

Source and distribution of organic matter in surface sediments from mangroves on the island of Itaparica, Bahia/Brazil

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Abstract Elemental analysis and isotopic composition evaluated the impact of human activity at the surface sediments in the largest island of Todos os Santos Bay, northeastern Brazil. Saturated hydrocarbons (n-alkanes and isoprenoids) by gas chromatography coupled with a flame ionization detector and ^{13}C by mass spectrometer were determined from 30 surface sediment samples in mangroves at the Itaparica Island (Bahia-Brazil) in the rainy and dry season. These data, distribution, and ratio of carbon/nitrogen showed a mixture of sources: continental, marine, and anthropogenic ones. From the chromatographic profiles, light oil contamination was observed in the dry regions of Baiacu, Campinas, and Ponta Grossa, while in Jiribatuba it was observed during the rainy season. However, $\delta^{13}\text{C}$ results during dry and rainy season in

the presence of oil also showed in Misericórdia and Cacha Pregó districts for both periods and Ponta Grossa during the rainy season. Principal component analysis, using a correlation matrix, revealed the latent relationships among all the surface sediment stations investigated and confirmed our analytical results.

Keywords Saturated hydrocarbons · $\delta^{13}\text{C}$ · Organic carbon · Mangroves · Estuary

Introduction

In the mangrove ecosystem, tidal power is bland and current velocity is low which favor the intense deposition of fine sediments and organic matter (Rossi and Mattos 2002; Zagatto and Bertolotti 2008).

The chemical composition of sedimentary organic matter may vary depending on the weather on the coast and the contributions of marine and continental organic matter residues (Queiroz and Celino 2008; Pait et al. 2012). The anthropogenic influence on the environment modifies the composition and concentration of organic matter, potentially affecting the local biota (Queiroz and Celino 2008; Ekpo et al. 2012).

Carbon and nitrogen are the two main components of organic matter. The carbon content in the pellet surface depends on a number of factors such as sedimentary characteristics, the rate of microbial degradation, column of water and land ratio of entries (Costa et al. 2011). The organic material from higher plants has low

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nitrogen content and therefore a high carbon/nitrogen (C/N) ratio. Therefore, high C/N ratios in marine sediments indicate a predominantly terrestrial source of organic matter, while sediments rich in marine organic matter have lower C/N ratios (Burone et al. 2003; Gonsalves et al. 2011). According to Bordovsky (1965), marine sediments near the river exhibit the highest C/N ratios, indicating entry of terrestrial material in the area. The input of inorganic nitrogen from sewage can contribute to the reduction of C/N proportion.

The carbon isotope ratio distinguish between sources of sedimentary organic matter, either in marine or terrestrial plants, mainly reflecting the dynamics of assimilation during photosynthesis and the isotopic composition of carbon source (Meyers 1997). According to Mahiques et al. (1999), using the values of $\delta^{13}\text{C}$, based on the subscriptions of different isotopes in C_3 plants (higher land plants), and C_4 (grass), in benthic organisms, zooplankton, and phytoplankton led to an increasing number of studies and better understanding of sediment dynamics in continental and coastal areas.

Hydrocarbons present in the sediments originate from petroleum inputs, partial combustion of fossil

fuels, forest fires, and diagenetic degradation of biogenic precursors (Readman et al. 2002; Killops and Killops 2005; Celino and Queiroz 2006), constitute an important amount of the organic material that reaches the sediments.

Concentrations of total aliphatic hydrocarbons in unpolluted intertidal and estuarine sediments are normally lower than $10 \mu\text{g g}^{-1}$ (Volkman et al. 1992). In organically enriched sediments, when there is a significant input of n-alkanes derived from higher plants, total aliphatic hydrocarbon concentrations may have reached values up to $100 \mu\text{g g}^{-1}$ (Venturini et al. 2004).

The positive correlation ($p < 0.05$) between total organic carbon and total aliphatic hydrocarbons could be related to the input of terrestrial plant materials (Venturini et al. 2004) as well as to the input of petroleum products (McGroddy and Farrington 1995).

Preferred Carbon Index evaluates the maturity of thermal oil and may be used to verify the origin of organic matter. Values much higher than 1 indicate a contribution of higher plants which is considered an immature oil; however, values equal to 1 indicate an increasing maturity of oil, thus presenting the presence of oil (Killops and Killops 2005).

$$\text{CPI} = \left[\left(\frac{n\text{-C}_{25} - n\text{-C}_{33}}{n\text{-C}_{24} - n\text{-C}_{32}} \right) + \left(\frac{n\text{-C}_{25} - n\text{-C}_{33}}{n\text{-C}_{26} - n\text{-C}_{34}} \right) \right] \quad (1)$$

(Moldowan et al. 2007)

Todos os Santos Bay, with an area of approximately 927 km^2 , is the largest on the northeastern Brazilian coast, with an approximate volume of $6.39 \times 10^9 \text{ m}^3$, a medium depth of 6.9 m and currents with medium speed of 41.0 cm s^{-1} (1.476 m h^{-1}). These factors contribute to the low water residence time in the bay, minimizing the effects of the industrial effluents to be discharged into the bay (Lessa et al. 2008).

Since 1950, the area around Todos os Santos Bay (TSB) has been suffering increasing industrialization and exploitation of its natural resources (Queiroz and Celino 2008). Presently, the extraction, transportation, and refinement of petroleum at TSB are the most prominent industrial activities. The Itaparica Island is outside the area of petroleum activities, at the extreme south of TSB (Fig. 1).

Principal component analysis (PCA) reduces the number of variables in the original data set into fewer factors (or principal components) without significant

loss in the total variance of the data. The load of each variable in the original data contributes to the major components and allows the grouping of data with similar behaviors (Celino et al. 2012; Praveena et al. 2012).

The aim of this study was to investigate saturated hydrocarbons (n-alkanes and isoprenoids) and stable carbon isotopic ($\delta^{13}\text{C}$) composition in the different seasons, in surface sediments samples, from various mangroves of Itaparica Island (Bahia–Brazil), in order to assess their possible origins, especially with respect to contamination from anthropogenic sources.

