Superficial distribution of aromatic compounds and geomicrobiology of sediments from Suruí Mangrove, Guanabara Bay, RJ, Brazil

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ABSTRACT

The distribution of selected aromatic compounds and microbiology were assessed in superficial sediments from Suruí Mangrove, Guanabara Bay. Samples were collected at 23 stations, and particle size, organic matter, aromatic compounds, microbiology activity, biopolymers, and topography were determined. The concentration of aromatic compounds was distributed in patches over the entire mangrove, and their highest total concentration was determinated in the mangrove's central area. Particle size differed from most mangroves in that Suruí Mangrove has *chernies* on the edges and in front of the mangrove, and sand across the whole surface, which hampers the relationship between particle size and hydrocarbons. An average $\simeq 10\%$ p/p of organic matter was obtained, and biopolymers presented high concentrations, especially in the central and back areas of the mangrove. The biopolymers were distributed in high concentrations. The presence of fine sediments is an important factor in hydrocarbon accumulation. With high concentration of organic matter and biopolymers, and the topography with *chernies* and roots protecting the mangrove, calmer areas are created with the deposition of material transported by wave action. Compared to global distributions, concentrations of aromatic compounds in Suruí Mangrove may be classified from moderate to high, showing that the studied area is highly impacted.

Key words: microbiologic activity, Guanabara Bay, biopolymers, phenol, Aromatic Polycyclic Hydrocarbons and Monoaromatics.

INTRODUCTION

The increase of human activity near the shores has led to serious pollution problems. Mangrove ecosystems, commonly found in the intertidal zones of tropical and subtropical regions, are frequently subjected to pollution stress representing sinks or receivers of various pollutants (Tam and Wong 1999, Zheng et al. 2000).

The effects of large, or even chronic, oil spills have been studied at different levels, from whole ecosystems down to more specific physio-metabolic processes. It has been observed that biological damages to aquatic organisms are a function of their spatial and temporal

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persistence, hydrocarbon bioavailability, the ability of each group to accumulate in the environment and the capacity of contaminants to interfere with the normal metabolism of organisms or communities (GESAMP 1993).

Polycyclic Aromatic Hydrocarbons (PAHs) are an important class of organic pollutants and are ubiquitous in the environment (Pereira Netto et al. 2000). PAHs are of environmental concern because they are widespread in the environment, and some of them have well-known carcinogenic compounds (Ohkouchi et al. 1999, Zakaria et al. 2002, Mai et al. 2003, Kannan et al. 2005). PAHs are introduced in the aquatic environment through accidental oil spills, industrial discharges, wastewaters, atmospheric precipitation, superficial drainage etc. In these ecosystems, PAHs become are due to their hydrophobic structures, become preferentially adsorbed in the sediment.

The contact of organisms with toxic oil fractions may lead to death by intoxication, especially associated to monoaromatic hydrocarbon (MHC) fractions. Among the most toxic components are benzene, toluene and xylenes that are considerably soluble in water (especially benzene). This fact makes marine organisms more vulnerable to them because they absorb these compounds through tissues, gills, by direct ingestion of water or by contaminated food. MHC show intense acute toxic effects, especially due to their high solubility and resulting bioavailability (GESAMP 1993).

Among the MHC, benzene is the most harmful compound, with well-known carcinogenic properties, and it is classified as carcinogenic to humans (1A) by IARC (2007). The other MHC (toluene, xylenes and ethylbenzene) are less toxic (IPCS 1996, 1997), but they are of concern at least because they add odor or taste to water at ppm concentrations (Day et al. 2001).

BTXs (acronym for the set benzene, toluene and xylene) frequently kill meroplankton, ichthyoplankton or other organisms in different life stages subjected to them in the water column, even at concentrations below 5mg/l. In addition to the toxic action of petroleum hydrocarbons and other chemical components, oil pollution may physically suffocate marine organisms (Kennish 1997). Many minor fuel components are of interest due to their toxicology. This is the case of PAHs and

BTX that have been studied in many media including air, water and soil (IPCS 1998, Menchini et al. 1999, Monod et al. 2001, Pereira Netto et al. 2002, 2004, Rego and Pereira Netto 2007).

Mangroves are also rich in polyphenols and tannins (Kathiresan and Ravi 1990, Ravi and Kathiresan 1990, Achmadi et al. 1994). As far as the chemical aspects, the presence of functional groups like carboxyls and phenolic hydroxyls leads the humic substances (HS) to show a polyelectrolytic role and act as complexing agents of metallic ions (Saar and Weber 1982, Alloway 1990). Intrinsic features of mangroves such as high organic matter and sulfide contents, the anoxic condition of the superficial sediment layer, low energy character of the environment and the reduced current flow favor deposition and accumulation of contaminants. High concentrations of heavy metals, PCBs and PAHs have been found in mangrove sediments and have been observed to persist for many years (Tam and Wong 1999, 2000, Tam and Yao 2002, Zheng et al. 2002).

This study was carried out at The Suruí Mangrove, Guanabara Bay, which is located in Magé Municipality (7.489.800 S, 694.280 W), Rio de Janeiro State, Brazil, with an area of about 80.000–100.000 m^2. Since it is located north of the Guapimirim Environmental Protection Area (APA), it shares features with the zone termed Norte-APA de Guapimirim (Fig. 1). Suruí Mangrove is bounded by Morro da Solina to the west, and by RJ at BR 116 highway to the north. Its importance increases by the presence of the Suruí River and the channel from Suruí to Mirim, both acting in some parts as boundaries of the Guapimirim APA, and by the fact that they flow into Guanabara Bay (Soares et al. 2006) (Fig. 1). Like most rivers of this region, Suruí Mangrove is constantly flooded because it has a predominantly flat topography, close to sea level, which consequently leads to the formation of *chernies* at its edges and fringe. The accumulation of sediments and the invasion of detritus from Guanabara Bay by its fringe and from Suruí and Suruí Mirim rivers its edges are also observed due to the tidal regime (L.F. Fontana et al., unpublished data).

