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Bioavailability of Organic Matter in the Superficial Sediment of Guanabara Bay, Rio de Janeiro, Brazil

Biodisponibilidade da Matéria Orgânica dos Sedimentos Superficiais da Baía de Guanabara, Rio de Janeiro, Brasil

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Abstract

Thirty superficial sediment samples were collected in Guanabara Bay in order to identify new trophic state and environmental quality descriptors for coastal systems. A biochemical approach was used for analyzing the quality and quantity of sedimentary organic matter and metabolic bacterial activity. The samples were analyzed for particle size; organic matter, protein, carbohydrate, lipid, biopolymeric carbon, and bioavailable carbon levels; and bacterial metabolic activity. The results show a homogeneous spatial distribution for the anaerobic bacteria web and for biopolymers (carbohydrates>lipids>protein). The NE area of the bay displayed sediment lipid levels above 1 mg/g, indicative of organic sewage input. Spatial distribution of the superficial sediments in relation to other variables was not significant ($p>0.05$). Biopolymers and labile organic matter showed a significant correlation with the average particle size of 80% of the fine particles. Despite the availability of labile organic matter, under the form of biopolymeric carbon, only 50% of the carbon was available to the trophic web. The bacterial consortia formed by sulfate reducing and denitrifying bacteria sustain the benthic trophic food web in Guanabara Bay.
Keywords: Biochemical composition, sediment, bacterial activity; organic matter; Guanabara Bay

Resumo

Foram coletadas 30 amostras de sedimentos superficiais na Baía de Guanabara, com o objetivo de identificar novos descritores de estado trofico e qualidade ambiental do ecossistema costeiro, usando análises bioquímicas para quantificar e qualificar a matéria orgânica sedimentar e o metabolismo bacteriano. Foram analisados a granulometria, teor de matéria orgânica, teores de proteínas, carboidratos, lipídeos, cabono biopolimérico, carbono biodisponível e atividade metabólica bacteriana. Os resultados mostraram uma distribuição espacial homogênea para a teia bacteriana anaeróbia e os biopolímeros (carboidratos>lipídeos>proteínas). O NE da Baía apresentou teores de lipídeos acima de 1 mg/g de sedimento, indicativo de aporte de esgoto orgânico. A distribuição espacial dos sedimentos superficiais em relação às variáveis não apresentou significância ($p>0,05$). Os biopolímeros e a matéria orgânica apresentaram correlação significativa com a granulometria média de 80% dos finos. Apesar da disponibilidade de matéria orgânica lábil, sob a forma de carbono biopolimérico, o carbono disponível para a teia trófica está em torno de 50%. O consórcio bacteriano formado por bactérias sulfato redutoras e desnitrificantes sustentam a teia trófica bêntica da Baía de Guanabara.
Palavras chave: Composição bioquímica, sedimento, atividade bacteriana; matéria orgânica; Baia de Guanabara

1 Introduction

The discharge of excessive nutrients from municipal and industrial waste waters, as well as urban and agricultural run-off, leads to an increase in inorganic and organic material in marine waters. This input, which results in eutrophication, is one of the major stresses to marine environment (Meyer-Reil & Koster, 2000).

Within aquatic ecosystems, bottom sediments have an important function as an efficient natural trap for various substances (including contaminants) and also as a natural regulator of the processes that occur within the sea floor. They can store large amounts of organic matter and affect the oxygen content of bottom water. Bottom sediments also constitute a source of nutrients for the water column above them, leading to benthic-pelagic coupling and influencing primary productivity (Jørgensen, 1996).

The sedimentary organic matter in coastal areas is mainly derived from primary and secondary production within the ecosystem, inputs of terrestrial material, and bacterial production in the sediments themselves. The relative importance of these sources is determined by local factors such as climate, nutrient supply, hydrodynamic conditions and biogeochemistry of the water. Changes in any of these factors, including human disturbance, may then be reflected on the sedimentary organic matter (Pinturier-Geiss *et al.,* 2002).

Sediments area ‘‘recorder’’ of water column processes and the final storage for the accumulation of autochthonous and allochthonous organic matter inputs (Fabiano and Danovaro, 1994). Therefore, extending Nixon’s concept of organic supply, we can assume that concentration and composition of the sedimentary organic matter are important indicators of the trophic state of marine environments (Fabiano *et al.,* 1995; Danovaro *et al.,* 1999).

Marine sediments are intensively colonized by microorganisms (bacteria, cyanobacteria, fungi, algae; size <<150 μm). Most are organized in biofilms, complex associations of microbes, immobilized on surfaces and embedded in an extracellular organic matrix, consisting of extracellular polymeric substances (EPS) secreted by the cells. By their organization in biofilms, the organisms create their own microhabitats with pronounced biological and chemical parameter gradients. Along these gradients they can use substrates and energy efficiently (Meyer-Reil, 1994). Microorganisms are present in high numbers in sediments (about 10^{10} cells g^{-1} d.w.). Their biomass is greater than the biomass of all other benthic organisms and their cell surface exceeds by far that of all other organisms. Microbes possess a high surface-to-volume ratio, indicating their high metabolic activity rates. Dissolved inorganic and organic substrates can be metabolized with high substrate affinity and specificity. Particulate organic matter can be decomposed in close contact with the substrate by hydrolytic enzymes. Beside oxygen, microbes may use alternative electron acceptors (nitrate, manganese, iron, sulfate, and carbon dioxide) for the oxidation of organic material. Combined with their logarithmic growth and short generation times (less than 1 h), microbes possess a high metabolic potential (Meyer-Reil & Koster, 2000).