Materials and methods

The TSB has two entrances separated by Itaparica Island (Fig. 1). The Itaparica Channel, on the southwest, which presents a smoother topography with an average depth of 10 m (Lessa et al. 2008). The circulation inside the bay is mostly tidally driven.

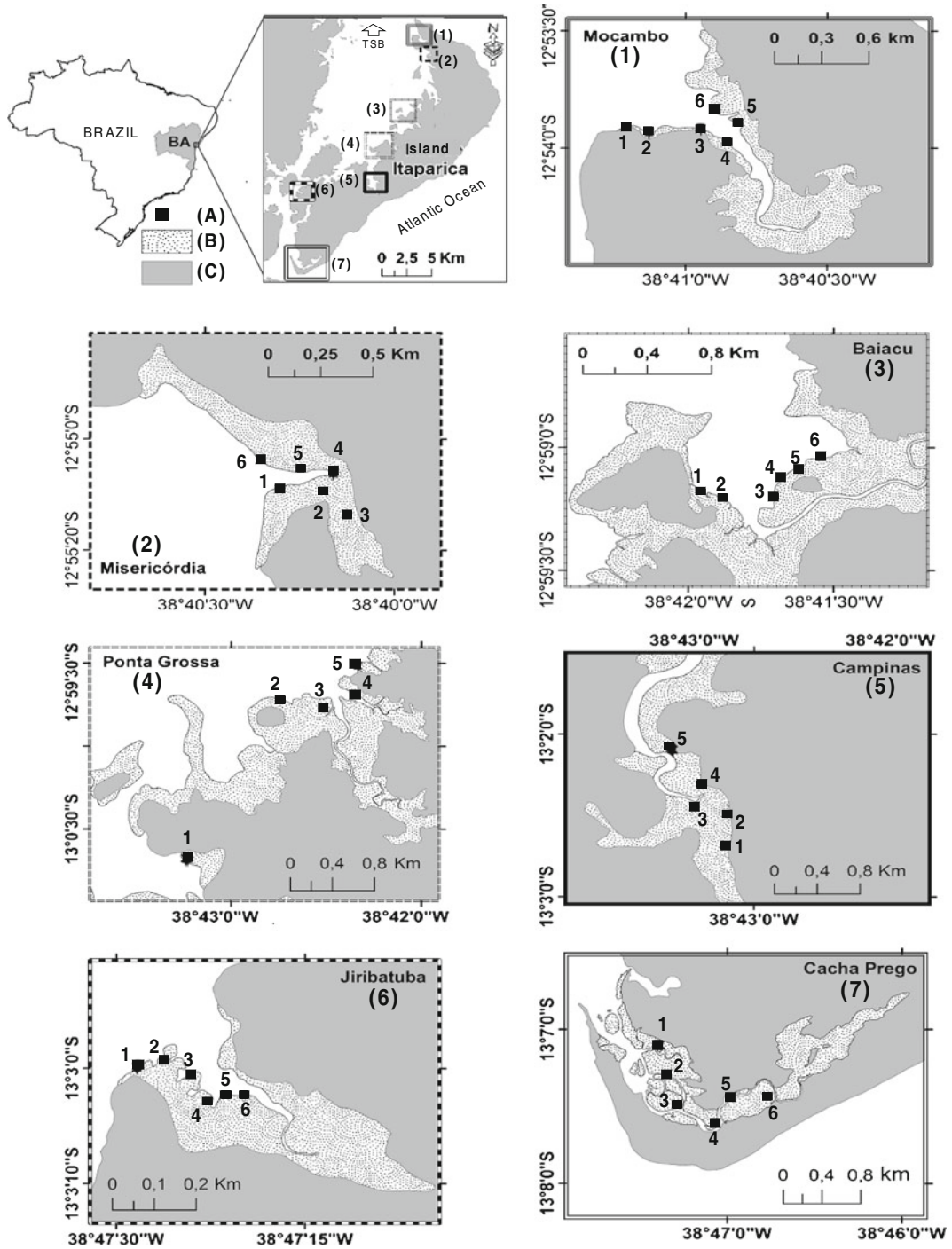


Fig. 1 Map of collecting stations Mocambo, Misericórdia, Baiacu, Cacha Prego, Ponta Grossa, Jiribatuba, and Campinas in Itaparica Island, Bahia, Brazil

During summer, the waters inside the bay have oceanic characteristics, while during winter there is a significant increase in freshwater fluxes (Souza et al. 2011).

The climate is tropical humid, with a 10-year average mean air temperature of 25.3 °C close to Salvador, and a 30-year mean rain fall of about 1,900 mm/year for the bay area (Lessa et al. 2008).

Sampling

Surface sediments (0.0 to 2.0 cm depth) were sampled twice (dry and rainy seasons) during low tide at the intertidal zone. Seven stations sampled from the Mocambo (MB), Misericórdia (MD), Baiacu (BI), Ponta Grossa (PG), Campinas (CA), Jiribatuba (JI), and Cacha Prego (CP) (Fig. 1). Composite sediment samples, within a 90×90-cm square, were collected from each station along a horizontal transect (0.1 km long), at every 10 m, by using a stainless steel spatula and transported to the laboratory in ice boxes (4±2 °C). Each sediment sample was well mixed and kept frozen until analysis.

Bulk sediment characteristics

pH measurements obtained with a SCHOTT Geräte Handylab 1, L7137A pH meter, by inserting the platinum electrode (pH) directly into the sediment (Berrêdo et al. 2008). The electrode for pH measurement was periodically calibrated with standard solutions pH 4, 7, and 10 (NIST). The temperature was measured with a SCHOTT Handylab 1, LF 513T/LF 613T portable tag apparatus by inserting the platinum electrode directly into the sediment due to a temperature sensor.

Samples previously lyophilized by L101 Liotop Lyophilizer for 48 h and homogenized with a stainless steel spatula. Around 12 g of the sample were transferred to a crucible and brought to the oven at 500 °C for 5 h to remove the organic material thereby obtaining a constant weight. Thereafter, the samples transferred to 2.00 mm (ABNT No. 10), 0.59 mm (ABNT No. 30), and 0.150 mm (ABNT No. 100) stainless steel sieves fitted one above the other, keeping the higher mesh above the lower one. After stirring these sieves for 5 min using a RETSCH AS200 mechanical stirrer, width 1.51 mm/g, the fraction retained on each sieve was weighed and removed (Embrapa, 1999).

