUR), Piedade (PIE) mangroves, and São João do Meriti, Sarapuí, Iguaçu, Suruí, and Macacu rivers

sampling stations of Guanabara Bay showed the highest values of quartz since these areas have a higher influence on hydrodynamic processes due to their proximity to the marine environment (Fig. 3).

The muscovite was generally abundant and had a higher incidence in northern and northeastern areas of the bay (Fig. 3), with average values of $27.3 \pm 11.7\%$. Stations with the lowest value were the stations corresponding to the entrance of Guanabara Bay BG-02, BG-03, BG-09, and BG-36 stations (Fig. 3). These stations were also the ones with the values of the highest coefficient of variation between the campaigns. Equivalent average values were observed in the areas of Surui and Piedade mangroves with an average value of $27.1 \pm 4.28\%$. The sediments of the rivers presented average values of $21.4 \pm 8.13\%$.

The distribution of kaolinite between sampling stations also showed a high frequency and high variability (Fig. 3). Kaolinite presented average values of $14.2 \pm 8.90\%$ in Guanabara Bay sediments, $6.27 \pm 3.48\%$ in Mangrove areas and average values of $12.8 \pm 8.58\%$ in sediments. High values, considering the average between the campaigns, were found

in the BG-30 station located in the northwest of the bay (Fig. 3). This value is due to this station is situated in a hydrodynamically stable area, without being under the influence of ocean waves and out of the influence of river discharges reach the bay. Higher values were found close to the stations BG-31 ($28.4 \pm 2.2\%$), BG-32 ($28.3 \pm 8.2\%$), and BG-33 ($27.4 \pm 2.5\%$). All these stations are located in the northwest of the bay. The lower mean values among the four campaigns were observed in the entry stations in Guanabara Bay, with average values of $0.8 \pm 1.6\%$ for BG-02 station, 9.7% for BG-09, and 0.0% for BG-02B and BG-03 station. Large variability was observed in the stations mentioned above, which showed the lowest values of kaolinite.

Relatively high values of albite were detected at stations near the Botafogo and Sao Francisco sounds (Fig. 4) stations BG-02 and BG-02b with $11.6 \pm 14.6\%$ and $12.6 \pm 14.3\%$. Low concentration values if compared to those described above were observed in the station BG-03 at São Francisco sound that presents $2.5 \pm 7.4\%$ as well in the Iguaçu River mouth, the stations BG-31 and BG-32 that present 2.4 ± 4.9 and $2.9 \pm 5.9\%$.

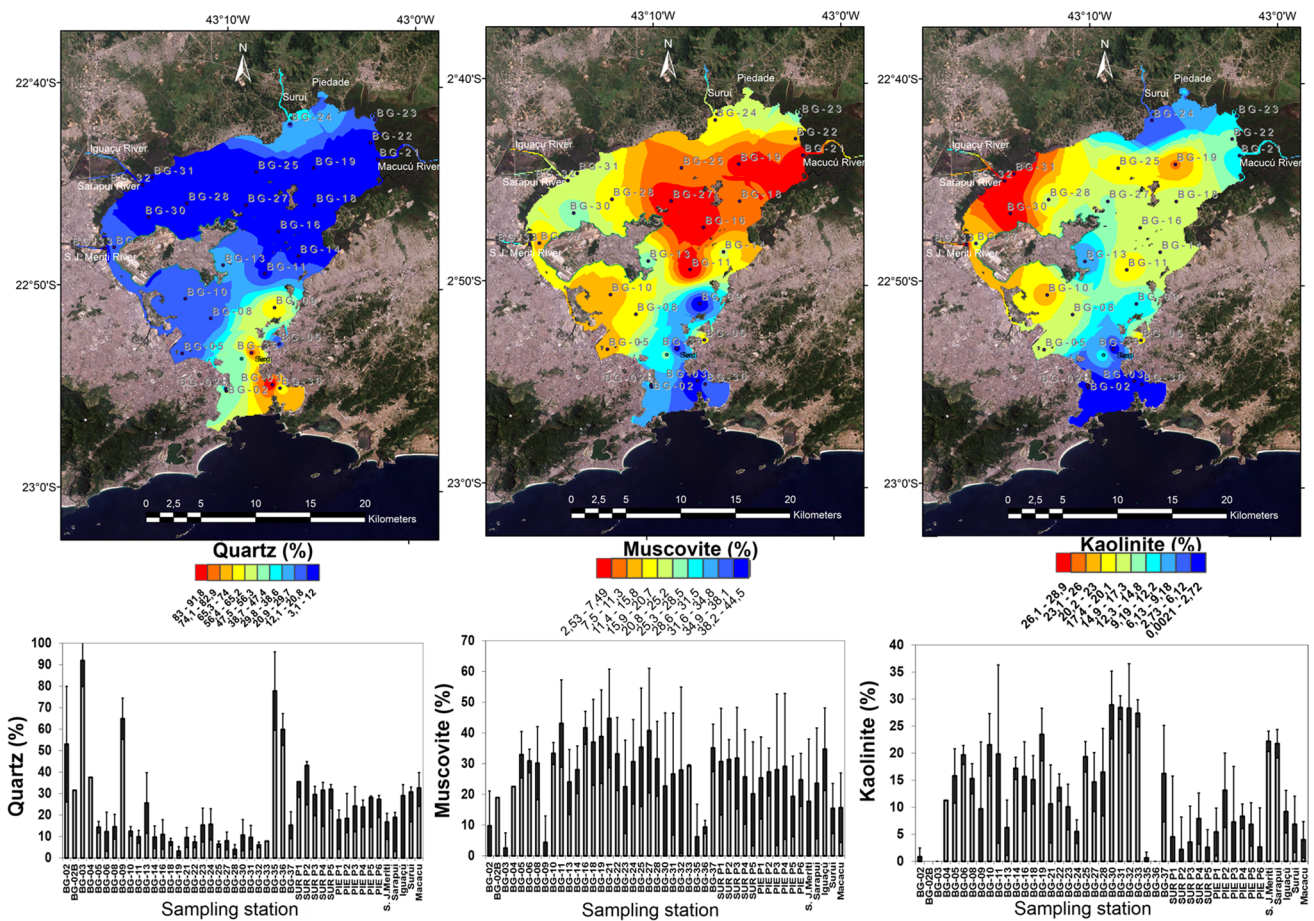


Fig. 3 Average distribution of quartz, kaolinite, and muscovite on maps and for each sampling point at Guanabara Bay (BG), Surui (SUR), Piedade (PIE) mangroves, and São João do Meriti, Sarapuá, Iguaçú, Suruí, and Macacu rivers

The aluminum hydroxide, gibbsite, presented average values of $1.56 \pm 1.51\%$ for Guanabara Bay sediments, $0.97 \pm 0.36\%$ for Surui and Piedade mangrove areas, and $0.66 \pm 0.86\%$ considering the sediment of the rivers studied. The gibbsite showed a gradient decrease in their average contribution from the interior of the bay to its mouth (Fig. 4). The highest value ($5.7 \pm 2.5\%$) was observed at station BG-19. The compartments toward the center of the bay had average contributions in the range of 3.6 to 1.5%.