The aim of this investigation was to identify new descriptors for trophic state and environmental quality of coastal systems, using a biochemical approach applied to the analysis of the quality and quantity of sedimentary organic matter and metabolic bacterial activity.

2 Environmental Setting

Guanabara Bay is located in Rio de Janeiro State, Southeast Brazil, 22°40`–23°00`S latitude and 043°00`–043°18`W longitude. It is one of the largest bays on the Brazilian coastline and has an area of approximately 384 km^2, including islands. According to Amador (1980), the bay coastline is 131 km long, and the mean water volume, $1.87 \cdot 10^9$ m^3. The bay measures 28 km from west to east and 30 km from south to north, but the narrow entrance to Guanabara Bay is only 1.6 km wide (Kjerfve *et al.,* 1997). Guanabara Bay has a complex bathymetry with a relatively flat central channel. The channel is 400 m wide, stretches from the mouth more than 5 km into the bay, and is defined by the 30-m isobath. The bay’s deepest point measures 58 m and is located within this channel (Kjerfve *et al.,* 1997). According to these same authors, north of the Rio de Janeiro-Niterói bridge, the channel loses its characteristics as the bay rapidly becomes shallower, with an average depth of 5.7 m, due to high rates of sedimentation, accelerated in the past century by anthropogenic activities in the catchment area.

Guanabara Bay lies within the tropics of southeastern Brazil, but, due to its coastal location, a humid sub-tropical climate with rainfall levels between 2,500 mm (high altitudes) and 1,500 mm (low altitudes) prevails between December and April. The mean annual temperature is 20 - 25°C (Nimer, 1989). The drainage basin of Guanabara Bay has an area of 4,080 km^2, consisting of 32 separate sub-watersheds (Kjerfve *et al.,* 1997). However, six of the rivers alone are responsible for 85% (JICA, 1994) of the 100 m^3 s^{-1} of total mean annual freshwater input. Nowadays, 11 million inhabitants live in the greater Rio de Janeiro metropolitan area, which discharges tons of untreated sewage directly into the bay. Brazil's second largest industrial site is found in this area. There are more than 12,000 industries in the drainage basin, which account for 25% of the organic pollution released into the bay (FEEMA, 1990). The bay also harbours two oil refineries along its shores, which process 7% of the nation's oil. At least 2,000 commercial ships dock in the port of Rio de Janeiro every year, making it the second biggest harbour in Brazil. The bay is also home to two naval bases, a shipyard, and a large number of ferries, fishing boats, and yachts (Kjerfve *et al.,* 1997).

In the last 100 years, the catchment area around Guanabara Bay has been strongly modified by human activities, in particular deforestation and uncontrolled settlement, which increased river flow velocities, as well as sediment load and transport to the bay. Consequently, the average rate of sedimentation has increased to 1–2 cm $year^{-1}$ (Godoy *et al.,* 1998).

3 Material and Methods

In August, November and December of 2005, thirty samples of surface sediment were collected in Guanabara Bay using a Van-Veen Grab sampler for sand and an Eckman sampler for mud sediment. These samples were stored in sealed polythene bags, conditioned in ice and taken to the laboratory (Figure 1).

Figure1 Map of the study area with the superficial sediment sample points.

The particle size analyses were carried out after organic matter destruction by a laser particle size analyzer CILAS1064L (Ziervogel & Bohling, 2003), , and then classified according to the textural classification proposed by Flemming (2000) in Table 1.

Code	Textural Class	Code	Textural Class
S	Sand	D-I	Extremely silty slightly sandy mud
A-I	Slightly silty sand	D-II	Very silty slightly sandy mud
A-II	Slightly clayey sand	D-III	Silty slightly sandy mud
B-I	Very silty sand	D-IV	Clayey slightly sandy mud
B-II	Silty sand	D-V	Very clayey slightly sandy mud
B-III	Clayey sand	D-VI	Extremely clayey slightly sandy mud
B-IV	Very clayey sand	E-I	Silt
C-I	Extremely silty sandy mud	E-II	Slightly clayey silt
C-II	Very silty sandy mud	E-III	Clayey silt
C-III	Silty sandy mud	E-IV	Silty clay
C-IV	Clayey sandy mud	E-V	Slightly silty clay
C-V	Very clayey sandy mud	E-VI	Clay
C-VI	Extremely clayey sandy mud		

Table 1 Letter-number codes and descriptive terminology for the 25 textural classes of the ternary diagram used for a revised textural classification of hydrodynamic subdivisions on the basis of sand/silt/clay ratios.