Organic carbon analysis

Approximately 3 g of each sample lyophilized and treated with 10 ml of HCl 1 mol L⁻¹ for carbonates removal. After 24 h, the samples were centrifuged for 1 min (3,000 rpm) and the supernatant discarded. The procedure repeated until no further effervescence

occurred in the sample. The samples washed and centrifuged three times with ultrapure water, dried below 50 °C, and weighed. Each sediment sample (10–12 mg) weighed into a tin capsule, sealed, and then subjected to elemental analysis (Costa et al. 2011). Organic carbon and nitrogen isotope values were determined by elemental analyzer ECS 4010 CHNS-O Analyser Costech Instruments. Isotopic analysis determined by the elemental analyzer coupled to a Finnigan Delta Plus mass spectrometer. The gases used in the product showed high purity (300 kPa of He and O₂ where He is the carrier gas). In the equipment, it was used a thermal conductivity detector whose combustion gas used in the samples was O₂ at 30 mL min⁻¹ for 5 s and oven operating temperature of 900 °C.

Instrumental analyses

The methodology used for the extraction of the fraction of hydrocarbons based on Banjo and Nelson (2005). Each sample of sediment previously lyophilized was weighed about 10 g and subjected to 30 mL of organic solvents mixture (DCM/hexane—1:1 v/v) in a USC 2800A Unique ultrasound bath, frequency 40 kHz, for 3 cycles of 10 min each. The organic extracts obtained were concentrated using a pre-rotavaporator, then, quantitatively, transferred to a vial and subjected to nitrogen gas stream. The determination of the hydrocarbons performed by gas chromatography coupled with a flame ionization detector (GC/FID, Varian CP3800). The dissolved samples in n-hexane and directly injected without flow divider in a gas chromatograph using a DB-5 30 m×0.25 mm×0.25 mm DB-5 stationary phase column (5 % phenyl, 95 % methyl silicone), with the injector at 280 °C, initial column temperature 50 °C, 1 min isothermal, 6 °C/min, heating rate to the final temperature of 310 °C, and 10 min isothermal.

The individual hydrocarbons (pristane (P), phytane (F), and *n*-C₁₀ to *n*-C₄₀) were measured in relation to the area of its external standard calibration.

Compound identification and quantification

Total organic carbon (TOC) was measured in triplicate with a standard deviation of less than 1 %. Analysis of blank reagent showed that the analysis system and the glass container for extraction were free of contamination.

Isotopic organic carbon ratios registered in ppm (‰) and calculated as following:

$$\delta^{13}\text{C}(\text{‰}) = \left\{ R_{\text{sample}} / R_{\text{standard}} - 1 \right\} \times 1,000,$$

Where R_{sample} and R_{standard} are $^{13}\text{C}/^{12}\text{C}$ standard and sample isotopes, respectively. Carbon isotope compositions measured by an international standard of known concentration (PDB—Pee Dee Belemnite). The values of ($\delta^{13}\text{C}$) carbon isotopic ratios reported to PDB international rating scale. Reproducibility based on triplicate analysis were $\pm 0.2\text{‰}$ ($n=6$).

Quantification was performed using internal standards and the analytical program was conducted under controlled laboratory conditions, following a laboratory quality assurance protocol that includes analysis of reference material (NIST-1941), procedural blanks and participation in international intercalibration exercises.

For the analysis of individual n-alkanes, the limits of detection were on average 9×10 and $9 \times 10^{-4} \mu\text{g g}^{-1}$ (dry weight). The limit of quantification (LQM) was $0.10 \mu\text{g g}^{-1}$ (dry weight).

Since natural samples consist of complex hydrocarbons mixtures, different parameters, in addition to absolute concentrations, were analyzed to evaluate the probable origin (anthropogenic or biogenic) of hydrocarbons.

Statistical analyses

The mean and standard deviation values were calculated. All concentration data prior to statistical analysis

were normalized by logarithm (log10) transformation. Differences among mangrove stands were analyzed by a parametric one-way analysis of variance (ANOVA). *F* test was performed to detect any difference between core samples collected.

In order to explore more latent relationships to the investigated stations, PCA was applied to the obtained results. PCAs reduce the scaling of the data and form a smaller set of orthogonal factors of easier interpretation. The principle is to transform the original set of variables in a smaller set of linear combinations, which accounts for the greater part of the variance of the original set. The primary function of this analysis is to reduce the number of variables maintaining the original information as much as possible, so that the variables with similar characteristics grouped into factors (Magalhães et al. 2007).

Statistical tests were performed using the computer software STATISTICA® (StatSoft 1997).

Results and discussion

Using ANOVA: single factor through *F* test, it was verified that the pH, Eh, TOC, temperature, silt+clay, $\delta^{13}\text{C}$, and C/N ratio variables show significant differences at a confidence level of 95 % between dry and rainy seasons.

The data showed normal distribution for the saturated hydrocarbons in the dry season (Table 1) and the rainy season (Table 2).

Table 1 Descriptive statistics of mangroves sediments of Itaparica Island in the dry season

	Valid <i>N</i>	Mean	G.M.	Median	Min.	Max.	Var.	Sd
Temp. (°C)	30	31.77	31.67	32.45	27.20	35.80	6.43	2.54
pH	30	7.03	7.01	7.04	5.91	8.29	0.44	0.66
Eh	30	36.33	24.18	32.50	1.00	98.00	659.50	25.68
Sand	30	77.84	77.43	79.01	56.78	87.06	60.59	7.78
Silt+clay	30	22.16	20.99	20.99	12.94	43.22	60.59	7.78
$\delta^{13}\text{C}$	30	-18.47	-	-20.85	-24.50	0.00	37.52	6.13
TOC	30	0.53	0.35	0.51	0.06	1.89	0.20	0.44
TOC/TN	28	10.67	10.21	10.00	6.00	19.00	9.06	3.01
CPI ₂₂₋₂₆	8	0.24	0.19	0.18	0.11	0.83	0.06	0.24
CPI ₂₆₋₃₆	15	0.47	0.36	0.32	0.13	1.54	0.17	0.41
Σ n-Alk	18	0.63	0.45	0.48	0.13	2.08	0.32	0.56

