

# Hydrocarbons in surface sediments of harbor areas in a tropical region (Ceará state, northeast Brazil)

Lucas Moreira Buruaem<sup>1</sup> · Satie Taniguchi<sup>2</sup> · Silvio Tarou Sasaki<sup>2</sup> ·  
Márcia Caruso Bicego<sup>2</sup> · Leticia Veras Costa-Lotufu<sup>3</sup> · Denis Moledo Souza Abessa<sup>1</sup>

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**Abstract** Sediment samples collected in two harbors of a tropical region of Brazil were investigated for the distribution of linear alkylbenzenes (LABs), aliphatic (AHs) and polycyclic aromatic hydrocarbons (PAHs). The levels of hydrocarbons in sediments from Mucuripe and Pecém harbors were lower than those reported in industrialized sites and threshold levels of sediment quality guidelines. Analysis of AHs revealed an input of biogenic compounds and, according to diagnostic ratios, PAHs in both harbors originated from pyrogenic sources, which can be related to harbor activities. The contribution of local and diffuse sources seemed to be less important, but not negligible. Deposition zones in both harbors are associated to sedimentation of particles, biogenic materials and hydrocarbons. The results of this study can assist in characterization and management of dredged material by providing information on the distribution and sources of hydrocarbons along the tropical zones, which is important for the identification of ecological risks associated with these compounds.

**Keywords** Dredging · Marine pollution · Sediment contamination · Tropical environments

## Introduction

Harbor activities have important roles in global economy. However, such activities are generally recognized as harmful to coastal environments. Negative impacts related to port installation and operation involve changes in sediment transport due the construction of jetties, dredging and removal of sediments, and increasing contamination due to generation of wastes and discharge of chemicals, such as petroleum and its derivatives (NRC, National Research Council 1997). These activities are often associated with marine pollution and the input of contaminants along the different environmental compartments. In this context, sediments constitute a sink and a secondary source of many compounds, presenting higher concentrations when compared to the water column (Burton 2002).

Port areas may receive loads of petroleum and derivatives and the distribution of these substances in the sediment can be assessed by aliphatic (AHs) and polycyclic aromatic hydrocarbons (PAHs) analysis. AHs are important petroleum derivatives and may also be biosynthesized by marine or terrigenous organisms (Volkman et al. 1992). PAH are released from natural sources such as biomass combustion, volcanic eruptions and diagenesis, while anthropogenic sources include coal and wood burning, oil combustion, industrial activities, effluents and accidental fuel spills (USEPA United States Environmental Protection Agency 2003). Linear alkylbenzenes (LABs) are hydrocarbons that have been released into the environment since the early 1960s as by-products of linear alkylbenzene sulfonate (LAS) detergents, which represents the most widely

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✉ Lucas Moreira Buruaem  
lburuaem@gmail.com

<sup>1</sup> Núcleo de Estudos em Poluição e Ecotoxicologia Aquática (NEPEA), Universidade Estadual Paulista (UNESP), Pça. Infante D. Henrique s/n°, São Vicente, SP CEP: 11330-900, Brazil

<sup>2</sup> Universidade de São Paulo, Pça. do Oceanográfico, 191, Butantã, SP CEP: 05508120, Brazil

<sup>3</sup> Universidade Federal do Ceará, Av. da Abolição, 3207, Meireles, Fortaleza CEP: 60165-081, Brazil

used anionic surfactants in the world. Their environmental occurrence has been related to sewage discharges and source of domestic and industrial wastes (Eganhouse 1986).

To deal with the problem of sediment contamination, different countries, such as much of the European Community, United States and Canada, have developed enforcements and criteria towards the characterization and classification of contaminated sediments (Burton 2002). In Brazil, nevertheless, some efforts have been employed into the development of regulations for marine and estuarine sediments. The Federal Resolution CONAMA 454/12 (Brasil 2012) was published with the purpose of establishing Sediment Quality Guidelines (SQGs) for dredging activities, however, such parameters were based on international values.

Some authors have demonstrated that the use of these SQGs may be ineffective to protect biota from tropical and subtropical areas and recommended the development of site specific values (Choueri et al. 2009; Buruaem et al. 2012). The achievement of this goal requires efforts to expand information on distribution and levels of contaminants in sediments from various sectors of the Brazilian coast, since different coastal areas present distinct climate and sedimentology in a continental-scale, as pointed by Lacerda and Marins (2005). These authors reported a dominance of clastic materials and fines particles in sediments from subtropical areas like in the southeast in relation to the Tropical ones as in the northeast, which is richer in calcium carbonates and sandy sediments.