Total organic matter: the calcination method was used and the sediment samples were conditioned in a previously weighed porcelain crucible. After being filled with the samples, the crucibles were weighed again and placed in a muffle at 450ºC for 24 hours. After that, the crucible weights were measured again so the concentration of organic matter in the samples could be calculated by the difference between masses (Byers *et al.,* 1978; Baptista-Neto, *et al.*, 2000; Crapez *et al*., 2003).

Protein (PRT) analyses were carried out after extractions with NaOH (0.5 M, 4 h) and were determined according to Hartree (1972), modified by Rice (1982), to compensate for phenol interference. Concentrations are reported as albumin equivalents. Carbohydrates (CHO) were analyzed according to Gerchacov & Hachter (1972) and expressed as glucose equivalents. This (?) method is based on the same principle as the widely used method of Dubois *et al.* (1956), but is specifically adapted for carbohydrate determination in sediments. Lipids (LIP) were extracted by direct elution with chloroform and methanol, and analyzed according to Marsh & Wenstein (1966). Lipid concentrations are reported as tripalmitine equivalents. For each biochemical analysis, blanks were made with the same sediment samples previously treated in a muffle furnace (450°C, 2 h). All analyses were carried out in 3–5 replicates. Protein, carbohydrate and lipid concentrations were converted to carbon equivalents by using the following conversion factors: 0.49, 0.40 and 0.75 ug of C ug^{-1}, respectively (Fabiano & Danovaro, 1994). The sum of protein, carbohydrate and lipid carbon was referred to as biopolymeric carbon (BPC, *sensu* Fichez, 1991), and the bioavailable organic carbon was determined according to the equation: [(total biopolymeric carbon x 100)/total biopolymers)] (Pusceddu *et al.,* 2004).

The metabolic bacterial activity -- aerobe, facultative anaerobe, denitrification and sulfate-reduction -- was analyzed using methodology described in Alef & Nannipieri (1995).

Statistical analyses were performed using 30 sediment samples and the correlation matrices from the program STATISTICA© 6.0 ($\delta = 0.349$). The different stations with their variables were investigated by multivariate analysis (ANOVA) in order to observe the significant spatial distribution of the samples. Ward's method with City-block (Manhattan) distance differs from all other methods in that it uses an analysis-of-variance approach to assess the distance between clusters. In short, this method attempts to minimize the Sum of Squares (SS) of any two (hypothetical) clusters that can be formed at each step. This distance is simply the average difference across dimensions. In most cases, it yields results similar to the simple Euclidean distance. However, note that in this measurement the effect of single large differences (outliers) is dampened (since they are not squared). Analyses were performed with organic matter, lipids, proteins, carbohydrates, biopolymeric carbon, clay, silt (fine, medium and coarse), and sand (very fine, fine and medium).

4 Results and Discussion

The bottom sediment samples from Guanabara Bay range from clay to sand, and sedimentary textures can be comprised of silt, from 62.65% to 85.63%; clay, 7.51% to 12.87%; and sand, 4.46% to 29.59%. According to the Flemming (2000) classification, the samples from Guanabara Bay were sorted into five main groups: Silt (EI – samples 6 to 9), Extremely silty slightly sandy mud (DI – samples 1 to 5 and 11 to 16), Very silty slightly sandy mud (DII – samples 27 to 30), Extremely silty sandy mud (CI – samples 17 to 26) and Very silty sandy mud (CII – samples 27 to 30) (Figure 2). Particle size of the Guanabara Bay sediments was classified mainly as silty mud. Only in samples 9, 12 and 27 to 30 were the levels of clay higher than 10%. At stations 17 to 26, the levels of fine to very fine sand were higher than 10%, and in samples 27 to 29 the presence of medium sand was higher than 2.36%.

Textural classification of the sediment can be explained by bay hydrodynamics. In Guanabara Bay, from the alignment of Forte Gragoatá to Santos Dumont Airport, the bay widens in the main channel, resulting in a reduction of current speeds and in an increase of the deposition of fine sediments on both sides of the channel. Sediments are primarily clayed-silt and silt-clays deposited as a function of the SSW waves and the tidal current. The north and center of the bay are characterized by the presence of muddy sediments. These areas are protected from the waves and tidal current action, and have very low hydrodynamic energy, accumulating mainly silt and clay sediments (Kjerfve *et al.,* 1997; Quaresma *et al.,* 2000; Catanzaro *et al.,* 2004; Baptista-Neto *et al.,* 2006). Ortega-Calvo *et al.* (1997) showed that contribution from the hydrophobic surface to clay mineral absorption is more significant when organic matter is above 6-8%. The continuous input of organic substance in the sediment of Guanabara Bay, reaching the levels mentioned above, generated an anoxic environment characterized by low values of the redox potential.