Temp. temperature, TOC total organic carbon, Σ n-Alk somatory of n-alkanes, G.M. geometric mean, Min minimum, Max maximum, Var variance, Sd standard deviation, - not calculated

Table 2 Descriptive statistics of mangroves sediments of Itaparica Island in the rainy season

	Valid <i>N</i>	Mean	G.M.	Median	Min.	Max.	Var.	Sd.
Temp. (°C)	30	29.21	29.17	29.00	26.20	32.30	2.60	1.62
pH	30	7.42	7.36	7.440	5.40	9.42	0.79	0.89
Eh	30	37.57	23.15	29.00	1.00	117.00	990.20	31.47
Sand	30	77.84	77.43	79.01	56.78	87.06	60.59	7.78
Silt+clay	30	24.66	22.44	23.07	6.23	52.77	111.70	10.57
$\delta^{13}\text{C}$	30	-19.88	-	-20.10	-26.00	0.00	26.28	5.13
TOC	30	0.60	-	0.39	0.00	2.05	0.29	0.54
TOC/TN	29	11.76	11.49	12.00	6.00	16.00	6.12	2.47
CPI ₂₂₋₂₆	8	0.30	0.25	0.20	0.13	0.77	0.05	0.22
CPI ₂₆₋₃₆	15	0.77	0.35	0.22	0.10	5.30	1.85	1.36
$\Sigma\text{n-Alk}$	18	1.03	0.74	0.66	0.21	5.50	1.48	1.22

Temp. temperature, TOC total organic carbon, $\Sigma\text{n-Alk}$ somatory of n-alkanes, G.M. geometric mean, Min minimum, Max maximum, Var variance, Sd standard deviation, - not calculated

Total organic carbon and total nitrogen ratios and grain size distribution

In the dry season, the content of total organic carbon (TOC, Tables 4 and 5) at all stations that ranged from 0.09 to 0.96 % but reached up to 2.05 % in the rainy season are presented in Tables 1 to 5. The TOC concentrations in sediment samples from mangroves of Mocambo (1) and Jiribatuba (6) villages were significantly lower in comparison to other stations in the same period.

The amount of total organic carbon in Itaparica Island compared to other countries and studies performed in TSB (Table 3) are lower in this study.

Total nitrogen (TN) values also show a wide range and distribution pattern similar to TOC. The lowest values of TOC and TN are found in the inner relict sands (TOC of 0.9 to 0.5 %) and higher values on the

outer silty clays. Elevated TOC (>0.75 %) and TN content are found off the river. TOC/TN ratios mostly range between 8 and 14.

A good relation is seen between the proportion of mud fraction (silt and clay) and TOC content (Fig. 4). Organic matter is known to be associated with fine-grained sediments because of the larger surface area which provides good binding sites for organic matter (Meyers 1997). The stations established in Jiribatuba and Mocambo are located in areas with high mobility of sediments caused by tidal movement (Lessa et al. 2008). In addition to the reasons above, the leaching can influence low TOC concentrations for some stations in the rainy season (Table 5). The relict-sand dominated areas have low TOC and TN content.

The range of TOC (0.09 to 1 %) on the Itaparica Island is similar to those major rivers in high tidal regimes like Amazon, Changjiang, Pearl River etc (Hu et al. 2009).

Table 3 Comparison of total organic carbon in sediments from different sites

Local	Total amount organic carbon (%)	Reference
Todos os Santos Bay—BA	2.4–4.18	Veiga et al. 2008
Mandovi—India	1–2.5	Harji et al. 2008
Marmugoa—India	0.6–2.9	
Dom João—BA	1.04–3.00	Celino et al. 2008a, b
Itaparica Island—BA	0.09–2.05	Presente estudo

Spatial and temporal distribution of saturated hydrocarbons

As a result, for comparison in the different regions sampled in this study, hydrocarbons results (Tables 4 and 5) investigated were expressed related to the dry sediment. Moreover, the n-alkane profile distribution (n-Alk) derived from biogenic and different petrogenic sources exhibit distinct typical pattern which can be evaluated by the so-called Preferred Carbon Index (CPI). The CPI is a dimensionless quantity that relates

Table 4 Median of physico-chemical parameters, pH, Eh, silt+clay, $\delta^{13}\text{C}$, TOC, TOC/TN, CPI, CPI_{16-20} , CPI_{22-26} , CPI_{26-36} , and $\Sigma\text{n-alk}$ the mangroves surface sediments of Itaparica Island, Bahia in the dry season

Site	T (°C)	pH	Eh	Silt+clay	$\delta^{13}\text{C}$	TOC	TOC/TN	CPI	CPI_{16-20}	CPI_{22-26}	CPI_{26-36}	$\Sigma\text{n-alk}$
1	34.8	6.48	52	24.0	-14.4	0.09	8.4	-	-	-	-	0.08
2	32.8	6.88	31	21.0	-21.8	0.96	12.2	-	-	0.16	0.37	0.65
3	32.4	7.22	-19	16.0	-20.1	0.58	12	1.2	-	0.14	0.31	0.74
4	n.d.	n.d.	n.d.	7.0	-16.5	0.21	9.7	1.5	0.52	2.9	0.13	0.56
5	n.d.	n.d.	n.d.	18.0	-23.7	0.41	14.3	2.7	-	0.38	0.34	0.33
6	28.3	6.34	63	20.0	-15.2	0.16	8	-	-	-	0.14	0.24
7	30.6	7.24	11	25.0	-23.4	0.50	11.5	-	0.65	0.18	0.47	1.01

n.d. not determined, - not calculated

the amounts of n-Alk series of odd and even carbon number. The value of this index indicates the predominance of hydrocarbons of these series which helps to infer that the n-Alk amount of n-Alk with odd number of carbon is dominant in its structure. This indicates a predominance biogenic for these compounds. When the CPI is less than unity the predominant n-Alk is the number of even carbons whose dominant source indicated is anthropogenic (Aboul-Kassim and Simoneit, 1996). However, if the CPI is equal or very close to unity an indication of its origin is petrogenic but should not be used isolatedly.