Water flow through the mangrove is reduced by mangrove plants, which characterizes complex current patterns, including jets, eddies and stagnant zones. Most of the suspended sediments settles down in the man-
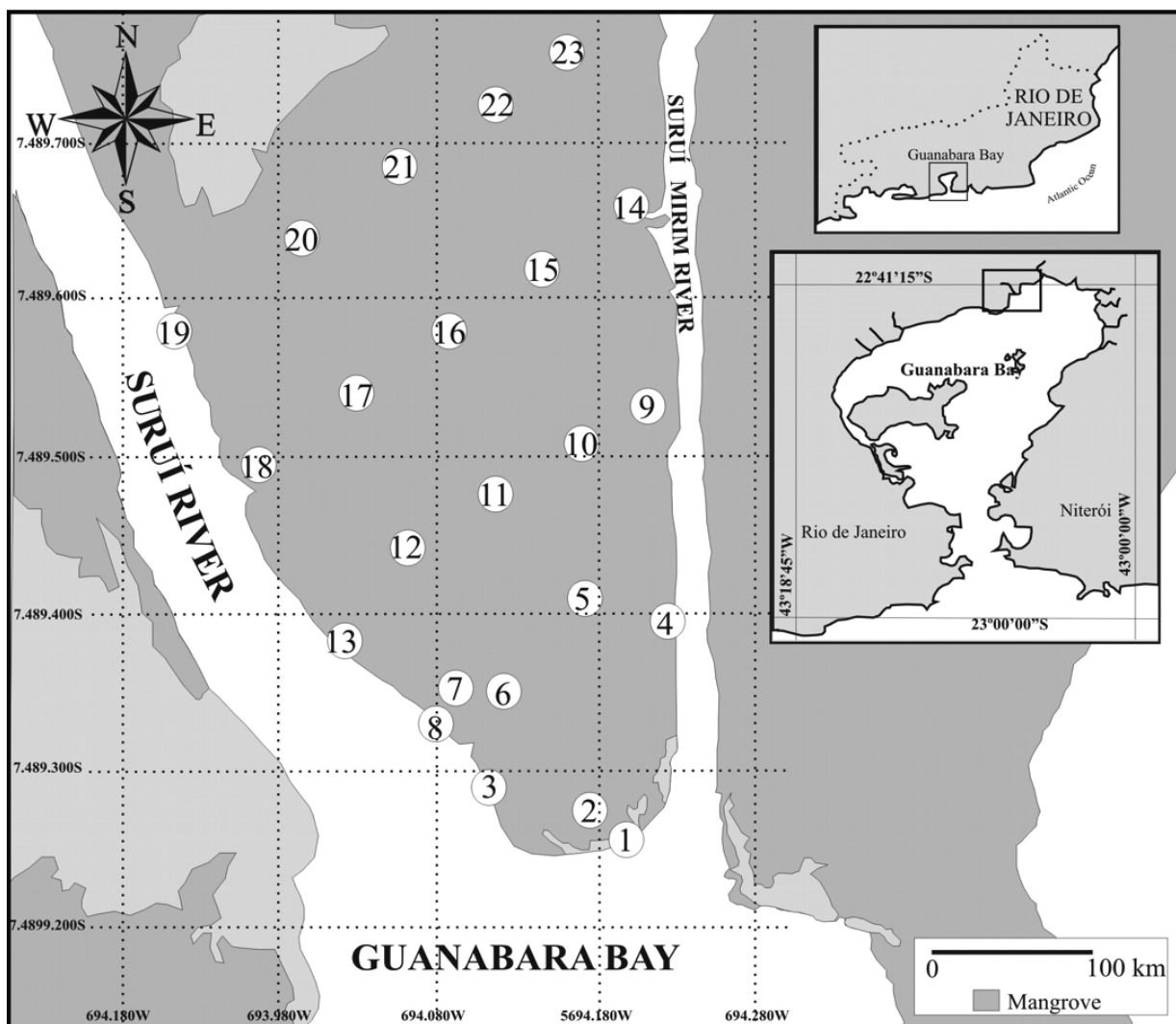
Fig. 1 – Suruí Mangrove (sampling grid).

grove itself, and is not reexported (Furukawa et al. 1997). The most predominant plant species in Suruí Mangrove and along most of the 3,600 m of the Suruí River (from Suruí City to the river mouth) is the white mangrove (*Laguncularia racemosa*). There are also, a few clusters of black mangrove interspersed (*Avicennia schaueriana*); close to the Suruí River mouth, some clusters of red mangrove (*Rhizophora mangle*) can be found. The mangrove is under a strong anthropic pressure. The predatory practice of crab catching with raffia traps next to the burrows, and the indiscriminate tree logging, landfilling, draining and deforesting alter hydrological conditions and, consequently, mangrove func-

tioning thus, hampering management and conservation constitutes a great impact over on Suruí Mangrove and all Guapimirim APA mangroves (Soares et al. 2006).

Just like the two other zones located north of the APA, environmental management of this zone also calls for close follow-up, although the urbanized area represents only around 10% of this area, with a low settlement density. Forest cover is practically nonexistent (just 0.2%), and this percentage points to strong deforestation near the preservation area, a process that ought to merit compensation. More auspiciously, 16.6% of the area is constituted by conserved mangroves *versus* 0.21% of degraded mangroves. The wetlands and

flooded areas together represent 12.1% or total area, which indicates the possibility of actions directed to future mangrove regeneration (Egler et al. 2003).

The oil spill that occurred in 2000 was one of the most severe ever recorded in Guanabara Bay, hitting several ecosystems in the region. It was the second accident in the same pipeline that had already leaked in 1997, which was caused by the rupture of an oil pipeline of Duque de Caxias Refinery (REDUC). According to Petrobras estimates, a total of about 1,300 m^3 of crude leaked, of which 25% (325 m^3) evaporated, 40% (520 m^3) was recovered, and the rest (455 m^3) was retained in mangroves and rocky shores (Michel 2000).

The aim of this study was to quantify contamination by selected aromatic compounds (ACs) (phenol, benzene, toluene, xylenes, naphthalene, phenanthrene and benzo[a]pyrene) at Suruí Mangrove, Guanabara Bay, Brazil, identify possible deposition sites, and assess the relationtship between these concentrations and other variables related to the microbiological characteristics of this area, such as the electron transport system activity, esterase activity, bacterial organic carbon, biopolymers (carbohydrates, proteins and lipids) and also environmental features such as sediment particle size, organic matter content and topography.

MATERIALS AND METHODS

SEDIMENT COLLECTION AND SAMPLING GRID

About 150 g of superficial sediment were collected at each point in a sampling grid comprising 23 sampling stations along Suruí Mangrove (Fig. 1). Sediments were collected from a layer of 2–3 cm deep without damaging the sedimentary layers. Samples were transferred to aluminum trays, kept in thermal boxes, and transported to the laboratory where they were kept in freezer until processing. All samples were collected in January 26th, 2006.

TOPOGRAPHY

For the topographical survey, a Trimble model 3305 class 2 (medium precision) Total Station, with 5″ angular precision and 2 mm ± 2 ppm linear precision was used. Georeferencing was done with GPS receptors, Astech model ProMark2, with 5 mm ± 1 ppm linear precision

and 10 mm ± 2ppm altimetric precision. Topographic survey was obtained with a closed polygon with 19 vertices and supported on two auxiliary stations with GPS receptors. Point coordinates were plotted in the UTM system, UTM, SAD 69, MC = 45° w degrees with orthometric altitudes. Data of the obtained polygon representing the study area are show in Table I. This data indicate that the studied area shows a very flat topography at nearly the sea level.

TABLE I
Data of closing of the polygon.

Parameter	Value
Angular closing	0°01′55″
Linear closing	0,176 m
Difference in E	–0.176 m
Difference in N	–0.005 m
Altimetric difference	–0.003 m
Relative precision	1: 6.793
Length of the polygon	1.195.294 m
Number of vertices	19

PARTICLE SIZE ANALYSIS

Sandy fractions ($>$0.062 mm) were sieved using sieves with 0.5 phi intervals. The Wentworth scale was used for classification. Muddy fractions ($<$0.062 mm) were analyzed by the pipette method (Suguio 1973). Particle size classification followed the one proposed by Flemming (2000), which is restricted to sand sediments ($<$2 mm). It employs the triangular diagram also used by other classification systems (Shepard 1954, Folk 1968), but with more subdivisions.

ORGANIC MATTER

Organic matter (OM) was determined as the difference between sediment dry weight (100°C, 24 h) and weight of the residue after combustion (450°C, 4 h) (Byers et al. 1978).

TOTAL BIOPOLYMERS

Determination of total biopolymers (carbohydrate, lipids and proteins) was performed in triplicate samples of wet sediment. All determinations were done by the spectrophotometric method. Carbohydrates (CHO) were quantified according to Gerchacov and Hachter

(1972) using the same principle as Dubois et al. (1956) and glucose as a standard, with slight modifications to sediment analysis. Lipids (LIP) were extracted with chloroform and methanol and analyzed according to Marsh and Wenstein (1966); tripalmitine was used as a standard. Proteins (PTN) were determined according to the method proposed by Hartree (1972) and modified by Rice (1982) to compensate for phenol interference. Bovine albumin, fraction V (Sigma), was used as a standard.

TOTAL BIOPOLYMERIC CARBON

Lipids, carbohydrates and proteins were converted into carbon equivalents using 0.75, 0.40 and 0.49 g.C g^{-1} conversion factors, respectively (Fabiano and Pusceddu 1998). The biopolymeric carbon fraction (C-BPF) was defined as the sum of carbohydrate, protein and lipid carbon (Fabiano et al. 1995).