The microcline presents mean values between the campaigns of $17.9 \pm 7.27\%$ for Guanabara Bay sediments, $23.3 \pm 5.77\%$ for mangrove areas, and $28.8 \pm 11.8\%$ considering the average values of sediments of the rivers. The highest mean values observed in Guanabara Bay sediments were found at stations BG-22 ($24.9 \pm 6.62\%$), BG-23 ($33.8 \pm 10.3\%$), and BG-24 ($25.0 \pm 6.72\%$), corresponding to areas of the mouth of the Guapi-Macacu and Guarai Caceribú Rivers (Fig. 4). The BG-05 station (Rio de Janeiro harbor) and BG-06 (Niterói Harbor) had high values of this mineral with an average of $20.8 \pm 5.04\%$ and $25.3 \pm 5.04\%$, respectively. Stations mouth of São João do Meriti and Iguaçú Rivers, BG-33/BG-37 stations, and BG-32 as well as stations BG-28

and BG-30 in the central sector of the northwestern sector of Guanabara Bay showed values above 20% (Fig. 4).

A low concentration of calcite was found. This contribution was on average, considering the four sampling campaigns in Guanabara Bay $1.88 \pm 1.89\%$, $0.23 \pm 44\%$ for mangrove areas and $0.05 \pm 0.11\%$ for river sediments (Fig. 5). The largest average contribution ($8.37 \pm 2.49\%$) was observed at station BG-24, corresponding to the area of the mouth of the Caceribú River (Fig. 5). Average contributions of 1.7% and near to the detection limit were also observed in different areas of the bay (stations BG-03, BG-6, BG-09, BG-18, BG-21, BG-23, and BG-28). Concerning the average contribution of aragonite, only two stations BG-02 and BG-02B had values of 3.3% and 6.3%, respectively (Fig. 5). In the other stations, the contribution of aragonite was less than 1% (Fig. 5).

Amorphous silica derived from diatomaceous algae structures and sponge spicules (Porifera) was frequently found in samples of Guanabara Bay showing the average values of $4.90 \pm 2.82\%$ (Fig. 5). The maximum average value was observed at station BG-13 ($11.7 \pm 13.3\%$). Probably the highest concentrations of silica in the central sector of Guanabara

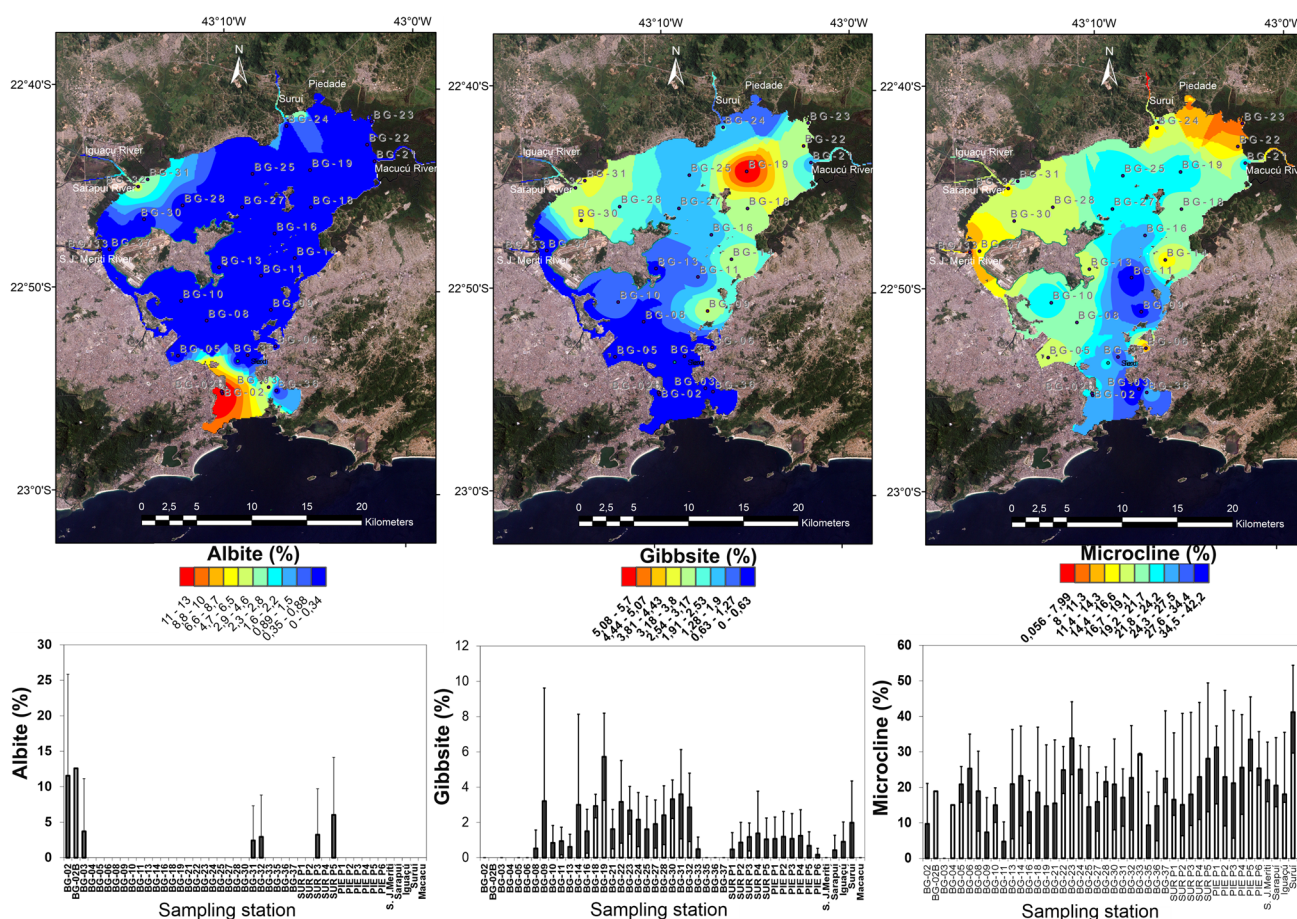


Fig. 4 Distribution of albite, gibbsite, and microcline contents in surface sediments on maps and for each sampling point at Guanabara Bay (BG), Surui (SUR), Piedade (PIE) mangroves, and São João do Meriti, Sarapuí, Iguaçú, Suruf, and Macacu rivers

Bay (Fig. 5) should be associated with diatom productivity, a fact to be confirmed by studies conducted with this group of organisms. The average values of amorphous silica found in the mangroves were $3.57 \pm 1.69\%$ similar to those found for Guanabara Bay. The average value found for the rivers was 0.69 ± 1.04 significantly lower than those observed for Guanabara Bay and mangroves (MW, $p < 0.05$).