The spatial distribution of hydrocarbons in sediments of mangrove swamps of Itaparica Island—BA studied by comparing the concentrations of n-Alk among different sampling sites (Mocambo, Misericordia, Baiacu, Ponta Grossa, Campinas, Jiribatuba, and Cacha Pregó) during dry and rainy seasons.

Looking at Fig. 2, concentrations of n-Alk were found above $2 \mu\text{g g}^{-1}$ dry sediment in BI4 and PG1 during dry season and CP2 and CP4 in the rainy season.

Concentrations found in the village of Mocambo were below LQM ($0.10 \mu\text{g g}^{-1}$ dry sediment) in the dry season. The other locations are plenty of high molecular weight n-alkanes ($>n\text{C}_{20}$), both in dry and in wet seasons. Carbon chain length in the range $n\text{C}_{23}$ $n\text{C}_{35}$ is characteristic of n-alkanes source land derived wax cuticle from vascular plants, depending on the local vegetation it can predominantly occur $n\text{C}_{25}$, $n\text{C}_{27}$, and $n\text{C}_{29}$, $n\text{C}_{31}$ (Veiga et al. 2008).

During the dry MD, BI and CA showed a mixture of organic matter of algal debris and vegetation due to predominant continental CPI_{22-26} and CPI_{26-36} (Table 4) (Commendatore et al. 2000; Stout et al. 2001). PG and CP also present predominance CPI_{22-26} and CPI_{26-36} is the presence of CPI_{16-20} due to phytoplankton and bacteria (Commendatore et al. 2000). JI organic matter presents continental vegetation due to predominant CPI_{26-36} (Stout et al. 2001). In the rainy season MD, BI and PG also present predominance in CPI_{22-26} and CPI_{26-36} is the presence of CPI_{16-20} due to phytoplankton and bacteria in

Table 5 Median physico-chemical parameters, pH, Eh, silt+clay, $\delta^{13}\text{C}$, TOC, TOC/TN, CPI, CPI_{16-20} , CPI_{22-26} , CPI_{26-36} , and $\Sigma\text{n-alk}$ the mangroves surface sediments of Itaparica Island, Bahia in the rainy season

Site	T (°C)	pH	Eh	Silt+clay	$\delta^{13}\text{C}$	TOC	TOC/TN	CPI	CPI_{16-20}	CPI_{22-26}	CPI_{26-36}	$\Sigma\text{n-alk}$
1	27.3	7.88	-27	19.0	-15.6	0.19	9.1	-	-	-	-	0.08
2	28.2	7.32	10	24.5	-22.9	1.42	12.8	-	-	0.16	0.37	0.65
3	30.6	7.18	-15	15.5	-19.7	0.35	10.8	1.2	-	0.14	0.31	0.74
4	27.8	6.58	49	14.0	-21.8	2.05	10.9	1.5	0.52	2.90	0.13	0.56
5	30.0	6.43	59	14.0	-20.3	0.08	11.7	2.7	-	0.38	0.34	0.33
6	28.7	7.49	5.0	35.5	-18.4	0.26	10.5	-	-	-	0.14	0.24
7	31.1	6.38	62	27.5	-25.5	0.81	14.8	-	0.65	0.18	0.47	1.01

n.d. not determined, - not calculated

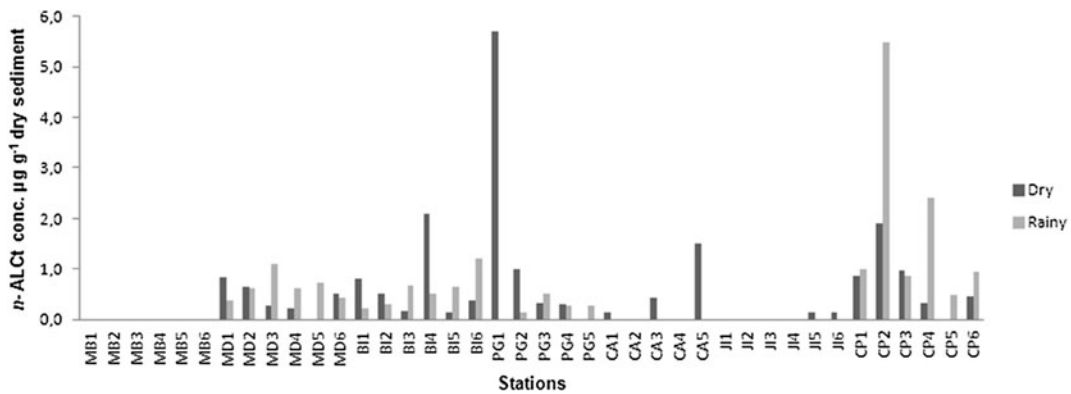


Fig. 2 Distribution of Σn -alk in surface sediments of the Itaparica Island—BA

Table 5 (Commendatore et al. 2000). CP showed a mixture of organic matter of algal debris and vegetation due to predominant continental CPI_{22–26} and CPI_{26–36} in Table 5 (Commendatore et al. 2000; Stout et al. 2001).