TOTAL BACTERIAL CARBON

Total bacterial carbon (BC) was enumerated by epifluorescent microscopy (Axiosp 1, Zeiss, triple filter Texas Red – DAPI – fluorescein isothiocyanate, 1.000 X magnification) and fluorochrome fluorescein diacetate (Kepner and Pratt 1994). Carbon biomass (μg C/cm^3) by the method described by Carlucci et al. (1986). Fluorochrome fluorescein diacetate allows the score of viable cells, morphologically differentiated as cocci, rods and spirilla.

ESTERASE ACTIVITY

Esterase enzyme activity (EST) was determined using the method described by Stubberfield and Shaw (1990). It is based on fluorogenic compounds, which are enzymatically transformed into fluorescent products that can be quantified by the emission with a spectrophotometer by enzymes that hydrolyze many polymeric biomolecules. The results are expressed in μg fluorescein/h/g of sediment.

ELECTRON TRANSPORT SYSTEM ACTIVITY

Electron transport system activity (ETSA) was determined using the method described by Houri-Davignon and Relexans (1989), without a surplus of electron donors (Trevors 1984). It is based on dehydrogenase

enzymes, which are the major representatives of oxidoreductase reactions. They catalyze the oxidation of substrates producing electrons that can enter into the electron transport system of the cell and be quantified by UV-visible absorption. The results are expressed in μl O$_2$/h/g of sediment.

DETERMINATION OF AROMATIC COMPOUNDS (ACS)

High performance liquid chromatography with an ultraviolet-visible detector (HPLC-UV) was used to determine concentrations of the studied aromatic compounds (phenol, benzene, toluene, xylenes, naphthalene, phenanthrene and benzo(a)pyrene). A Shimadzu LC-10 AT VP system was used, and detection was performed at 254 nm. A standard solution of the studied compounds was prepared by dissolving 100 mg of each substance into a final volume of 10.0 ml of acetonitrile, followed by a dilution of 1.00 ml of this solution to 100 ml with acetonitrile. Calibration curves were evaluated between 2.00 and 100 mg/L, with standard solutions after the adequate dilutions of this solution in acetonitrile.

The determination of aromatic compounds was undertaken considering the following methods: Method 610-E.P.A. (Environmental Protection Agency) – Determination of polynuclear aromatic hydrocarbon in water; Method 6440-B-E.P.A. (Environmental Protection Agency) – Method for liquid extraction in water; and Standard CSN N3 PR 120815 – Operation of high performance liquid chromatography apparatus (HPLC).

Limits of detection (LODs) and limits of quantification (LOQs) were obtained by dividing respectively three and ten times the signal to noise ratios by the angular coefficients of the calibration curves. Signal to noise rations was estimated by the standard deviations of the peak areas obtained after 10 subsequent injections of the 2.00 mg/L standard. LODs and LOQs were expressed in terms of sample volume by dividing the obtained values by the ratio of the analyzed sample (3 g) and the final volume of the concentrated extract (20 mL).

Quantification limits were better than 0.30 μg/g for all studied aromatic compounds.

STATISTICAL ANALYSIS

Statistical analyses were performed using 9 variables with the correlation matrices by the program STATIS-

TICA$^{©}$ 7.0 (δ = 0.349). Ward's method with City-block (Manhattan) distance is different from all other methods because it uses an analysis of variance approach to evaluate the distances between two 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, this distance measures yields results similarly to the simple Euclidean distance. However, in this measure, the effect of single large differences (outliers) is dampened (since they are not squared). Nine variables, namely phenol, BTX (sum of benzene, toluene and xylene concentrations), PAH (sum of naphthalene, phenanthrene and benzo[a]pyrene concentrations), percentages of fine sediments and organic matter (OM), total of carbohydrates (CHO), lipids (LIP), proteins (PTN) and porosity, and their values at the 23 sampling stations are summarized in Table II.

RESULTS

The assessment of mangrove topography was performed on October 16th 2007. Suruí Mangrove comprises an area about 80.000–100.000 m^2. Suruí Mangrove topography features an elevation at the mangrove front reaching 2.3 m, and two lower areas ranging from 0.3 to 0.6 cm, one 200 m long on the Suruí River side, and the other along the entire Suruí Mirim Channel. The mangrove topography indicates that it is almost totally flat at its center and back. This higher area, which is a placed in front of the mangrove, together with the mangrove plants, protects it from the inflow of Guanabara Bay waters that invade the mangrove when the tide rises, which configures complex current patterns that prevent the reflux of water out of the mangrove and lead to sediment to settlement in the flatter areas (Fig. 2).

Sand is the dominant particle size fraction of the sediments. Most stations presented small percentages of silt. However, samples 4, 7, 11, 12, 15, 16, 20, 21 and 22 presented 30 to 55% of silt. The highest clay concentrations (around 30%) were found at station 7, 12 and 17. Station 21 presented 61% of clay, and station 12 was the only one with more comparable grain proportions. Suruí Mangrove displayed a range from sand to very clayey to slightly sandy mud, according to the classification by Flemming (2000) (Fig. 3).

Biopolymers were distributed all over the mangrove, with concentrations that ranged widely. CHO, which varied between 398 μg/g (station 3) and 1760 μg/g (stations 7), showed a large range when compared to that of PTN and LIP. PTN ranged from 118 (station 1) to 220 μg/g (station 11). However, a continuous increase in PTN concentrations was observed from station 12 to 23 (325 to 824 μg/g). LIP varied very little over the whole mangrove. The smallest concentration was observed at station 6 (12.4 μg/g), and the largest at station 7 (154 μg/g) (Fig. 4). As a consequence of these data, total biopolymeric carbon ranged all over the mangrove. The largest concentration was found in the station 17 (936 μg/g), and the lowest at station 6 (247 μg/g) (Fig. 5).

BC varied from 0.27 μg C/cm^3 (station 1) to 10.24 μg C/cm^3 (station 21). The station 21 clearly presented a much higher value than the others, which were always below 3.72 μg C/cm^3. The mean for BC values, excepting station 21, was 2.01 μg C/cm^3. Stations located at the mangrove front (1 to 8) presented values below the mean (Fig. 6). Enzymatic activity values ranged over the whole mangrove. The highest value was found at station 21 (6.52 μg fluorescein/h/g) and the smallest one at station 19 (1.35 μg fluorescein/h/g), with a mean of 3.92 μg fluorescein/h/g. The high esterase enzyme values indicated hydrolysis of molecules heavier than 600 Da.

ETSA, which is related to biomass production, also displayed a very variable activity over the whole mangrove. ETSA values ranged from 0.004 μl O$_2$/h/g (station 10) to 0.62 μl O$_2$/h/g (station 16), with a mean of 0.13 μl O$_2$/h/g. Stations 3 to 12, which are located close to the mangrove front, showed ETSA close to the mean (Fig. 7). The highest OM percentage was found at station 21 (23%), and the lowest at station 8 (1%). A high OM percentage, with a mean of 10% (Fig. 8), was found for the entire mangrove.

The results of selected aromatic compounds determination are shown in Table II. Compounds that showed the largest concentrations were phenanthrene, at station 14 (436 μg/g), followed by xylene at 27.80 μg/g (station 1), and phenol at 25.40 μg/g (station 2). Except in the case of stations 1, 2, 7, 15, 17 and 23, benzene concentrations were always below the limit of detection

TABLE II
Data summary.