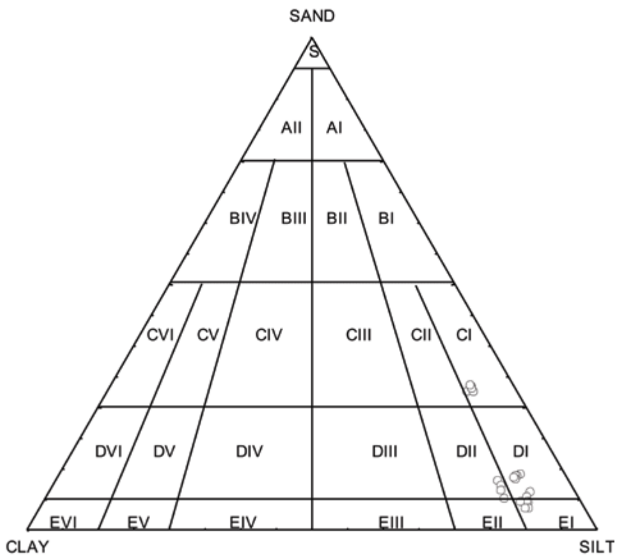

Figure 2 Particle size distribution in the superficial sediment from Guanabara Bay, based on the classification proposed by Flemming (2000).

The organic matter in the superficial sediments ranged between 0.59% – 7.99%. Samples 9, 10, 17 and 20 displayed concentrations of organic matter ≤3.89%. In samples 14 and 15, it ranged from 4% to 5%, while in samples 1 to 6, 8, 11, 12 and 26, it ranged between >5%-6%. In samples 7, 13, 16, 19, 21 and 25, and 27 to 29, it was ≥6%. The levels of organic matter in the sediment show the highest concentration at station 28 (8.35%), and the lowest concentration at station 30 (0.59%), with an average of 5.62% for all 30 stations in Guanabara Bay (Table 2). The average levels of organic matter in the superficial sediments of Guanabara Bay ranged from 4% to 6%, values similar to the ones found by Catanzaro *et al.* (2004) and Baptista-Neto *et al.* (2006). In all of the 30 sediment samples, the highest levels of organic matter (8.4%) were found in areas close to the Guapimirim APA (a protected environment area), which still boasts one of the most protected mangrove areas. This mangrove zone thus contributed more organic matter to this area than to the northwest part of the bay, where the mangrove system was nearly destroyed by oil industry (Mendonça-Filho *et al.,* 2003). However, at the Fundão Island channel, near the bay's northwestern region, high concentrations of organic matter (around 15% – 27%) were found, as well as a high load of fine sediments with high plasticity (Barbosa *et al.,* 2004). Other levels of organic matter, ranging from 0.97% – 15.35 %, were found in Ubatuba Bay in 38 superficial sediment samples (Burone *et al.,* 2003). Dell`Anno *et al.* (2002), in a study on the Apulian coast in Italy, found the total organic matter varying from 1.8% – 5.4% along the first study year.

The organic compounds aggregated onto the clay minerals in the water column were deposited in environments with low oxygen tension, accumulating and forming sediment rich in organic matter and suboxide and anoxic conditions (Premuzic, *et al.,* 1982; Hedges *et al.,* 1997). The biogenic component is generated *in situ* externally by biological processes and includes microorganisms (bacteria, fungi, protozoans), plankton, decaying remains of organisms, fecal matter and marine and terrestrial plant debris, or, from a biochemical standpoint, proteins, carbohydrates, lipids and pigments (Luthy *et al.,* 1997).

Proteins in the superficial sediments ranged from 0.022 to 0.111 $mg.g^{-1}$ (0.05 ± 0.0 $mg.g^{-1}$). In samples 10 and 30, from the main channel of the bay, and in sample 16, from the mangrove channel, the values were ≥0.105 $mg.g^{-1}$. Carbohydrates ranged between 0.219 – 1.483 $mg.g^{-1}$ (0.92 ± 0.3 $mg.g^{-1}$), with concentrations ≥1.006 mg.g^{-1} in samples 3, 5, 6, 9, 16, 19, 21 and 26. Lipids ranged between 0.064 – 1.711 mg.g^{-1} (0.60 ± 0.4 mg.g^{-1}), with concentrations ≥1.077 mg.g^{-1} in samples 1, 3, 6, 8 and 16. Biopolymeric carbon ranged between 0.191 – 1.684 mg.g^{-1}, with an average of 0.85 ± 0.4 mg.g^{-1}. Samples 1, 3, 5 – 8 and 16 were the ones that presented values ≥1.088 mg.g^{-1} of BPC. In terms of the bioavailable carbon, all samples presented an average of 52.84 ± 4.7% (Table 2). The total values found in this work for carbohydrates, proteins and lipids were similar to the data from the literature. Pusceddu *et al.* (1999), in Italy, in the western Mediterranean, found 0.76-70.53 mg of carbohydrates/g, 2.16-12.1 mg of proteins/g and 0.26-4.47 mg of lipids/g in the sediments, respectively. Dell'Anno *et al.* (2002), in the Apulian Coast of Italy, obtained 4.6 mg/g for carbohydrates, 0.37-2.1 mg/g for proteins and >1 mg/g for lipids. The total biopolymeric carbon in this work was also similar to the results found in the literature. Pusceddu *et al.* (1999) found values ranging from 2.5-36.1 mg C/g in the sediments. However, Dell'Anno *et al.*(2002) found a variation of 0.9-6.9 mg C/g in the sediments.