Bulk organic matter

The concentrations of organic carbon values were within the range of 1.47 to 21.8%, as also reported by previous studies in several areas of Guanabara Bay (Baptista Neto et al. 2000; Carreira et al. 2002; Kehrig et al. 2003; Farias et al. 2007). The highest TOC concentrations were observed in a mangrove located in an area of great urban densification and impacted by domestic sewage (Kehrig et al. 2003).

The values of COT for sediments of Guanabara Bay considering the four sample campaigns were average and standard deviation of $3.78 \pm 1.93\%$. These average values were similar to the values of $3.58 \pm 2.94\%$ observed for sediments

of the studied rivers. Mangrove sediments presented relatively higher values concerning the other two compartments of $5.56 \pm 2.69\%$, however, not significantly different between them (MW, $p < 0.05$). Considering the spatial distribution in Guanabara Bay, the minimum value of $0.03 \pm 0.001\%$ was observed for the station BG-03. Minimum values, considering average values for the four sampling campaigns, lower than 1% were observed for stations BG-02, BG-02B, and BG-09 (Fig. 6). The highest mean value for the four campaigns was observed in Guanabara Bay at station BG-08, reaching $6.20 \pm 0.25\%$. In general, it was observed that the area with the highest concentrations of carbon is located in central stations in the northern sector of the bay outside the influence of river discharges, which correspond to stations BG-30, BG-28, BG-25, and BG-18 (Fig. 6).

The C/N ratio showed variations which comprised range values between 6.21 which represents a predominantly phytoplankton source in Guanabara Bay and 20.9 in the mangrove, this value denotes a lignocellulosic source of mangrove vegetation. Guanabara Bay presents an average of 10.5 ± 2.44 according to algae productivity significantly lower

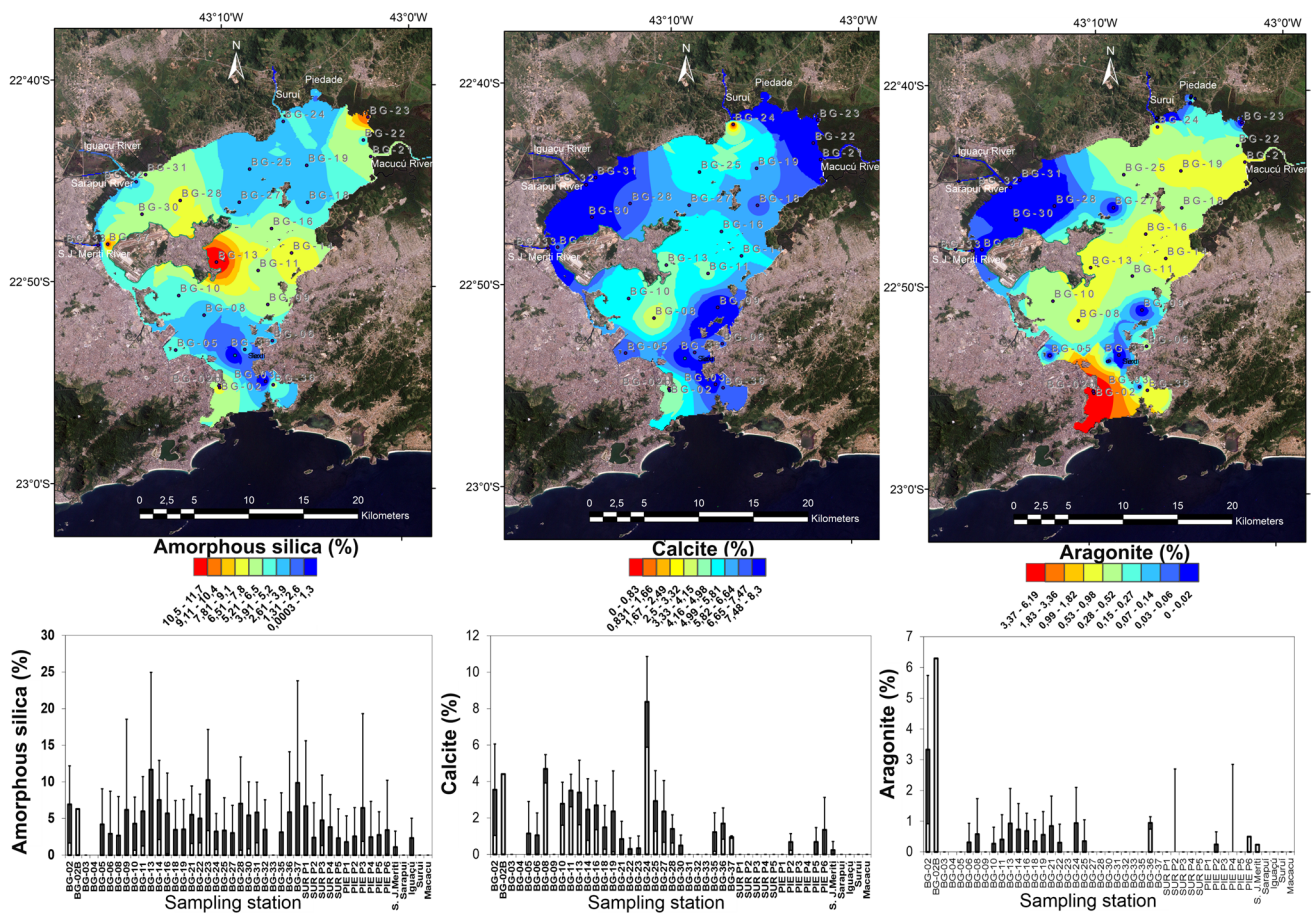


Fig. 5 Distribution of amorphous silica, calcite and aragonite on maps and for each sampling point at Guanabara Bay (BG), Surui (SUR), Piedade (PIE) mangroves, and São João do Meriti, Sarapuí, Iguaçu, Suruí, and Macacu rivers

(KW, $p < 0.05$) than the C/N ratio of mangrove areas with 18.8 ± 1.12 . The C/N ratio in the river’s sediment presents intermediated values considering the bay and mangroves sediments with average values of 12.6 ± 1.98 (Fig. 6). Higher values of this ratio were found at stations adjacent to the river’s mouth, testifying input lignocellulosic refractory material, from the sub-drainage basins of the rivers and mangrove areas. The highest value in Guanabara Bay of 16.1 ± 3.20 was found in BG-23 station at the mouth of the Guapi-Macacu river that drains an extensive area of forest and mangrove remnants (Fig. 6). The average C/N ratio is slightly higher in the sectors representing the north sector at sample stations adjacent to mangrove areas, which present lignocellulosic contributions. These values were more pronounced than in the central sector of the bay to which it presents a greater influence of phytoplankton source on organic matter (Fig. 6).