Samples	Phenol	BTX	PAH	Fine sediments (%)	OM(%)	CHO	PTN	LIP	Porosity
1	22.9	47.0	22.0	40.0	6.20	865.6	166	66.5	1.00
2	25.4	15.1	<LOQ	31.0	4.40	692.2	204	34.8	0.90
3	5.59	10.2	19.7	11.0	4.90	292	156	139	0.50
4	9.56	8.32	36.8	48.0	6.60	639	127	108	1.20
5	11.4	7.91	<LOQ	30.0	5.00	831	190	40.2	1.00
6	18.8	14.4	<LOQ	18.0	2.80	398	161	12.4	0.50
7	12.0	13.8	23.9	77.0	17.8	1760	154	154	0.60
8	2.84	3.16	<LOQ	3.0	1.20	408	200	19.6	0.40
9	2.35	0.89	<LOQ	33.0	6.90	942	118	105	1.10
10	2.54	0.69	<LOQ	32.0	12.5	1074	215	55.2	0.60
11	8.16	1.20	266	58.0	22.0	1358	221	117	0.70
12	4.03	0.47	27.8	68.0	16.0	1361	325	121	0.60
13	<LOQ	1.24	5.10	13.0	14.2	1022	417	132	0.50
14	1.80	6.55	436	30.0	7.20	1068	344	95.5	1.20
15	3.28	13.6	<LOQ	57.0	9.30	1242	396	104	1.20
16	1.67	6.40	192	61.0	18.3	1573	455	92.2	0.70
17	1.97	7.99	32.8	73.0	9.10	1282	656	135	1.20
18	1.41	4.55	<LOQ	10.0	5.80	417	487	21.9	0.40
19	1.01	1.58	2.50	28.0	4.60	692	392	30.9	1.00
20	2.18	8.92	<LOQ	64.0	20.5	1022	824	106	0.60
21	3.51	15.5	<LOQ	87.0	23.3	1113	531	103	0.80
22	1.22	5.94	<LOQ	53.0	7.50	768	563	110	1.10
23	2.46	14.1	28.0	18.0	4.30	473	539	88.2	0.90

<LOQ – minor quantification limit.

(LOD) of the employed method. Concentrations of the other monoaromatics were larger than those of benzene at all stations. Toluene concentrations ranged from 0.33 to 17.5 μg/g; xylene concentrations varied between < LOD and 27.8 μg/g.

Naphthalene was detected only at station 8, and at all other sites it was below the limit of detection (LOD) of the employed method. Phenanthrene concentrations varied widely at the studied stations (<LOQ to 436 μg/g). Benzo[a]pyrene varied in a low range (<LOQ to 2.5 μg/g). Phenanthrene predominated among PAHs and was found in most samples. This substance is of concern to aquatic biota since phenanthrene, pyrene and fluoranthene were previously found to be responsible for most of runoff toxicity to aquatic biota (Boxall and Maltby

1997). The sum of concentrations of the aromatic compounds (AC) ranged from 3.26 to 436 μg/g, and only 3 stations presented values above 100 μg/g. Station 14 showed a higher concentration of total ACs (444 μg/g), followed by stations 11 (275 μg/g) and 16 (201 μg/g) (Table III).

STATISTICAL ANALYSIS

In order to evaluate the relationships among different sampling station, cluster analysis (CA) was used. Ward's method and Manhattan distances were considered for station clustering. Concentrations below LOQs were replaced by values between LOD and LOQ in order to avoid a large number of invalid values. CA results are shown in Figure 9.
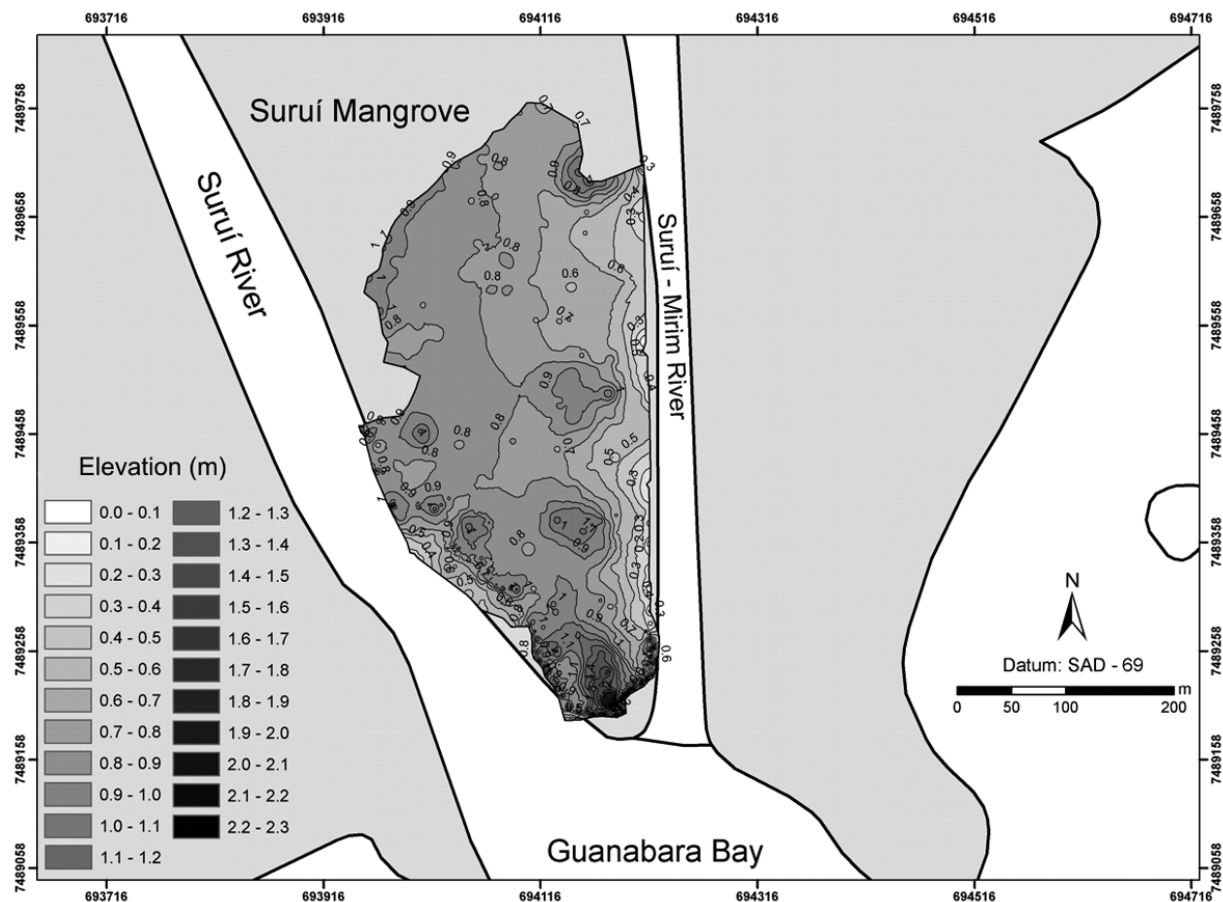
Fig. 2 – Suruí Mangrove topography.

Manhattan analysis, using nine variables – namely phenol, BTX (sum of benzene, toluene and xylene concentrations), PAH (sum of naphthalene, phenanthrene and benzo[a]pyrene concentrations), percentages of fine sediments and organic matter (OM), total of carbohydrates (CHO), lipids (LIP), proteins (PTN) and porosity – and 23 cases yielded 4 groups. Two main station groups can be observed with a Dlink/Dmax value of around 40. The first group is mainly formed by samples from the center to the back of the mangrove (11, 12, 13, 14, 15, 16, 17, 20, 21 and 22), which presents only one sample from the mangrove front (7). The second group was mostly comprised of samples from the frontal part of the mangrove (1, 2, 3, 4, 5, 6, 8, 9,10), and included three samples (19, 18 and 23) from the back.