In all 30 superficial sediment sample stations in Guanabara Bay, polymers presented an average of 1.57 ± 0.6 mg.g^{-1}. Carbohydrates represent 59% of the biopolymers in surface sediments, followed by lipids (38%) and proteins (3%). The representative relationships of the biochemistry of the superficial sediments were not similar to the ones found in the literature for superficial sediments, because in this work there is a higher percentage of lipids than proteins, with the maintenance of carbohydrate levels. Pusceddu *et al.* (1999) and Dell'Anno *et al.* (2002) found the following relationship: CARBOHYDRATES > PROTEIN > LIPIDS. In relation to the functional role of proteins, Dell'Anno *et al.* (2002) assigned it to the high primary productivity levels, while Pusceddu *et al.* (1999) defined it as a limiting factor for benthic organisms. Higher lipid levels are associated with fine sediments from less hydrodynamic areas (Kjerfve *et al*., 1997, Amador, 1980). Dell'Anno *et al.* (2002) associated the increase in lipid levels to the increase in depth, which was not seen in our results. In Guanabara Bay, the most abundant polymers after carbohydrates were lipids, due to the association with hydrophobic organic micropollutants (HOMs; including halogenated hydrocarbons, plasticisers, fused-ring hydrocarbons and pesticides) (Turner & Millward, 2002). A raw sewage input in the order of 20 m^3 s^{-1} (derived from a population of about 7.3 x 10^6 inhabitants) is a major cause of environmental concern (Feema, 1998). The uneven distribution of non-point sources of sewage has resulted in pronounced spatial gradients of contamination in water and sediments from the bay (Kjerfve *et al*., 1997; Valentin *et al*., 1999; Crapez *et al.,* 2000; Baptista Neto *et al*., 2005; Brito *et al*., 2006). Carreira *et al.* (2002 e 2004) and Pinturier-Geiss *et al.* (2002) pointed out that the preservation of lipids in the sediments was linked to the prevailing anoxic condition in the sediments.

Dell'Anno *et al.* (2002) and Pusceddu *et al.* (1999) also established a protein/carbohydrate ratio as an indicator of eutrophication levels in coastal systems: mesoligotrophic (proteins <1.5 mg/g; carbohydrates <5 mg/g), eutrophic (proteins <1.5-4 mg/g; carbohydrates 5-7 mg/g) and hypertrophic (proteins >4 mg/g; carbohydrates >7 mg/g). Although several authors have already detected a process of eutrophication in Guanabara Bay, the biopolymeric ratio indicates that levels are not yet comparable to ones in the Mediterranean Sea, and the indicators devised by Dell'Anno *et al.* (2002) and Pusceddu *et al.* (1999) cannot be applied to the Guanabara Bay estuarine ecosystem.

Bacterial respiratory activity (Figure 3) indicated that there exists an overlapping of results of aerobe and facultative anaerobe, and only samples 2, 26, 27 and 30 displayed aerobic processes. Sulfate-reduction, denitrification and anaerobic processes also overlapped in almost all the superficial sediment samples from Guanabara Bay. These results indicate that the metabolism responsible for the organic matter and nutrient cycles are affected by an anaerobic bacterial food web, which can use electron acceptors like nitrogen, iron, manganese and sulfur derived from continental and coastal erosion, according to Turner & Millward (2002). After polymer break, monomers and oligomers are carried into the cell, becoming available for the oxidation-reduction reactions that will culminate in energy production. However, facultative anaerobe, denitrification and sulfate-reduction processes produce only 50, 100 and 170 kJ/mol, respectively, as opposed to the aerobic process (500 kJ/mol) (Edwards *et al.,* 2005).

Among anaerobic bacteria, sulfate-reducing bacteria (SRB) have been important organisms through much of Earth's 4.6 Gy history. Isotopic evidence indicates that sulfate reduction evolved at least 3.7 Gy ago, well before the evolution of oxygenic photosynthesis and cyanobacteria (Shen & Buick, 2004). SRB are expected to facilitate precipitation of calcium carbonate ions in solution. These bacteria impact the pH, because for every