Isotopic composition of organic matter

The $\delta^{13}C$ values found in this work varied between -27.4‰ (recorded in mangrove area) and -20.5‰ (found in

sediments from the bay) (Figs. 7 and 8). The average value from Guanabara Bay of $-22.8 \pm 1.7\text{‰}$ is heavier than observed in mangrove and riverine sediments that present average values of $26.8 \pm 0.42\text{‰}$ and $25.4 \pm 0.51\text{‰}$, respectively. The difference between Guanabara Bay sediments and mangrove sediments was significant (KW, $p < 0.05$), corroborating a phytoplankton influence for bay sediments and suggesting the predominance of lignocellulosic-derived organic matter as the main source in mangrove sediments. The $\delta^{13}C$ rivers samples values suggest a more strong influence of domestic sewage discharges. The elemental analysis presented above is in agreement with these interpretations. The spatial variation of the data and the relationship between the isotopic signatures show a distinction between the isotopic composition that comes from the estuarine pelagic system, more enriched in ^{13}C , mangrove vegetation remaining and riverine organic matter from the drainage system vegetation and sewage discharges. The latter two less enriched in ^{13}C , while the river environment generally had intermediate values observed in the two other types of environment.

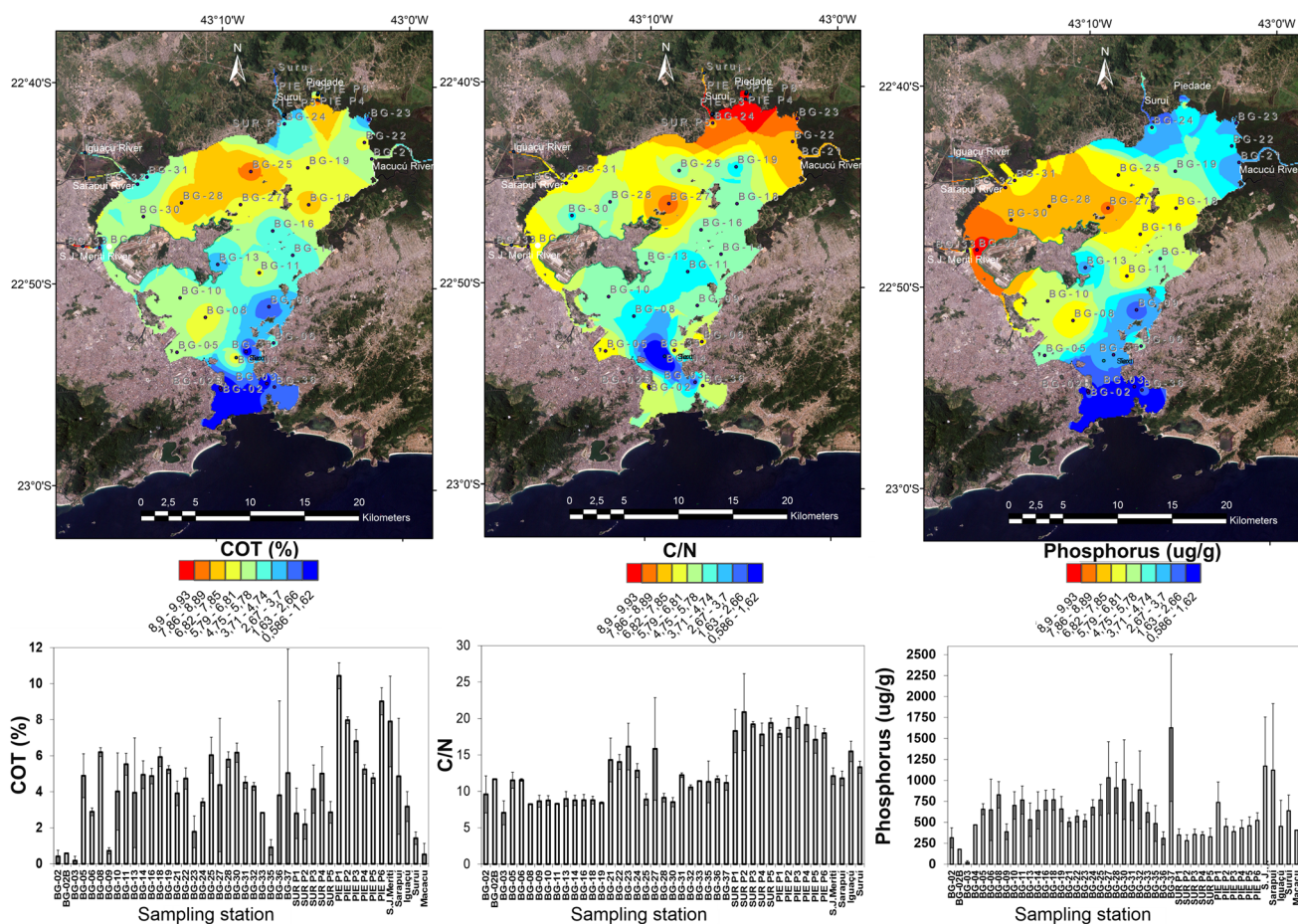


Fig. 6 Distribution of total organic carbon, the C/N ratio, and phosphorus on maps and for each sampling point at Guanabara Bay (BG), Suruí (SUR), Piedade (PIE) mangroves, and São João do Meriti, Sarapuá, Iguaçú, Suruí, and Macacú rivers

The Guanabara Bay sediment presents a high influence of the biogeochemistry fractioning of primary productivity. The carbon isotope fractionation between CO_2 (aq) and phytoplankton decreases in environments with increased productivity and high concentration of dissolved inorganic C dominated by HCO_3^- , which has a concentration of $\delta^{13}\text{C}$ around 0‰. The incorporation of inorganic C dissolved in marine phytoplankton generates $\delta^{13}\text{C}$ values typically between $-22‰$ and $-20‰$ (Meyers 2003). Another mechanism of the increase in $\delta^{13}\text{C}$ values can be increased by the removal of algae ^{12}C leaving the dissolved inorganic carbon isotopically heavier (Meyers 2003). In agreement with the results of the higher C/N ratio, the carbon isotopic analysis showed that mangrove sediments and environments near the mangrove area of the APA Guapimirim were less enriched in ^{13}C , while the sediments of the other areas showed an isotopic signature more characteristic of autochthonous production influence of assimilation of HCO_3^- from marine origin. Freshwaters, which in these rivers are rich in nitrate and silica, are also lower in DIC

than marine waters. High nutrient levels combined with low DIC levels may have caused less isotope discrimination against the heavier DIC as observed by Matson and Brinson (1990) in estuaries of North Carolina explains the low values of ^{13}C in sediments near the Guanabara entrance (BG-03, BG-02, BG-02B).