Each of these two main groups may be subdivided into two subgroups. The first, formed by stations 13, 1, 15, 17, 20, 21 and 22, showed similarities especially in the variation of CHO concentration (767.78 to 1282.3 μg/g). The second, formed by stations 7, 11, 12 and 16, is grouped by variation of PTN concentration (153.52 to 455.25 μg/g). A third group, formed by stations 3, 6, 8, 18 and 23, showed similarities in LIP contents (12.44 to 138.5 μg/g), PAHs and predominance of sand in the sediments (80%). The fourth group, comprising stations 1, 2, 4, 5 9, 10 and 19, was grouped by the contents of OM, BTX, phenol and porosity. In the variables diagram, grouping depended on sediment particle size and porosity, which suggests that the mineral matrix served as a first aggregation support for LIP and PAHs. The accumulation of phenol in the sediment that can also be derived from plant primary production became a substrate for final aggregation of LIP, CHO and PAHs, since PTNs, representing live biomass,
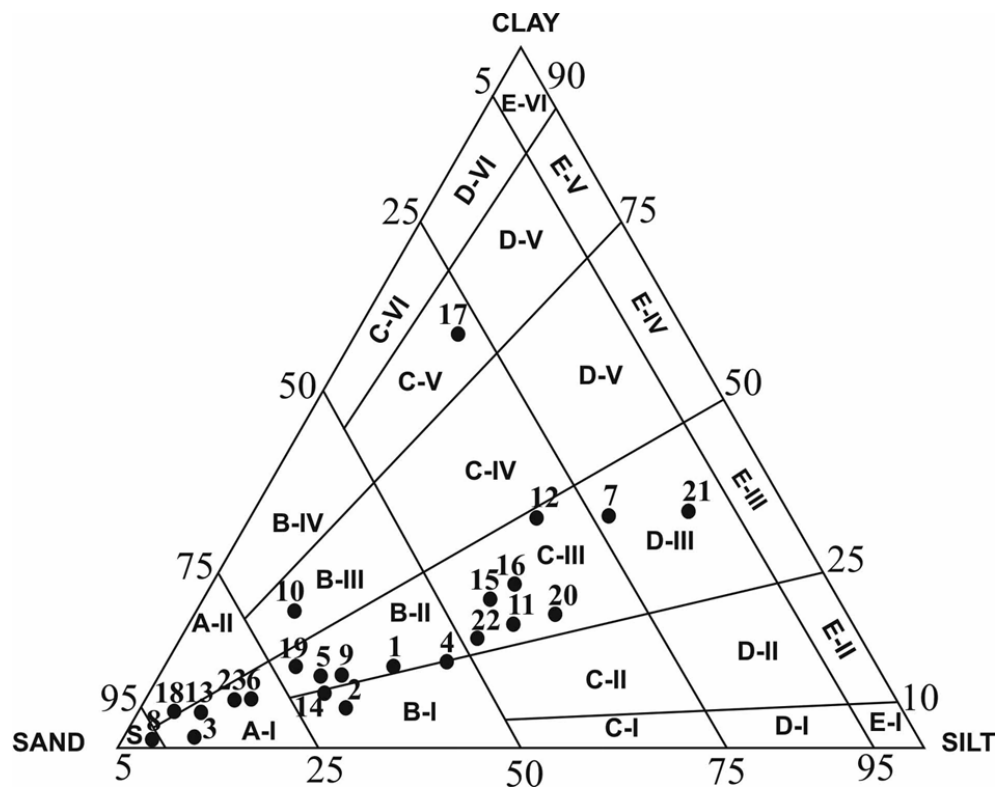
Fig. 3 – Triangular diagram of textural classes (Flemming 2000). Subdivisions are based on sand/silt/clay percentages.
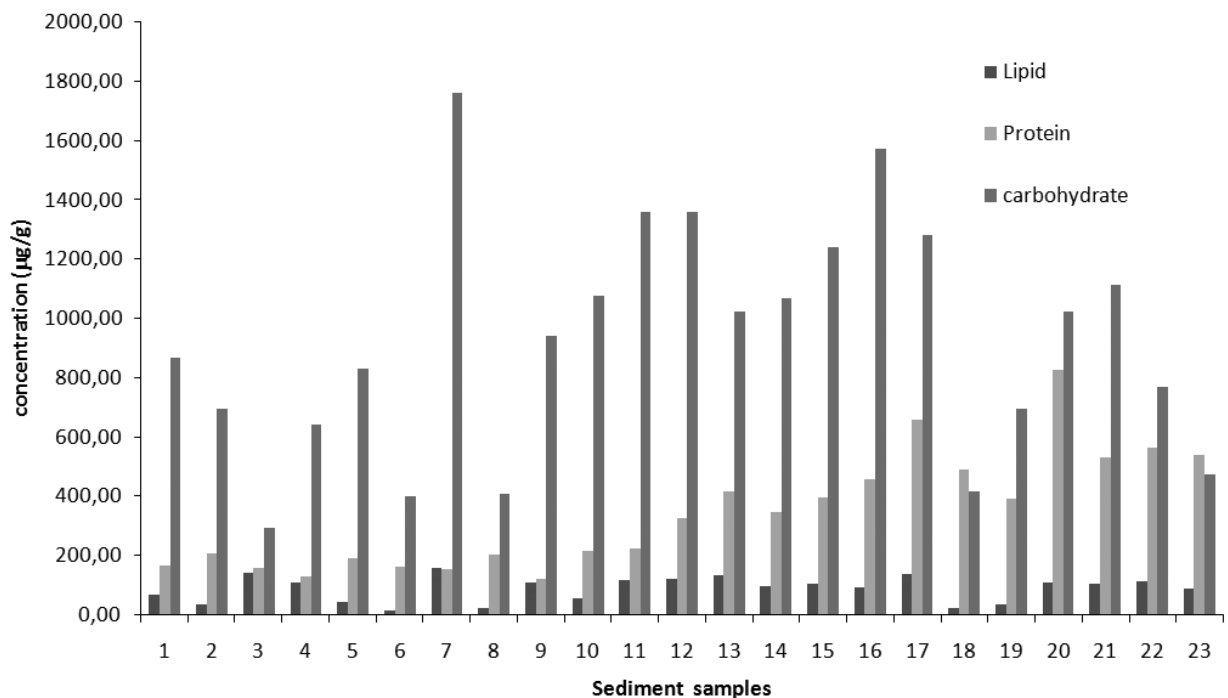