Samples	OM (%)	Biopolymers ($mg.g^{-1}$)				Biopolymeric carbon ($mg.g^{-1}$)	Bioavailable carbon (%)
		Carbohydrate	Lipid	Protein	Total		
01	6.01	0.826	1.077	0.04	1.947	1.16	59.6
02	6.19	0.932	0.58	0.06	1.576	0.839	53.2
03	6.50	1.082	1.317	0.05	2.453	1.447	59.0
04	6.72	0.868	0.785	0.05	1.702	0.96	56.4
05	5.37	1.106	0.982	0.04	2.13	1.199	56.3
06	6.35	1.483	1.322	0.05	2.856	1.61	56.4
07	7.06	0.956	0.906	0.05	1.915	1.088	56.8
08	5.83	0.956	1.711	0.04	2.704	1.684	62.3
09	3.50	1.006	0.442	0.06	1.504	0.762	50.7
10	0.76	0.314	0.17	0.11	0.59	0.305	51.7
11	6.13	0.613	0.49	0.04	1.145	0.633	55.3
12	5.33	0.799	0.573	0.05	1.421	0.773	54.4
13	7.72	0.778	0.645	0.06	1.479	0.822	55.6
14	4.82	0.554	0.461	0.03	1.043	0.581	55.7
15	4.95	0.567	0.831	0.05	1.448	0.875	60.4
16	6.09	1.126	1.233	0.11	2.465	1.427	57.9
17	3.89	1.038	0.39	0.05	1.479	0.733	49.6
18	4.40	1.114	0.611	0.05	1.777	0.929	52.3
19	6.20	1.049	0.616	0.02	1.687	0.893	52.9
20	2.08	0.613	0.329	0.06	1	0.521	52.1
21	6.68	1.06	0.446	0.04	1.546	0.778	50.3
22	6.89	1.26	0.24	0.04	1.538	0.702	45.6
23	6.84	1.193	0.277	0.03	1.5	0.7	46.7
24	6.08	1.078	0.252	0.05	1.378	0.644	46.7
25	7.99	1.132	0.27	0.02	1.424	0.666	46.8
26	5.42	1.249	0.274	0.03	1.549	0.718	46.4
27	7.47	0.706	0.281	0.02	1.01	0.504	49.9
28	8.35	0.972	0.226	0.05	1.25	0.584	46.7
29	6.50	0.943	0.339	0.03	1.313	0.646	49.2
30	0.59	0.219	0.064	0.11	0.395	0.191	48.4

Table 2 Biopolymers, biopolymeric carbon and bioavailable carbon in 30 samples from Guanabara Bay.

sulfate and every two organic carbon units consumed, one calcium carbonate unit can potentially precipitate (Baumgartner *et al.,* 2006). SRB were found in all sediment samples from Guanabara Bay. They use electron acceptors based on the energy field: first oxygen, then nitrate/nitrite and after that sulfur compounds (e.g., sulfate, sulfite, thiosulfate and elemental sulfur) (Krekeler & Cypionka, 1995). SRB and denitrifying microorganism associations could also explain our results. When SRB reduce nitrate/nitrite and produce ammonia nitrogen, the denitrifying bacteria can carry out their anaerobic oxidation (anammox), with generation of dinitrogen gas (Shivaraman & Shivaraman, 2003).

Spatial distribution of the 30 superficial sediment samples in relation to the variables was not significant ($p > 0.05$). In the grouping of surface sediment samples, group A, located in the central channel, represents samples with the lowest concentrations of organic matter and polymers. Group B, the one with the highest distribution in the harbour area, congregated samples with 1 $mg.g^{-1}$ carbohydrate and protein equivalents. Group C, located near the drainage basin of the Guapimirim protected environment area (APA), includes samples with the highest concentration of polymers and organic matter. Group D, from the northwestern area of the bay, which receives the input from the drainage basin of Rio de Janeiro's west zone, shows intermediate organic matter values and lipid concentrations above 1 $mg.g^{-1}$ (Figure 4).