The $\delta^{15}\text{N}$ values ranged between 1.19 and 6.77‰ (Fig. 7). The average values of $\delta^{15}\text{N}$ considering the four sample campaigns were $4.45 \pm 1.59‰$ for bay sediments, $3.72 \pm 0.85‰$ for mangrove sediments, and $3.95 \pm 0.26‰$ for river sediments. As observed for the isotopic carbon composition, $\delta^{15}\text{N}$ also showed seasonal and spatial variability in the bay (Fig. 7). The lowest average values were found in the southern sector and on the west and north shores of Guanabara Bay where organic sewage discharges are most pronounced. The stations adjacent to the mangroves of Suruí and Piedade also present low values in the range of 0.78 to 3.95‰. In the central compartment, the $\delta^{15}\text{N}$ values are higher with average values in the range of 4.16 to 5.98‰. The values increase toward the eastern sector of the Guanabara Bay,

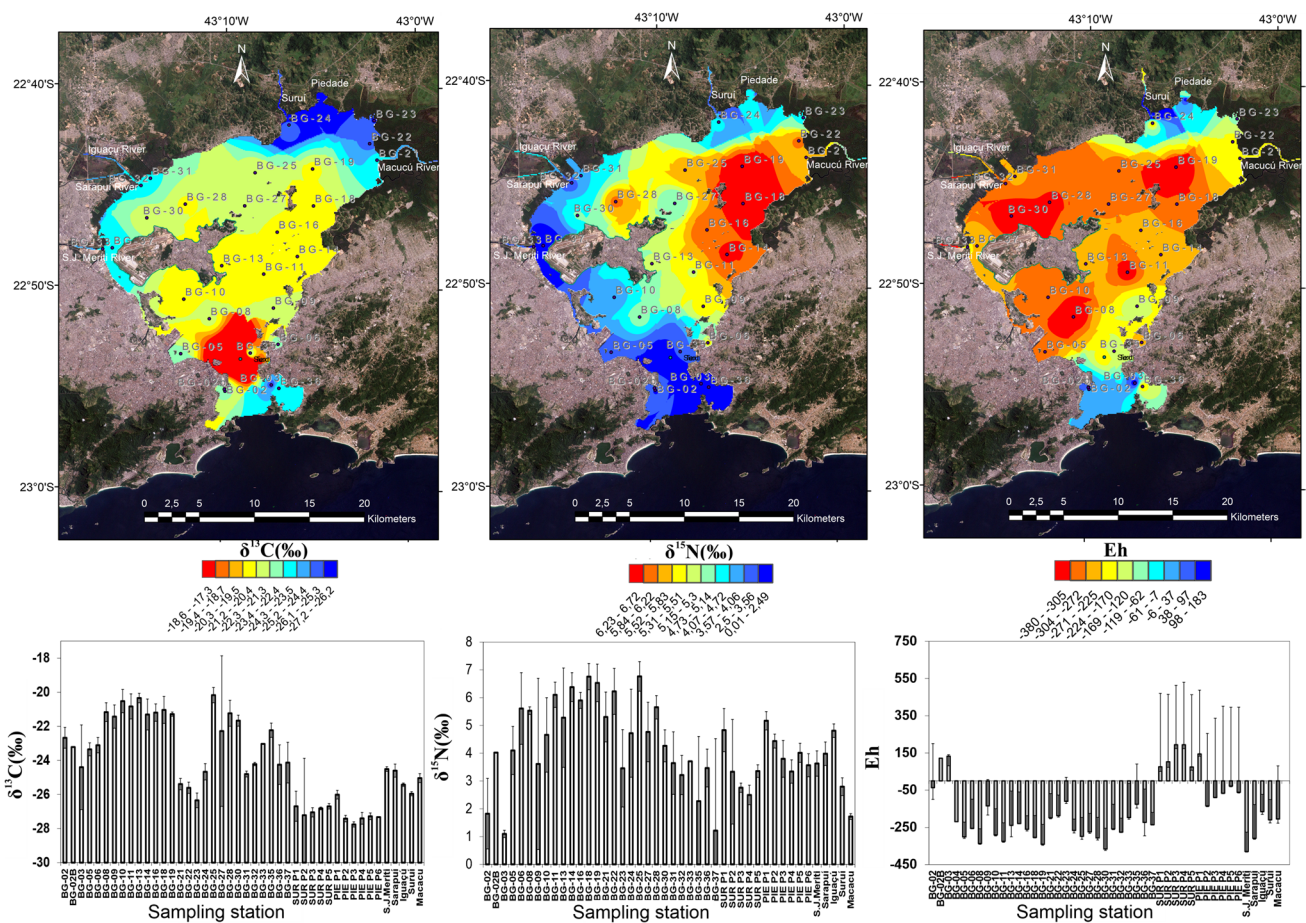


Fig. 7 Distribution $\delta^{15}\text{N}$, $\delta^{13}\text{C}$, and Eh in surface sediments layers on maps and for each sampling point at Guanabara Bay (BG), Surui (SUR), Piedade (PIE) mangroves, and São João do Meriti, Sarapu, Iguacu, Surui, and Macacu rivers

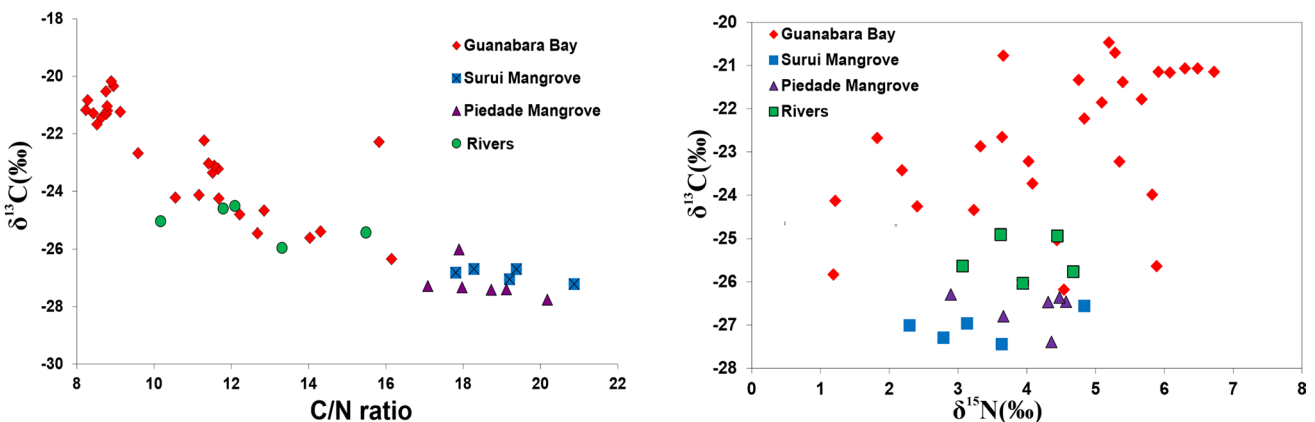


Fig. 8 Carbon isotopic composition versus C/N ratio (a) and versus nitrogen isotopic composition (b) in surface sediment samples

which can show intense primary productivity processes with values above 6.00‰ (Fig. 7).

Increased organic N load from municipal sewage discharge along the lower reaches of the river is another

potential N. The generation of urea and solid human and animal waste can produce sources of NO_3^- and NH_3 enriched with ^{15}N by atmospheric loss of ^{14}N (Herczeg et al. 2001). However, in the north-west sector, low values

of $\delta^{15}\text{N}$ can be observed, which implies that atmospheric fixation processes may be predominant. Even in an area with low redox potential (Fig. 7) in the western sector of Guanabara Bay where intense denitrification processes would be expected, values of $\delta^{15}\text{N}$ are observed to decrease. Two factors may be contributing to this finding: biogeochemical processes of methanogenesis and fixation of atmospheric nitrogen by Cyanophyceae. Nitrogen-fixing species (cyanobacteria in general) can fix atmospheric N when the concentration of dissolved inorganic nitrogen in the system is low. This setting results in $\delta^{15}\text{N}$ values, coming close to those found for the atmospheric nitrogen (N_2).