Fig. 4 – Total biopolymer concentrations in the studied samples (lipids, proteins and carbohydrates).
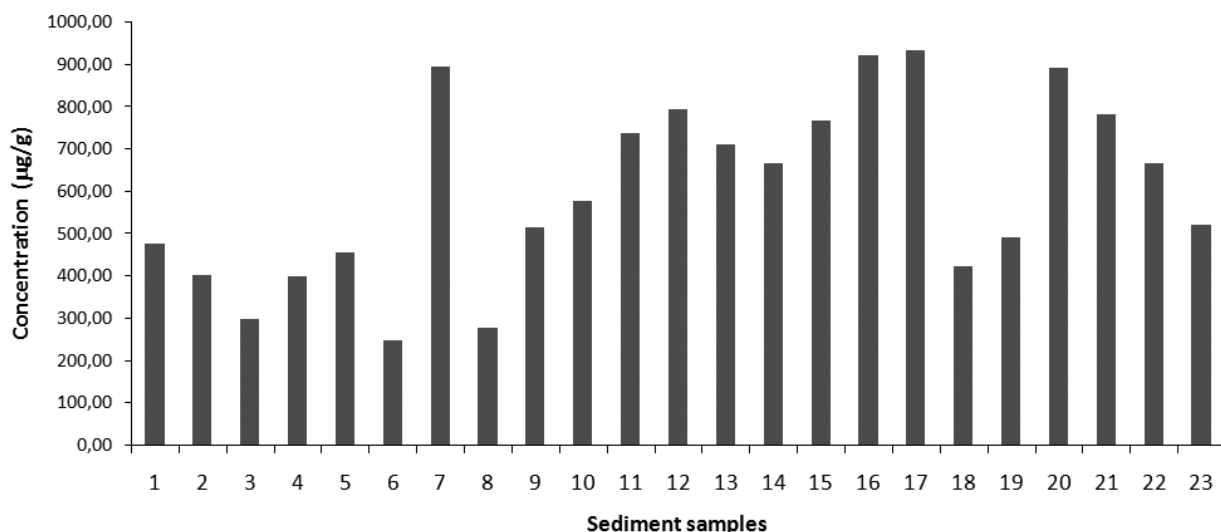
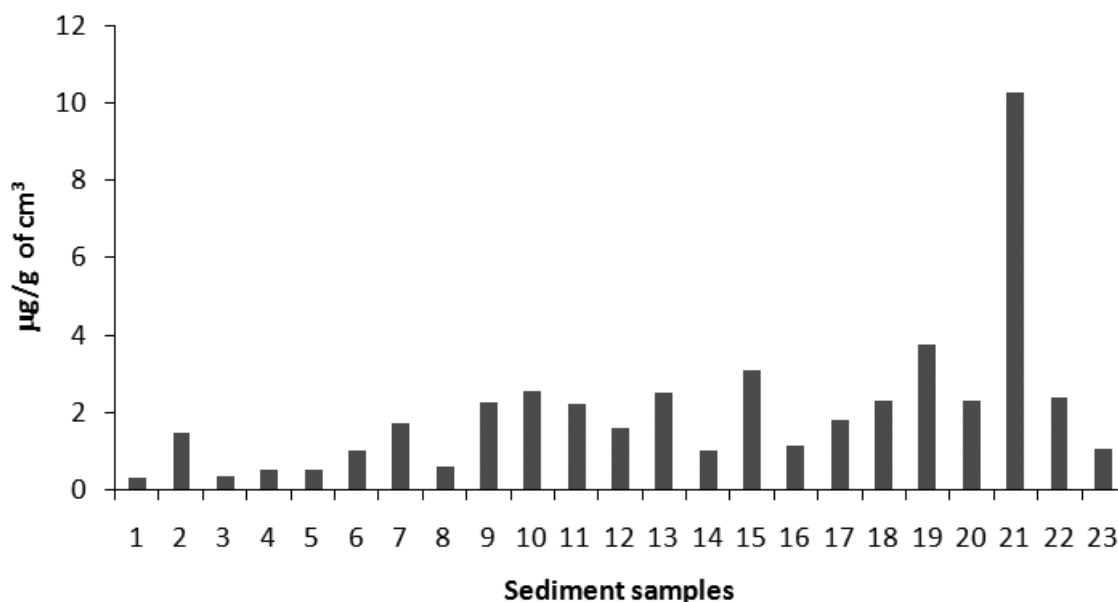Fig. 5 – Total biopolymeric carbon concentrations.

Fig. 6 – Bacterial carbon concentrations.

are also in this group. The correlation matrix among variables is show in Table IV. Significantly correlated variables ($P<0.05$) are show in bold.

DISCUSSION

The study of the topography of Suruí Mangrove revealed an almost flat area with a discrete elevation at its center and the back with a light elevation, which, together with plant roots, works as a protection against sea impact over mangrove sediments. These topographic characteristics play an important role in the patterns of mangrove development and maintenance. Substrate elevation and topographical variations have been recognized as important criteria in the success and patterns of mangrove seedling establishment (Anthony 2004, Ellison 1998, Kitaya et al. 2002, Saenger 2003, Cohen et al. 2005, Lara and Cohen 2006). Both topography and plant distribution serve as a pattern for the accumulation of organic matter (such as hydrocarbons) and inorganic (such as metals) species.
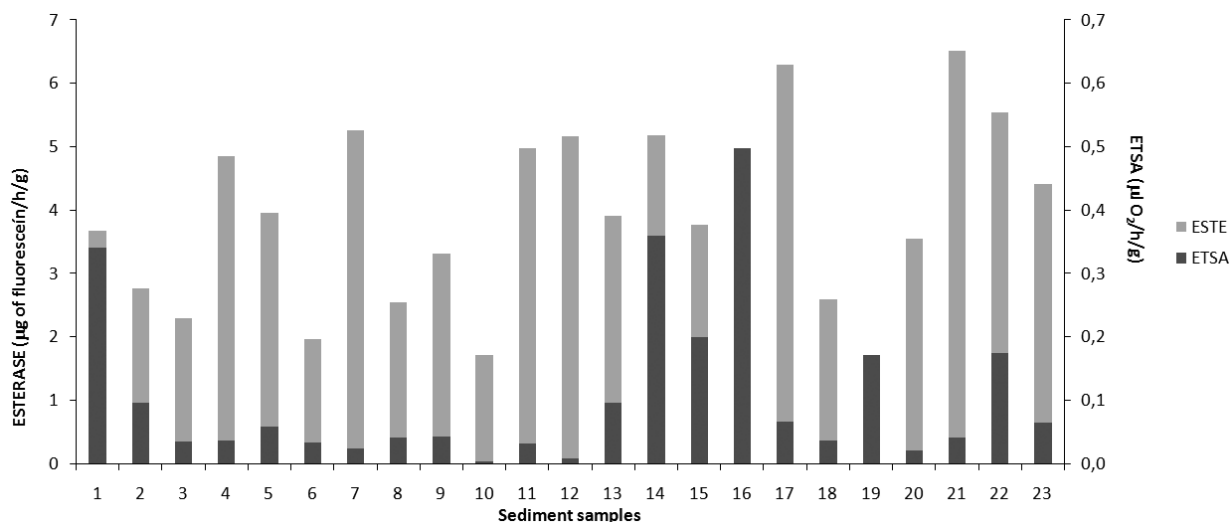
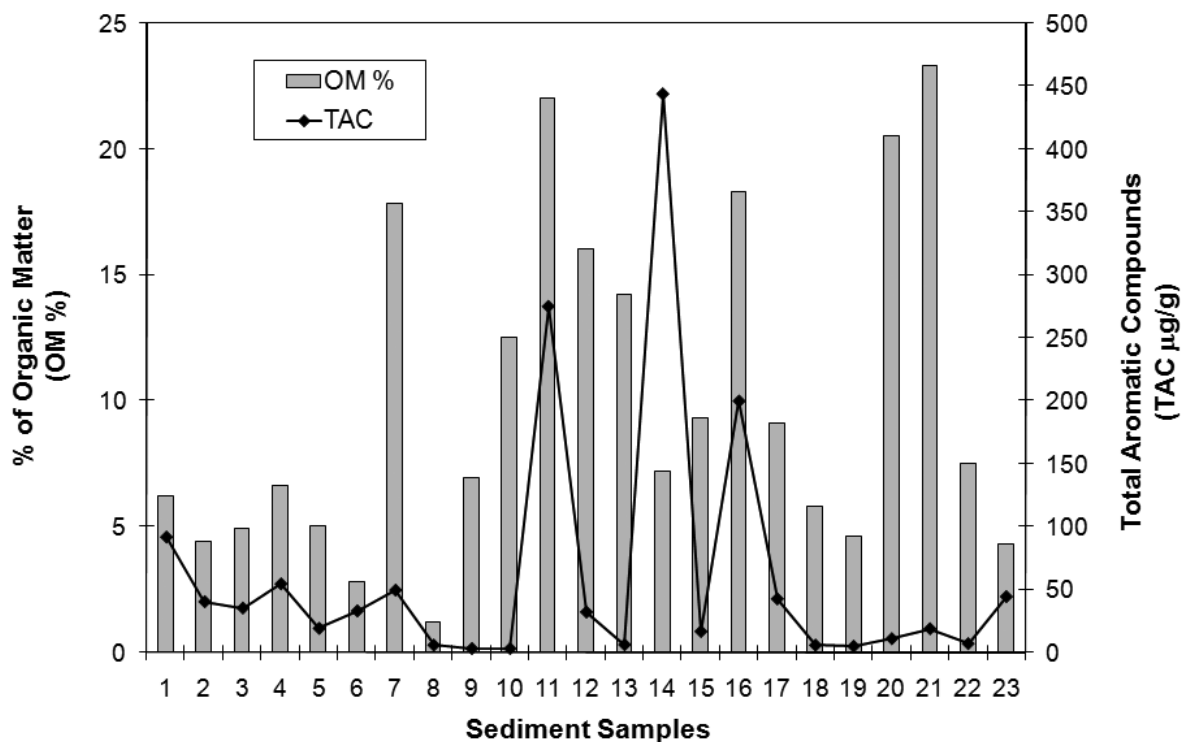Fig. 7 – ETSA and ESTE enzymatic activity concentrations.