In the rainy season, the JI (Fig. 5) maximum concentration values in nC_{27} are predominantly observed. n -alkanes of high molecular weight abound ($>nC_{20}$), in which the concentration of odd over the even ones is predominantly typical of higher plants (mangrove)

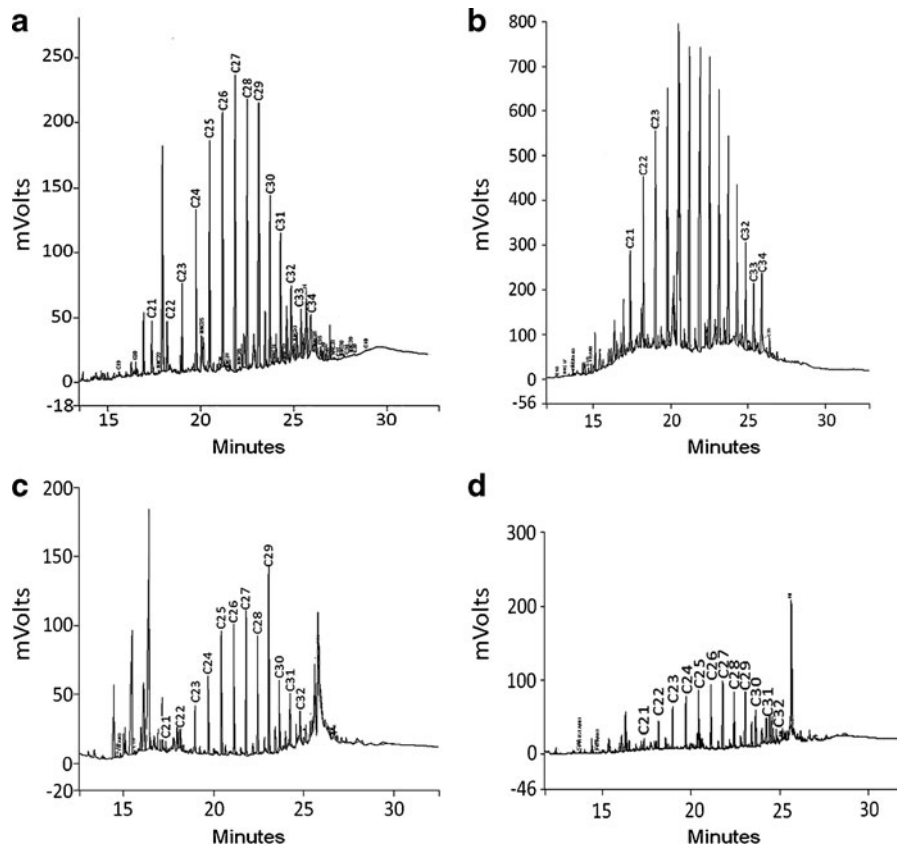
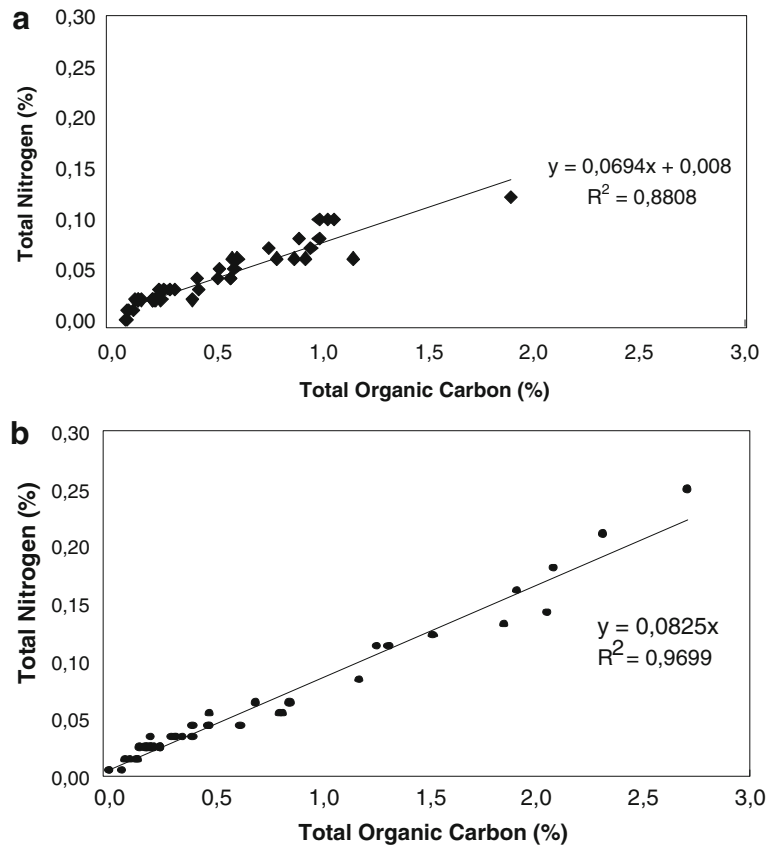


Fig. 3 Chromatograms showing the distribution of n -alkanes of the dry period: **a** B14 Station BI, in the village of Baiacu, **b** PG1 PG station in the village of Ponta Grossa, **c** CA3 station CA in

the town of Campinas and JI5 in JI station during rainy season in the village of Jiribatuba in Itaparica Island—BA

Fig. 4 % TN versus % TOC the dry period (a) and rainy season (b) in sediments of the Island Itaparica, Bahia, Brazil



(Le Dréau et al. 1997), evidenced by nC_{25} and nC_{29} that exhibit maximum peak concentrations. The chromatogram shows a typical profile of a mixture of contribution of organic matter illustrated by the marked depletion of the compounds nC_{21} , nC_{22} , nC_{31} , and nC_{32} , suggesting a mixing source with strong oil influence (Fig. 3).

One side of Itaparica Island faces the Atlantic Ocean and the other one faces the TSB, where there are the mangroves of Misericórdia, Baiacu, Ponta Grossa, Campinas, and Jiribatuba. This side works as a source of protection due to the influence of ocean currents bringing the hydrocarbons into the TSB (Lessa et al. 2008).

The establishment of contamination levels by hydrocarbons is related to their concentration in the environment. In harbor areas, industrial and urban petrogenic hydrocarbons may have concentration between 10 and 1,000 $\mu\text{g g}^{-1}$ dry sediment (UNEP, 1992). Some studies were carried in TSB, such as Wagener et al. (2010), who studied TSB sediments and found concentration ranging from 0.47 to 18.69 $\mu\text{g g}^{-1}$ dry sediment. Celino et al.