During periods of high productivity due to lack of availability of nutrients in the environment, phytoplankton can assimilate the available, the dissolved nitrogen, which tends to be more enriched in ^{15}N , when compared to periods of lower productivity (Meyers 1997). This is caused by a breakdown of the isotope that decreases with the decrease in nutrient availability (Macko and Estep 1984; Macko and Pereira 1990). Phytoplankton assimilates N isotopic composition due to the natural enrichment of assimilable N (NO_3 or NH_4) (Herczeg et al. 2001).

One of the most important biogeochemical mechanisms governing N transformation is denitrification (Lofton et al. 2007). The process of denitrification is an important process of isotopic fractionation enriching the remaining forms of nitrogen in the water column with the heavier isotope $\delta^{15}\text{N}$ presenting the most positive value. This is a process that can contribute to the increase of $\delta^{15}\text{N}$ values in sediments with low redox potential in Guanabara Bay. The sediments of mangrove areas, since they are most exposed to atmospheric oxygen at low tide, are more restricted to the denitrification processes (Fig. 8).

In the diagram of the relationship between $\delta^{13}\text{C}$ and C/N ratio (Fig. 8) could be seen the separation between two sedimentary environments: (1) The $\delta^{13}\text{C}$ values around -22‰ and low values of C/N suggest an enhanced contribution of phytoplankton to the sedimentary organic matter pool, responsible to inorganic carbon assimilation of marine origin in the form of HCO_3^- (Fig. 8). These values correspond to stations in Guanabara Bay. (2) The second group is characterized by mangrove sediments that have $\delta^{13}\text{C}$ values around -27‰ and high values of the C/N ratio (Fig. 8). A clear trend is observed in phytoplankton origin in the central sector with ranging values of $\delta^{13}\text{C}$ between -21 and -20‰ (Fig. 8).

The diagram proposed by Meyers (2003), in which values of $\delta^{13}\text{C}$ are plotted against C/N ratios, evidenced a very clear distinction between the source of the organic matter that characterized the sediment recovery in the

bay, riverine, and mangroves zones (Fig. 8). It was possible to separate the stations into two groups related to the characteristics of organic matter. The first comprising the organic matter of planktonic origin and another predominantly an organic matter of terrestrial/mangrove origin.

Palynofacies

The concept of palynofacies was first introduced by Combaz in 1964 to describe in the palynological studies the total assembly of the particulate organic matter contained in the sediment after removal of the sediment matrix by HCl and HF (Ercegovac 2006). However, currently, there are different definitions and classifications of palynofacies in the literature. Powell et al. (1990) defined as palynofacies an assembly characteristic of organic matter insoluble in HCl and HF, whose composition plays a specific sedimentary environment. Cornford et al. (1979) defined “organofacies” as an organo-petrographic parameter and geochemical features that have a particular association of the sediments. Rogers (1980) used the term palynofacies to define the organic content of the sediment, the source of organic matter, and the depositional environment (Ercegovac 2006). The palynofacies is strongly affected by the origin and the stage of biodegradation of organic matter (Ercegovac 2006) and can be divided into three groups: palynomorphs, phytoclasts, and amorphous. The phytoclasts and palynomorphs present structured forms and amorphous are unstructured. The phytoclasts represent fragments derived from plants or their degradation, and the amorphous components are all unstructured organic particles, including organic matter derived from phytoplankton or bacteria and higher plants resins and amorphous products of diagenesis macrophytic tissue (Tyson 1995).

The particles considered autochthonous or allochthonous may vary according to the depositional environment. The autochthonous organic matter can include not only phytoplankton but also particles of aquatic plants, while the allochthonous organic matter (terrestrial) comprises particles weathered from the watershed (Sebag et al. 2006).

In the group of phytoclasts, there are two categories: (1) preserved fragments (cuticle and lignocellulosic translucent), which have initial biogenic structures and (2) fragments processed (gelled material, lignocellulosic opaque, and charcoal), which have characteristics resulting from their degradation or thermal maturation (Sebag et al. 2006). The plant fragments are observed in various degradation stages: cuticle and translucent lignocellulosic correspond to the better preservation stage. The gelled material corresponds to the phytoclasts degradation in reducing environment, and lignocellulosic opaque and

oxidized charcoal match phytoclasts in reducing environment, the second being formed only at high temperatures (Sebag et al. 2006). The cuticles are extra-resistant cell layers covering the epidermis of higher plants and are characterized by the cellular structure unchanged and the presence of stomata and palisade parenchyma, with a structure more or less visible (Ercegovac 2006). Cuticles are typical of fluvial environments—deltaic, prodelta, estuarine—mangrove, or underwater environments nearby (Ercegovac 2006).

The most distinct lignified structures (lingo-cellulosic translucent) seen in palynological preparations are portions of the xylem, including tracheids and vessels. Lignified wood is extremely common in palynofragments of marine and non-marine, but is highly dependent on proximity to the source. This category is usually present in areas near the deltas, increases with the addition of sand or silt components, and decreases with decreasing grain size (Ercegovac 2006). The category opaque lignocellulosic fragments appear as opaque highly degraded/corroded/damaged, elongated shapes and angular edges. It is generated by the change of lignocellulosic fragments in an oxidizing environment, the normal or elevated temperatures, maybe abundant or common in muddy areas (coastal plain), delta-front and prodelta, freshwater marsh, pond, lake, and river sediments (Ercegovac 2006).

The amorphous organic matter can also be originated from the degradation of plant material by bacteria, or fecal remains of zooplankton and can be either diffuse, reddish, or opaque. The diffuse amorphous organic matter comes mainly algal and bacterial organic matter that is mainly amorphous red macrophytes and terrestrial plants, organic matter, and amorphous, opaque phytoclasts highly altered and oxidized by repeated cycles of degradation.

The diffuse amorphous organic matter comprises a large proportion of dead or live bacteria and often represents an intimate association with clay minerals. Sedimentary processes of “amorphization” take place in the photic zone, where much of the consumption and remineralization of biomass occurs at or near the sediment–water interface (Ercegovac and Kostić 2006). Predominantly the organic matter found in Guanabara Bay is characterized as diffuse amorphous organic matter. The sediments of Guanabara Bay presented values of diffuse amorphous organic matter of $76.5 \pm 8.4\%$. In Guanabara Bay, the diffuse amorphous organic matter was found with values between 38.9 and 84.5%. The average values for Guanabara Bay did not differ significantly from those observed for mangrove areas and for the sediments of the rivers which presented values of $78.3 \pm 1.68\%$ and $77.4 \pm 6.15\%$, respectively. A higher concentration was observed at the entrance of the bay (BG-35) and in the eastern sector adjacent to the Governor’s Island

(BG-13). The distribution and variations of this category can be seen in Fig. 10. Given that diffuse MOA represents organic matter from phytoplankton and bacteria, and that it is therefore expected to be found in much higher percentages in bay bottom sediments than in rivers and mangroves, it is plausible to assume that the rivers and mangroves analyzed are being eutrophicated. This eutrophication is probably occurring due to the large contribution of domestic sewage.