Fig. 8 – Organic matter and total aromatic compounds (TAC) concentrations in samples.

As in other studies, high organic matter content was found over the entire mangrove. Organic matter content was comparable to other estuaries: Itacorubi/SC, 3.38–5.4% (Da Silva et al. 2005) and 0.005–6.13%, Guanabara Bay (Vilela et al. 2003, Carreira et al. 2001, Baptista Neto et al. 2000). The high organic matter per-

centages, with a patch distribution pattern and associated to particle size, are typical of mangrove environment (Wasserman et al. 2001, 2006, Kehrig et al. 2003). The lowest organic matter percentage was found at station 8, where about 100% of sediment particle corresponded to sand.

TABLE III
Aromatic compound concentrations (μg/g) in sediments from Suruí Mangrove.

Samples	Phen	Ben	Tol	Xyl	Total BTX	Naph	Phen	B[a]P	Total PAHs	Total ACs
1	22.9	1.7	17.5	28.0	47.2	<LOQ	22.0	<LOQ	22.0	92.1
2	25.4	<LOQ	<LOQ	15.1	15.1	<LOQ	<LOQ	0.2	0.2	40.7
3	5.59	<LOQ	2.4	7.7	10.2	<LOQ	19.7	<LOQ	19.7	35.4
4	9.56	2.1	4.6	1.7	8.3	0.1	36.7	<LOQ	36.8	54.8
5	11.4	<LOQ	0.8	7.2	7.9	<LOQ	<LOQ	0.1	0.1	19.5
6	18.8	<LOQ	0.6	13.8	14.4	<LOQ	<LOQ	<LOQ	<LOQ	33.2
7	12.0	2.6	2.7	8.6	13.8	<LOQ	23.4	0.5	23.9	49.8
8	2.84	<LOQ	1.4	1.8	3.2	<LOQ	<LOQ	<LOQ	<LOQ	6.0
9	2.35	<LOQ	0.4	0.5	0.9	<LOQ	<LOQ	0.1	0.1	3.4
10	2.54	<LOQ	0.3	0.4	0.7	<LOQ	<LOQ	<LOQ	<LOQ	3.2
11	8.16	<LOQ	1.2	<LOQ	1.2	<LOQ	265.0	0.5	265.5	275
12	4.03	<LOQ	0.5	<LOQ	0.5	<LOQ	27.7	0.1	27.8	32.3
13	<LOQ	<LOQ	<LOQ	1.2	1.2	<LOQ	5.1	<LOQ	5.1	6.30
14	1.80	<LOQ	2.9	3.7	6.6	<LOQ	436.0	0.1	436.1	445
15	3.28	0.7	5.0	7.9	13.6	<LOQ	<LOQ	0.1	0.1	17.0
16	1.67	<LOQ	2.5	3.9	6.4	<LOQ	192.0	0.1	192.1	200
17	1.97	0.4	3.4	4.1	8.0	<LOQ	32.6	0.2	32.8	42.7
18	1.41	<LOQ	1.4	3.1	4.6	<LOQ	<LOQ	<LOQ	<LOQ	5.91
19	1.01	<LOQ	1.3	0.3	1.6	<LOQ	<LOQ	2.5	2.5	5.11
20	2.18	<LOQ	3.8	5.1	8.9	<LOQ	<LOQ	0.1	0.1	11.2
21	3.51	<LOQ	5.4	10.1	15.5	<LOQ	<LOQ	0.2	0.2	19.2
22	1.22	<LOQ	2.5	3.5	5.9	<LOQ	<LOQ	<LOQ	<LOQ	7.22
23	2.46	0.9	8.6	4.6	14.1	<LOQ	28.0	<LOQ	28.0	44.6

Phen (Phenol), Ben (Benzene), Tol (Toluene), Xyl (Xylene), Naph (Naphtalene), Phen (Phenantrene) and B[a]P (Benzo[a]pyrene). LOQ. = quantification limit.

TABLE IV
Correlation matrix of the studied variables.

	Phenol	BTX	PAH	Fines (%)	OM (%)	CHO	PTN	LIP	Porosity
Phenol	1	**0.663**	−0.128	−0.043	−0.239	−0.138	**−0.537**	−0.307	0.050
BTX		1	−0.131	0.104	−0.136	−0.079	−0.120	−0.077	0.227
PAH			1	0.090	0.218	0.330	−0.027	0.186	0.184
Fines				1	**0.741**	**0.781**	0.336	**0.565**	0.281
OM					1	0.761	0.345	**0.555**	−0.230
CHO						1	0.147	**0.569**	0.139
Ptn							1	0.196	0.015
Lip								1	0.202
Porosity									1

Phenol was detected in all stations except at station 13. Kueh and Lam (2008) detected phenol in Tolo Harbor, inner Deep Bay, Hong Kong. The results indicated that land-based discharges are unlikely to be the main source of trace organics in marine water because sewage contains large amounts of phenolic compounds that are commonly found in household, commercial and industrial products. Moreover, oil refinery effluents may con-
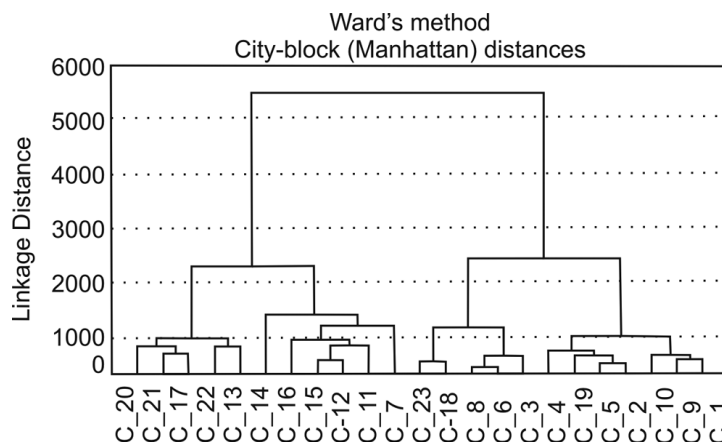
Fig. 9 – Clustering of sampling points considering the 9 variables from Table I.

tain many different chemicals at different concentrations including phenol, although the exact effluent composition cannot be generalized as it depends on the refinery characteristics and on which units are in operation at any given time. It is therefore difficult to predict the effects that an effluent may have on the environment (Kueh and Lam 2008). Buikema et al. (1981) looked at the effects of ammonia, phenol, chromates and fuel oil, on the reproduction and growth of *Mysidopsis bahia*. When exposed to phenol, chromate and fuel oil, these animals exhibited reproductive impairment. Phenol also caused growth inhibition.

It is therefore very difficult in areas with other sources of pollution to pinpoint the exact source of the observed effects (Wake 2005). Suruí and Suruí-Mirim Rivers, industrial complexes and refineries being close Suruí Mangrove are propable sources of sewage pollution and industrial effluents, which hampers the identification of pollution sources. The differences on hydrocarbon distribution at Suruí Mangrove showed patch distribution, and the presence of sand in the mangrove did not facilitate natural dampening of ACs. On the contrary, the high concentrations of organic matter and biopolymers allowed pollutants sequestration because internal micropores between organic matter and its constituents kept a high sorption. Thus, both the smallest and the highest AC values were found in stations that showed large sand levels, which suggests a preferential linkage to organic matter and its constituents.