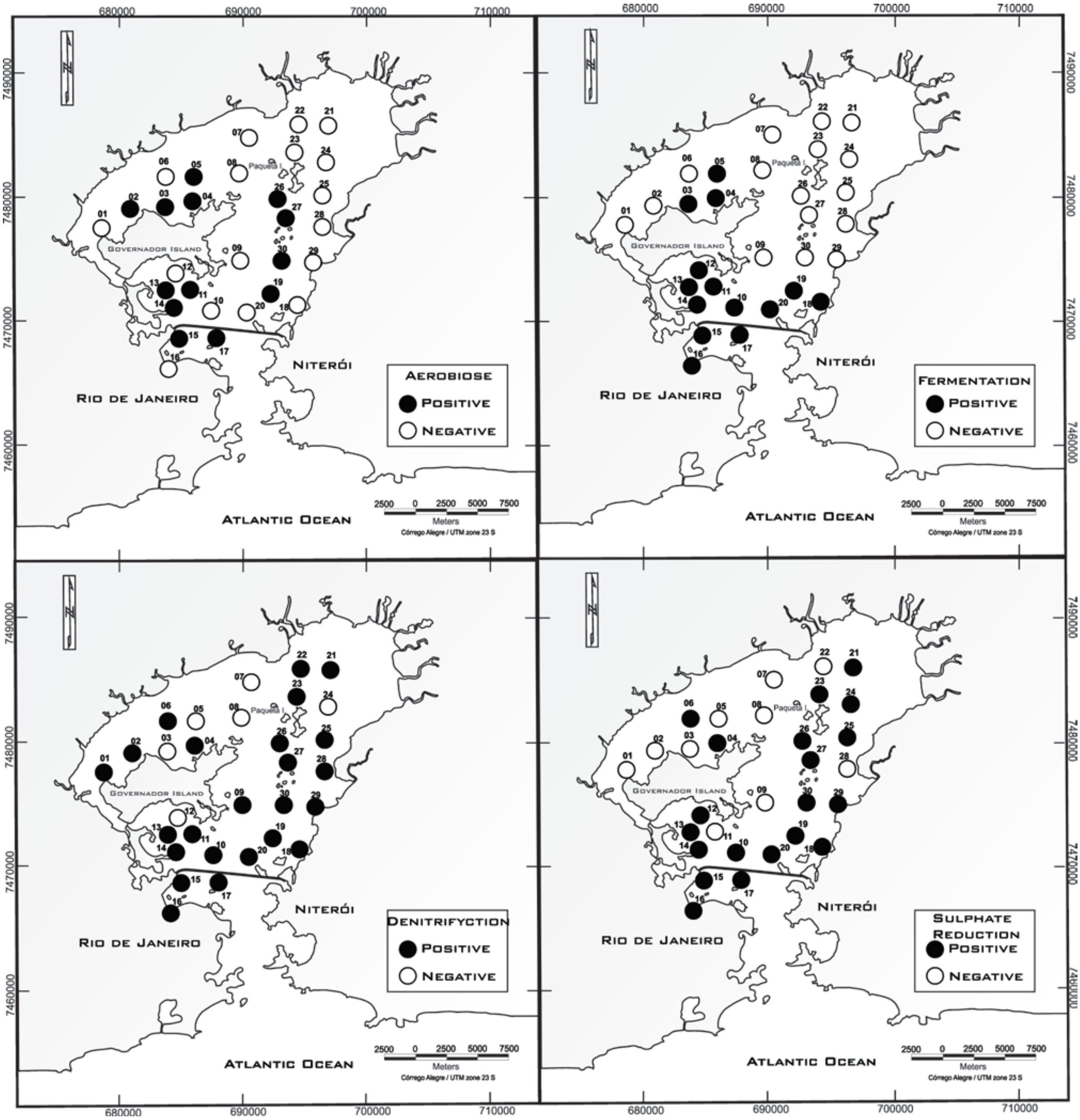

Figure 3 Metabolic bacterial activity in Guanabara Bay – RJ State.

The presence of clays showed a highly significant correlation with medium and fine silt (r=0.904 and r=0.814). Organic matter, lipids, carbohydrates and biopolymeric carbon showed a positive correlation with coarse and medium silt (r=0.390, r=0.448, r=0.468, r=0.380, r=0.496, r=0.422 and r=0.470, respectively). Carbohydrates showed a positive correlation with very fine sand (r=0.462). Proteins had a negative correlation with all variables. Organic matter had a positive correlation with carbohydrates and biopolymeric carbon (r=0.577 and r=0.362, respectively). Lipids and carbohydrates had a positive correlation with biopolymeric carbon (r=0.957 and r=0.561, respectively) (Table 3).