The reddish amorphous organic matter consists of groups of colloidal particles that appear dark red under transmitted light (Graz et al. 2010) and present a more degradation state and was found in three sampling points at Guanabara Bay sediments. The average values for reddish organic matter in Guanabara Bay sediments were $0.35 \pm 1.01\%$. For the mangrove areas, the average value was $0.026 \pm 0.062\%$ and absent in the rivers studied.

The gelified material corresponding to the degradation of phytoclasts material in reducing environment found in higher percentages on the shores of the bay from the west to the northeast sector focusing on the River São Joao do Meriti mouth (BG-37), near the Rio Iguacu mouth (BG-31) and close to the Guapi-Mirim environmental protection area (BG-21, BG-22, BG-23, and BG-24). Gelified material presents an average value of $3.37 \pm 1.50\%$ for Guanabara Bay sediments, $5.09 \pm 1.28\%$ for mangroves area, and $2.87 \pm 0.62\%$ for riverine sediments. Its distribution and its variations can be observed in Fig. 9.

Translucent lignocellulosic debris showed average values of $5.09 \pm 1.28\%$ for Guanabara Bay, for mangrove areas and rivers studied the average values were $6.50 \pm 1.61\%$ and $6.23 \pm 1.48\%$, respectively. Translucent lignocellulosic found mainly at the border of the northeast sector of the bay, near the area of the Guapi-Mirim environmental protection area (BG-21, 22, 23, 24 stations) and in the central bay, between the Rio-Niteroi Bridge and Governador Island (BG-08). Its distribution and its variations (Fig. 10) must reflect the deposition of terrigenous organic matter with a palustrine origin deposited (Boussafir et al. 2012) in an oxidizing environment. When we look at the map of the lignocellulosic translucent distribution in Guanabara Bay, we can see that the highest percentages occur near the APA Guapi-Mirim and mangrove areas, these areas, which are probably being the source of this material to the Guanabara Bay.

The second more representative type of organic material was the opaque lignocellulosic, but in a much smaller quantity. The category of lignocellulosic opaque was found with values between 6.31 and 18.3%, i.e., much lower percentages than the diffuse amorphous organic matter. In Guanabara Bay, the average concentration was $11.4 \pm 2.6\%$. In the mangrove areas, the mean values were $9.68 \pm 2.23\%$ and $13.7 \pm 4.76\%$ to rivers sediments. The highest concentrations were observed at stations near the

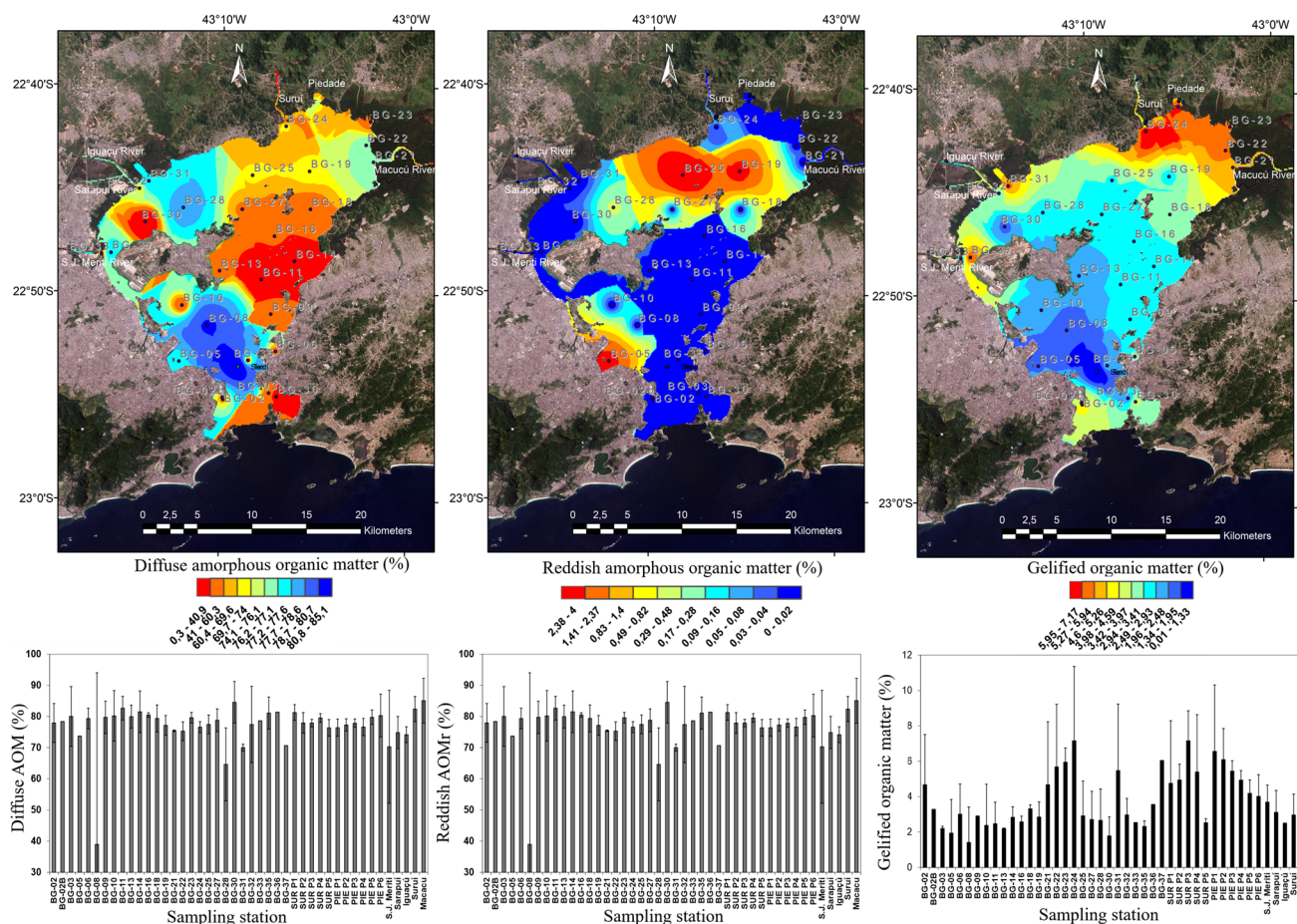


Fig. 9 Organic matter petrography types: diffuse amorphous organic matter, reddish amorphous organic matter and gelified organic matter on maps and for each sampling point at Guanabara Bay (BG), Suruí

(SUR), Piedade (PIE) mangroves, and São João do Meriti, Sarapuí, Iguaçú, Suruí, and Macacú rivers

Marina da Gloria sound (BG-02 and BG-02B), close to São Gonçalo (BG-16 and BG-18) and in the southwestern sector Bay, the Rio de Janeiro harbor (BG-05). However, the highest values were found in stations BG-28, BG-31, and BG-33, all located in the northwest of the bay (Fig. 10). This distribution appears to be associated with areas where the degradation of organic matter is so anaerobic.