Mucuripe and Pecém are the two main harbors of Ceara state, located on the northeast region of the Brazilian coast. These ports account for shipping most goods that are produced and traded in this Brazilian region. Thus, these areas are vulnerable to emissions of contaminants typical of harbor areas. Mucuripe is located within Mucuripe bay, in Fortaleza city, state capital of Ceará, and its area comprises the access channel, anchorage areas and evolution basins, which are protected by a long jetty (1900 m). On the other hand, Pecém port terminal is located in the municipal district of São Gonçalo do Amarante, about 50 km west from the capital, and is an “offshore” terminal assembled 2000 m from shoreline.

Fortaleza is one of the most important cities in Brazil, with over 2.3 million in habitants distributed across an area of 313 km<sup>2</sup> in its metropolitan region. Different anthropogenic contamination sources are situated along the coastline, such as vehicular emissions (e.g., deposition of particles and gases), harbor areas, drainage from urban pluvial water system (urban runoff) and industrial wastewater, transport and refinement of oil, and sewage discharges (Cavalcante et al. 2009; Cavalcante et al. 2010). Considering the lack of data on the contamination of

marine sediments, especially considering tropical regions, the present study aims to determine the composition, levels and sources of hydrocarbons in superficial sediments from the vicinities of Mucuripe and Pecem harbors through the analysis of LABs, AHs and PAHs, once these areas are affected by the potential sources of such compounds.