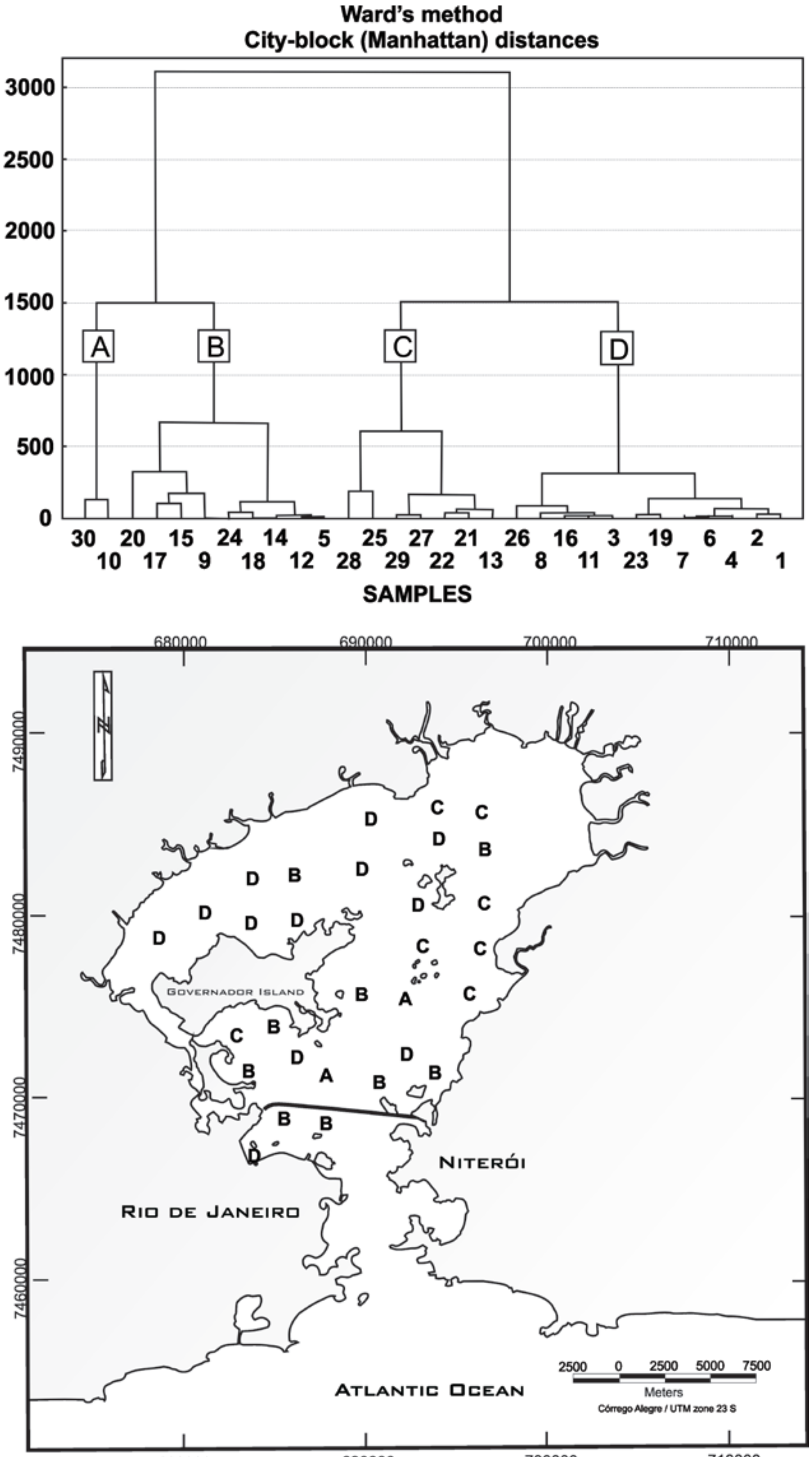

Figure 4 Grouping of samples and parameters.

5 Conclusion

Organic matter in the 30 sediment samples displayed a homogeneous spatial distribution in relation to the anaerobic bacterial food web and the polymers (carbohydrates>lipids>protein). The polymers correlated significantly with the particle size average of 80% of the fine material. Despite the availability of labile organic matter, under biopolymeric carbon form, the available carbon for the trophic food web was around 50%.

The bacterial consortia formed by sulfate reducing and denitrifying bacteria sustain the

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	OM	LIP	PRT	CHO	BPC	CLAY	SILT F	SILT M	SILT C	SAND VT	SAND T	SAND M
OM	1.000											
LIP	0.230	1.000										
PRT	-0.606	0.019	1.000									
CHO	0.577	0.298	-0.436	1.000								
BPC	0.362	0.957	-0.090	0.561	1.000							
CLAY	0.272	0.086	-0.133	0.032	0.080	1.000						
SILT F	0.251	0.365	-0.007	-0.038	0.302	0.904	1.000					
SILT M	0.390	0.468	-0.152	0.074	0.422	0.815	0.934	1.000				
SILT C	0.448	0.380	-0.483	0.496	0.470	0.280	0.268	0.527	1.000			
SAND VT	0.162	-0.167	-0.409	0.462	-0.010	-0.334	-0.543	-0.333	0.581	1.000		
SAND T	0.054	-0.486	-0.358	0.346	-0.320	-0.262	-0.610	-0.529	0.224	0.868	1.000	
SAND M	0.201	-0.580	-0.327	0.117	-0.473	0.300	-0.074	-0.182	-0.213	0.133	0.549	1.000

Table3 Table of parameter correlation for 30 samples from Guanabara Bay.

benthic trophic food web in Guanabara Bay. The anaerobic bacterial metabolism, besides producing organic acids and sulfate, and releasing nitrogen to the atmosphere, usually produces less intracellular energy than aerobic organisms, generating, on a macroscale, a low carbon and nutrient cycle in the anoxic sediment.

This situation results from a large daily contribution of untreated, or only primarily treated, sewage to the bay. Thus, this estuary differs from other coastal systems in the literature due to its lipid levels, which are higher than 1 mg/g in the northwest area of the bay. The preservation of labile molecules, such as lipids, in the sediment results from their linking to HOMs and metals. These anthropogenic components include sewage solids, plastics, tar, solvents, surfactants, coal dust and fly ash, and may occur as discrete particles, or as non-aqueous phase liquids adhered to or entrapped within the particle matrix.

Analyses of particle size associated with bacterial metabolism and the quantification of biopolymers can be an extremely useful tool in the study of carbon and nutrient cycle/scavenge in the marine sediment. Moreover, more studies like the present one need to be conducted in other Brazilian estuaries in order to establish biopolymer levels indicative of eutrophication in tropical coastal systems

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