The category cuticle found in very few percentages, which was concentrated on the shores of the northeastern sector of the bay, downstream of the Suruí and Piedade rivers (BG-24). A large value was observed at station BG-08. This station showed anomalous behavior for several parameters, which may be an area influenced by the dumping of dredged material.

In the principal component analysis considering the studied variables (Fig. 11), it can be observed that the sample stations at the entrance of Guanabara Bay had an influence of quartz, aragonite, and albite associated with

a high-energy environment with high particle size. The primary production processes are evidenced mainly in the central sector, notably, in stations BG-13, BG-24, and BG-10 with an association between high values of $\delta^{13}C$, diffuse amorphous organic matter both representative of algal material and gelified organic matter representative of the anaerobic oxidation in the interface water–sediment. The association of these variables with amorphous silica suggests that some of the primary production is highly influenced by diatomaceous production. Mangrove areas present notably high C/N ratios denoting a predominance of lignocellulosic organic matter. The mouths of the rivers and adjacent stations have an association of organic matter with opaque lignocellulosic organic matter and opaque amorphous organic matter showing extremely reducing conditions in these environments.

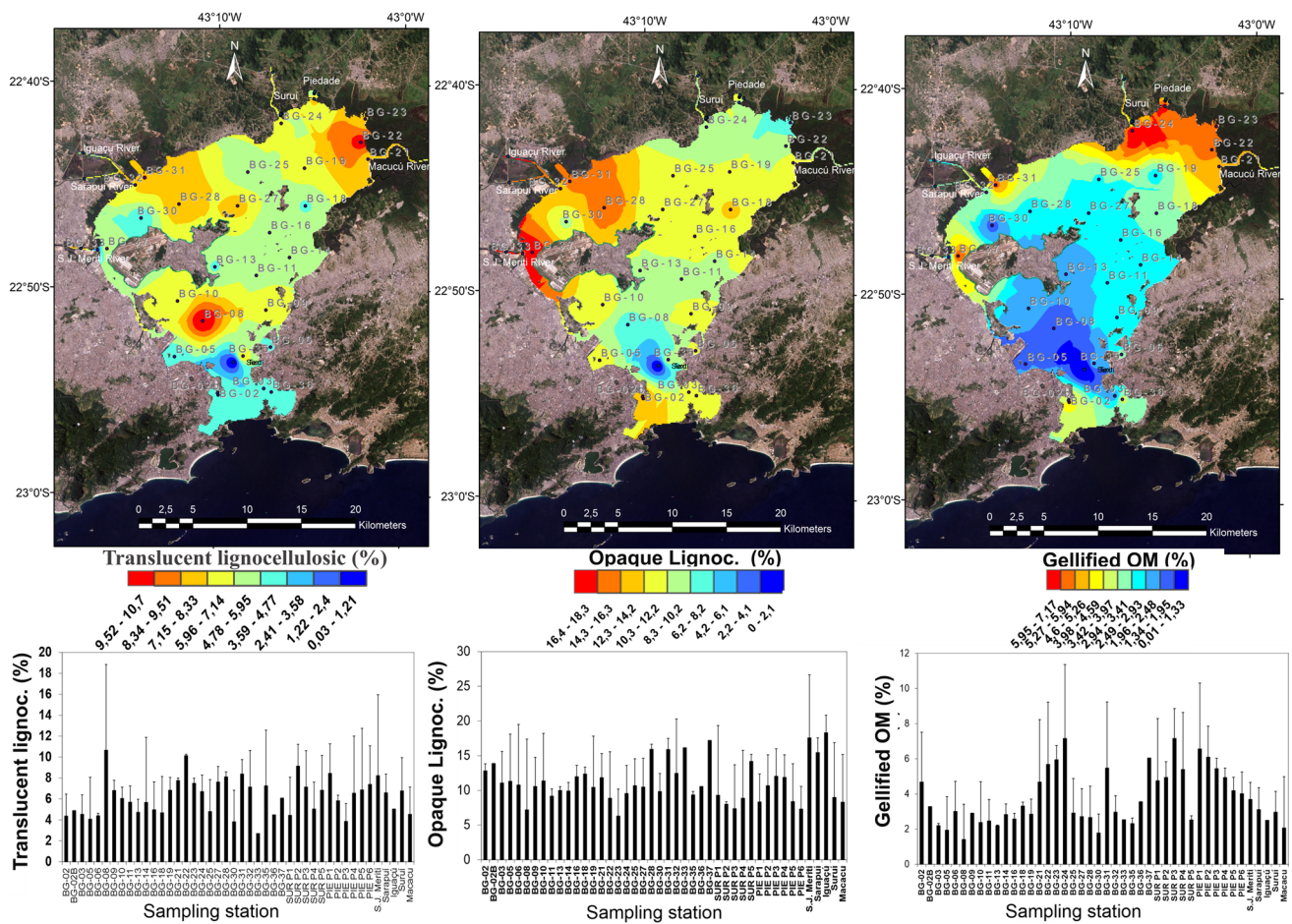


Fig. 10 Organic matter petrography types: Translucent lignocellulosic, opaque lignocellulosic, and gellified particles on maps and for each sampling point at Guanabara Bay (BG), Surui (SUR), Piedade (PIE) mangroves, and São João do Meriti, Sarapuú, Iguaçú, Suruí, and Macacu rivers

Conclusion

Guanabara Bay presented a variety of depositional environments attested by sedimentological, organic, and mineral indicators. Considering the sampling grid, a clear distinction between marine and continental environments and their respective gradients was observed. The southern sector of the bay showed a trend for higher concentrations of quartz minerals and carbonates such as calcite and aragonite. In contrast, the northern sector showed a significant trend for the deposition of minerals normally linked to clay and silt such as kaolinite, muscovite, and microcline. River discharge carries fine-textured mineral particles such as kaolinite, muscovite, and microcline which are deposited in river mouths adjacent areas with lower hydrodynamics. It should be noted that the northwestern sector of the Guanabara Bay due to the low hydrodynamics presented the

highest concentrations of kaolinite making this sector more susceptible to the adsorption of contaminants.

As the mineral elements of finer texture, the organic matter studied showed a tendency for the increase of its concentrations within a northward gradient. A marked increase in total organic carbon concentrations was observed in the north-central sector, at stations where the estuarine and river hydrodynamics is softer. The river mouths of the northwestern sector presented lower average carbon values than the adjacent central areas probably due to the higher hydrodynamics attested by a higher concentration of quartz in relation to those adjacent areas. Total phosphorus values were high in these areas due to the large discharge of domestic sewage. Nitrogen isotope data characterized the central-eastern sector as probably one area of intense cycling is an important organic matter, mainly related to the high productivity process that occurs in these areas.

Concerning the organic matter sources, there was a clear separation between the areas under influence of lignocellulosic organic matter at the river mouths and mainly in

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