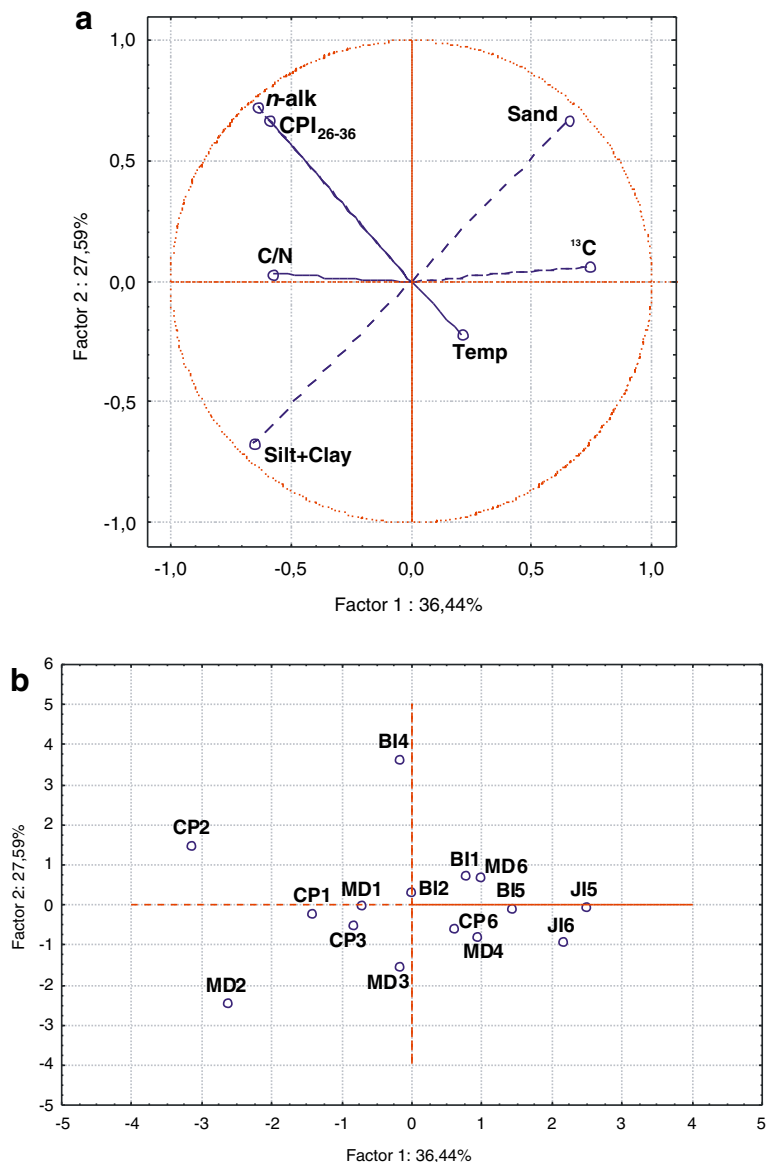
(2008a, b) studied the Northern TSB and found concentration ranging from 1.0 to 5.7 $\mu\text{g g}^{-1}$ dry sediment. In the present study the concentration was between 0.14 and 5.7 $\mu\text{g g}^{-1}$ dry sediment in the dry season and 0.21 to 5.5 $\mu\text{g g}^{-1}$ dry sediment during the rainy season, implying that the contamination found in Itaparica Island is lower when compared to studies in TSB (Fig. 4).

Sources of organic matter

TOC/TN ratio has been used to identify the source of organic matter. Some authors have suggested different values of TOC/TN ratio, according to the source of organic matter. Saito et al. (1989) suggested ratio greater than 20 to ground source and 5 to 7 as marine source. Additionally, Stein (1991) recorded values below 10, what suggests marine origin and values around 10 are components of both marine and terrestrial sediment.

In this study the TOC/TN ratio ranged from 8 to 14.3 in the dry season (Table 4) and from 9.1 to 14.8 in the rainy season (Table 5). Analyzing TOC/TN values

Fig. 5 **a** Graphic scores for the dry season regarding the variables of mangroves surface sediment samples in Itaparica Island, Bahia, Brazil. **b** Weights chart for the dry season of mangrove surface sediment samples of Itaparica Island, Bahia, Brazil



in surface sediments in the dry season for MB5, the MD1 MD6, BI1, BI2, BI5, PG1, PG3, PG4, MP5, CA1, CA3, CA4, CA5, JI1, CP1, CP2, CP3, and CP4 indicated a mixture of organic matter origin in marine-terrestrial, except for the MB2, MB4, MB6, BI3, BI4, BI6, PG2, and CA2, the JI2, JI6, CP5, and CP6, whose origin is marine. MB2 in the rainy season, the MD1 MD6, BI1, BI3, BI5, BI6, and PG2, the MP5, CA3, CA5, JI1, JI2, JI3, JI6, and CP1 to CP6 showed a mixture of marine-terrestrial organic matter origin except for MB1, MB3, MB5, MB6, BI2, BI4, PG1, CA1, JI4, and JI5 which presented marine origin.

Low TOC/TN ratios have been ascribed to higher portion of soil-derived organic carbon (Hu et al. 2009).

The stable carbon isotopic composition ($\delta^{13}\text{C}$) has also been used to distinguish the organic matter, either from marine sources or terrestrial plants sources (Schubert and Calvert 2001). Marine organic matter typically has $\delta^{13}\text{C}$ values ranging from -19 to -21‰ . Terrestrial plants with C_3 have an average value of $\delta^{13}\text{C}$ -27‰ (-22 and -33‰), while for C_4 it varies from -9 to -16‰ , with an average -13‰ (Hu et al. 2009). Most oils show $\delta^{13}\text{C}$ values in the range of -21

to -32% . The frequency distribution shows a strong peak between -28 and -29% (Mook and Vries 2001).