AC distribution indicates several contamination sources, with a first notification in 2000 (Michel 2000).

Highest AC concentrations were determined between the center and the back of the mangrove that are possible deposition sites being formed by tide reaching. Our results agree with those by Kim et al. (1999) who proposed that sediment properties, such as organic matter and particle size, may influence the distribution and concentration of PAHs and other hydrophobic organic compounds. Another PAH study established the important role that mangrove sediments play as oil sinks (Díaz et al. 2000). The entrance of water breaks the *chernies*, scattering sand all over the surface of Suruí Mangrove and hampering the relationship between particle size and AC sequestration.

A direct comparison of our data with previously published PAH ones is difficult due to several factors including: a) differences in analytical and sampling methods; b) set of studied PAHs; c) different physical, biological and geological characteristics of the studied area. Indeed, our results indicate that total PAH concentrations are larger in several points than indicated by previous studies at the same area. Maciel-Souza et al. (2006) determined total PAH concentrations of 11.53 to 28.28 μg/g in a transect along a mangrove close to the petroleum refinery, at the back of Guanabara Bay, and of 1.23 μg/g at a station on the Estrela River, close to Suruí Mangrove. In samples of superficial sediments from the same mangrove, total PAHs over 20 μg/g were determined 10 days after the 2000 Guanabara Bay oil spill (Gabardo et al. 2000). In 4 samples, our results were higher than those of Gabardo et al. (2000), even 6 years after the spill. However, such high values sug-

gest that this area may experience from other sources of contamination as discussed above.

Comparing these results in a more global context, PAH levels in Guanabara Bay were 2 to 6 times higher than the concentrations in 4 Hong Kong mangroves and 14 other sites at China, the Caribbean and Puerto Rico, where the highest PAH levels reported were 2.2 μg/g (Tam et al. 2001). Medeiros et al. (2005) studied the distribution of total PAHs in an estuarine lagoon in southern Brazil, highlighting that in the sediment near the petroleum distribution site values reached 11.8 μg/g and, in the refinery sediments, 4.4 μg/g. These sites were 100 and 40 times more contaminated than a nearby lagoon, and were described as chronic pollution sites. Zakaria et al. (2002) found different PAH concentration levels, ranging from 0.001 to 760 μg/g, with modal concentrations of 1–10 μg/g in rivers, lakes, estuaries, harbors and coastal areas. 80% of these regions presented values lower than 1 μg/g, and only in highly industrialized sites were they greater than 10 μg/g.

Due to the anoxic sedimentary environment, hydrolysis of organic matter biopolymers may be carried out by anaerobic bacteria, with high esterase enzymes activity and lower electron transport system activity. Anaerobic processes like fermentation, denitrification and sulfate reduction are energetically less efficient, but are responsible for the biogeochemical cycles in Guanabara Bay sediments (Silva et al. 2008). This hypothesis is supported by the low electron transport system activity, which is responsible for the energy synthesis process and, concomitantly, of biomass. Other studies have corroborated these results (Relexans 1996, Fenchel et al. 1988, Edwards et al. 2005). Bacterial carbon, which is present in the whole mangrove, reached a mean of 8^{10} cells/g, with no great variation among the studied stations. Bacteria are present in the sample in great numbers (10^{10} cells/g), and their biomass is higher than other benthic organisms due to the function and structure of microbial biofilms (Meyer-Reil and Koster 2000).

Crapez et al. (2001) determined 0.54 μg of fluorescein/h/g of esterase activity, and 0.31 μl O_2/h/g of electron transport system activity in sandy sediments from Praia de Boa Viagem, Niterói. Crapez et al. (2003) found different patterns in enzymatic determinations performed in different seasons of the year. Silva et al. (2008) stud-

ied superficial sediments of 30 points along Guanabara Bay and found a mean esterase activity value of 3.20 μg of fluorescein/h/g and electron transport system activity in only 15 stations. Mangrove trees contribute considerable amounts of autochthonous organic matter to the sediment, but also receive waters contaminated by sewage due to the river system that flows through industrial and residential areas close to Suruí Mangrove. The high organic matter levels allow the sequestration of aromatic hydrocarbons, making them unavailable for biodegradation (Kubicki and Apitz 1999) and thus explaining the presence of volatile compounds, such as benzene, toluene and xylene, in Suruí Mangrove sediments (Fontana et al. 2006). According to Pignatello (2003), most forms of natural organic matter contains internal micropores irreversibly deformed, which act to maintain a more or less linear sorption that competes with a slow desorption.

The carbohydrate, protein, lipid and total biopolymeric carbon values determined in this study are inferior to data from the literature. Pusceddu et al. (1999) found 760–70530 μg/g of carbohydrates, 21600–1210 μg/g of proteins and 260–4470 μg/g of lipids in the west Mediterranean (Italy). Dell'Anno et al. (2002), also in Italy, found 4600 μg/g of carbohydrates, 2100 μg/g of proteins and 1000 μg/g of lipids. The lower hydrodynamic areas showed the highest lipid concentrations, which are associated to fine sediments (Kjerfve et al. 1997, Amador 1980).

The protein/carbohydrate ratio may be used as an eutrophication level indicator in coastal systems. The ratio for an eutrophic environment is <1500–4000 μg/g for proteins, and 5000–7000 μg/g for carbohydrates (Dell'Anno et al. 2002, Pusceddu et al. 1999).

Although several authors have indicated the existence of an eutrophication process in Guanabara Bay, in the case of Suruí Mangrove that biopolymeric ratio cannot be applied due to high variation of the carbohydrate values determined and, probably, the greater velocity of physicochemical reactions in tropical environments.

CONCLUSIONS

The topography of Suruí Mangrove allows the inflow of Guanabara Bay water, which breaks the *chernies* and spreads the sandy fraction all over the sediment. The central and back areas act as deposition sites. Grain size

is an important factor in natural attenuation decrease of hydrocarbons. However, the high organic matter contents, even in samples with homogeneous distribution of sand/silt/clay, facilitated the maintenance of ACs in the sediments, together with biopolymers such as carbohydrates and proteins.

Mangroves are highly vulnerable to oil impact and play important roles in the maintenance of shorelines and as nurseries for several species. ACs in Suruí Mangrove are not washed by the tide nor naturally attenuated because, aside from the organic matter, the almost flat topography and vegetation disposition allow the sequestration of these compounds.

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RESUMO

A distribuição de compostos aromáticos selecionados e a microbiologia foram avaliados em sedimentos superficiais do Manguezal de Suruí, Baía de Guanabara. Amostras foram coletadas em 23 pontos e determinados a granulometria, matéria orgânica, compostos aromáticos, atividade microbiológica, biopolímeros e a topografia. A concentração dos compostos aromáticos foi distribuída em manchas por todo o manguezal e sua concentração total mais elevada foi encontrada na área central do manguezal. A granulometria diferiu da maioria dos manguezais, uma vez que no Manguezal de Suruí existem *chernies* nas bordas e na frente dos manguezais e areia através da superfície inteira, impedindo o relacionamento entre granulometria e os hidrocarbonetos. Uma média de 10% p/p da matéria orgânica foi obtida e os biopolímeros apresentaram concentrações elevadas, especialmente na área central e fundo do Manguezal. Os biopolímeros se distribuíram em altas concentrações. A presença de finos sedimentos é fator importante na acumulação de hidrocarbonetos. Na concentração elevada de matéria orgânica e de biopolímeros, topografia com *chernies* e as raízes que protegem os manguezais, áreas mais calmas são criadas, com depósito do material transportado pela ação das ondas. Comparadas às distribuições globais, as concentrações das substâncias aromáticas neste manguezal podem ser classificadas de moderadas a elevadas, demonstrando que a área estudada está altamente impactada.

Palavras-chave: atividade microbiológica, Baía de Guanabara, biopolímeros, fenol, Hidrocarbonetos Aromáticos Policíclicos e Monoaromáticos.

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