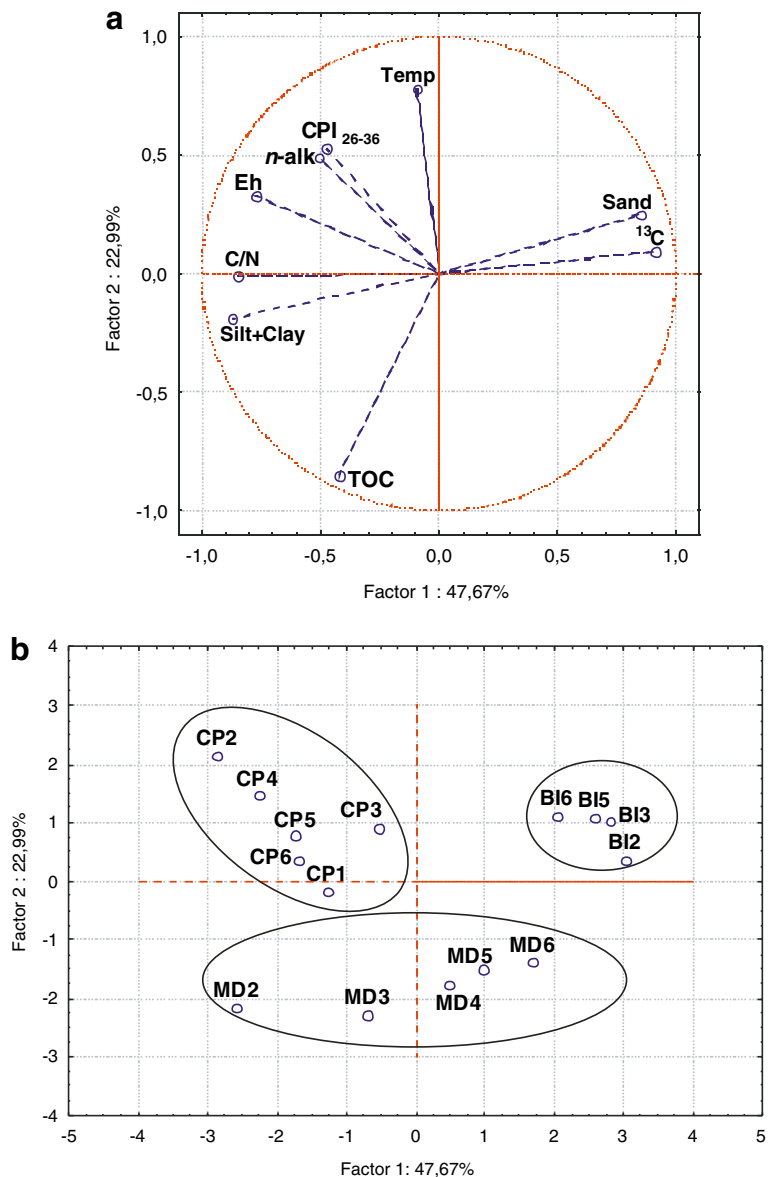
The $\delta^{13}\text{C}$ in the present study ranged from -14.4 to -23.7% (Table 5) during the dry season and -1 and TOC/TN ratio has been used to 5.6 to -25.5% during the wet season, suggesting a mixture of marine/land source to organic matter. From MD, CA and CP in the dry season, one can infer that the oil presence results from $\delta^{13}\text{C}$ -21.8 , -23.7 , and -23.4% , respectively. In the rainy season MD, CP and PG showed traces of oil $\delta^{13}\text{C}$ -22 , -25.5 , and -21.8% , respectively. For both periods the isotopic composition range approaches the

terrestrial plants range due to oil isotopic composition being considered lighter than sea carbonates (Mook and Vries 2001).

In order to verify the behavior of saturated hydrocarbons over the dry and rainy seasons it was used PCA, using 7.0 Statistica program made from pre-processed and normalized data through self-scheduling. The significance assessment occurred by ANOVA: single factor at 95 % confidence.

For dry season a data set with seven variables and 15 samples was made. PC1 and PC2 explained 64.03 % of the total variance. Figure 5 is observed in

Fig. 6 **a** Graphic scores for the variables of mangroves surface sediments samples of Itaparica Island, Bahia, Brazil. **b** Chart weights of the rainy season for the points of mangroves surface sediments samples of mangroves of Itaparica Island, Bahia, Brazil



PC2 positive correlations between sand, CPI_{26-36} and n -Alk contributing to the classification of CP2 and BI4 (Fig. 5). The $\delta^{13}C$ (Fig. 5) contributes to JI5 classification (Fig. 5). There was a negative correlation for PC2 regarding silt+clay ratio (Fig. 5) contributing to MD2 (Fig. 5), temperature (Fig. 5) for MD4, JI6 and CP6 classification (Fig. 5).

In the rainy season, a set of data samples 9 and 15 variables was made. PC1 and PC2 explained 70.66 % of the total variance. Figure 6 is observed in PC2-positive correlations among temperature, CPI_{26-36} , Σn -alk, and Eh, contributing to the formation of an assembly made by CP1, CP2, CP3, CP4, CP5, and CP6 (Fig. 6). $\delta^{13}C$ and sand (Fig. 6) contribute to the formation of an assembly made by BI2, BI3, BI5, and BI6 (Fig. 6). Negative correlation is observed in PC2 for silt+clay and TOC (Fig. 6) contribute to the formation of an assembly made by MD2, MD3, MD4, MD5, and MD6 (Fig. 6).

No statistically significant correlation was found between TOC and Σn -alk. Regarding plants derived from n-alkanes, this can be expected due to n-alkanes differential degradation and some carbon and organic material fractions from lignins and humic matter (Wagener et al. 2010).

Conclusion

Organic matter content correlates well with grain size and comparatively higher organic matter content is present fine-grained inner sediments and lower organic in the outer relict sands. Comparatively low rates of processing of soil carbon from source region floodplains and rapid burial on the shelf leads to better preservation of terrestrial carbon in the continental shelf sediments (Ramaswamy et al. 2008).

Although mangroves have presented a mixture of hydrocarbon sources, from terrestrial and marine origin, both TOC/TN ratio and stable carbon isotopic composition ($\delta^{13}C$), indication of oil presence was found through the chromatographic profiles for BI4, C3, and PG1 during dry season and JI5 during rainy season, as well as $\delta^{13}C$ which presented information about the presence of oil in Misericordia and Cacha Prego during dry and rainy season, in Campinas during dry season, and Ponta Grossa in the rainy season. The concentrations of Σn -alk were between 0.14 and $5.7 \mu\text{g g}^{-1}$ dry sediment in the dry season and 0.21 to

$5.5 \mu\text{g g}^{-1}$ dry sediment in the rainy season, implying that the contamination found in Itaparica Island is lower when compared with studies in TSB.

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