## Materials and methods

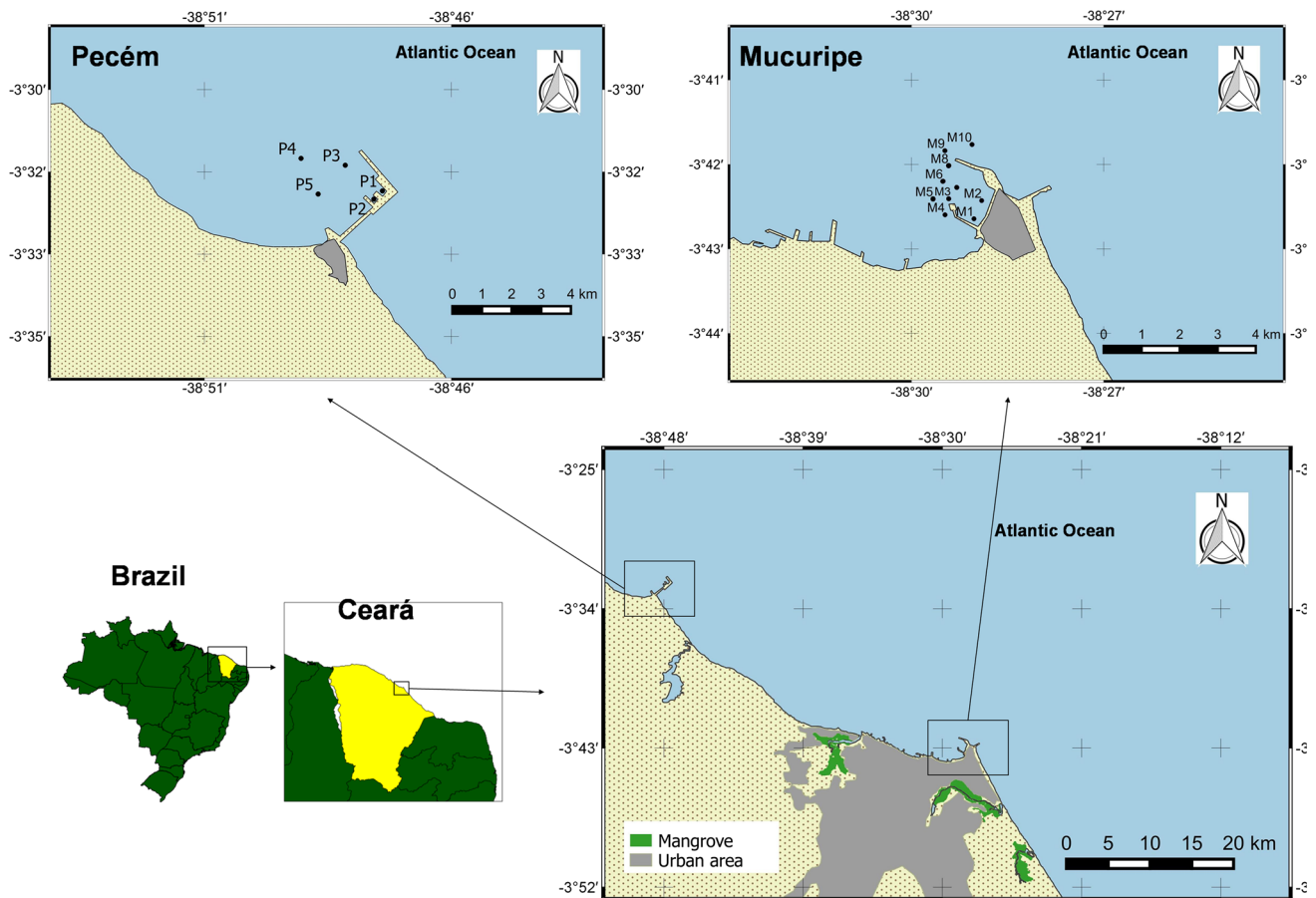
### Sediment sampling and handling

In Mucuripe harbor, sediment sampling was carried out in August 2007 and comprised 10 stations (Fig. 1): M1 and M2 were located at the commercial docks; M3 to M5 were close to tanker piers; M6 and M7 were situated at the access channel; and M8 to M10 were positioned in unsheltered areas. In Pecém terminal port, the collection was carried out in January 2008 and covered five stations (Fig. 1): P1 and P2 were close to the docking piers; P3 and P4 were at the access channel; and P5 was in an unsheltered area. Samples were collected using a *Van Veen* grab and only the top 2 cm of surface sediment were sampled. An aliquot was air-dried (Loring and Rantala 1992) and packed in plastic containers for analysis of sediment characteristic, and a second aliquot was stored in aluminum boxes at  $-20\text{ }^{\circ}\text{C}$  for subsequent analysis of hydrocarbons.

### Sediment analysis

Grain size distribution was measured by the wet sieving method (Mudroch and MacKnight 1994). Calcium carbonate contents ( $\text{CaCO}_3$ ) estimation was conducted by HCl digestion and gravimetry (Gross 1971). Decarbonated sediments were separated for total organic carbon analysis (TOC), determined on a TOC analyzer model SHIMADZU TOC-V series coupled with SSM-5000A and organic matter content analysis (OM), determined by the method of ignition and gravimetry (Luczak et al. 1997).

The sediment samples were freeze-dried and homogenized. An amount of 20 g was Soxhlet-extracted with a 50 % mixture of *n*-hexane and dichloromethane for 8 h according to UNEP (UNEP United Nations Environment Programme 1992). Before extraction, *n*-hexadecene (for AHs), *d*<sub>8</sub>-naphthalene, *d*<sub>10</sub>-acenaphthene, *d*<sub>10</sub>-phenanthrene, *d*<sub>12</sub>-chrysene, *d*<sub>12</sub>-perylene (for PAHs), and dodecyl 1-benzene (IC<sub>12</sub>-LAB for LABs) were added as surrogates to all the samples, blanks and reference material. The hydrocarbon extracts were fractionated into F1 (AHs hydrocarbons and LABs) and F2 (PAHs) by silica gel-alumina column chromatography. Twenty-six AHs hydrocarbons (*n*-C<sub>17</sub> to *n*-C<sub>35</sub>, including pristane and phytane)



**Fig. 1** Sites of sediment sampling in Mucuripe and Pecém harbors

were determined on a gas chromatography 6890 from Agilent Technologies with flame ionization detector (GC-FID). Thirty-three PAHs and thirty LABs were quantitatively analysed by an Agilent 6890 gas chromatograph coupled to a 5973 N mass spectrometer (GC/MS) in a selected ion mode (SIM). The results from all the compounds analyzed are presented in the Supplementary data (Appendix A, B and C).

Quality assurance and quality control (QA/QC) were based on the analysis of procedural blank, blank spike, matrix spike, matrix duplicate and standard reference material. The mean recoveries of surrogates and target compounds were within 65 and 102 %. The precision ranged from 1.8 to 12 % for AHs, 1.0 to 17 % for LABs and 1.6 and 19 % for PAHs. The method accuracy was ensured by the analyses of standard reference material from International Atomic Energy Agency (IAEA 417). GC/MS and GC-FID detection limit (DL) was 0.025 ng for LAB and PAH, and 0.13 ng for AH. Method detection limit (MDL) was based on the standard deviation ( $3 \times \sigma$ ) of seven replicates of a sediment sample containing target compounds at a level of one to five times the expected MDL.

## Results and discussion

Sediment characteristics are shown in Table 1. The sediments from Mucuripe and Pecém are composed mainly of sand, with higher levels of fine particles (mud) occurring in sheltered areas (M1–M7 and P1–P4). This can be associated with the occurrence of depositional areas induced by jetties, given the high hydrodynamics of this region, and the predominance of trade winds in E–W determines the constant transport of sediments towards West (Maia et al. 1998). Calcium carbonates, organic matter and TOC also presented higher levels in depositional areas.

According to Freire et al. (2004), sediments of the coast of Ceará are originated from organogenic and terrigenous facies. Organogenic substrates are derived from calcareous algae (*Lithothamnium* sp and *Halimeda* sp), contributing in up to 95 % of calcium carbonate deposition, and organic matter contents ranging, from 20 to 40 %. Sediments from terrigenous facies are characterized by siliciclastic material and clay. The texture of the outer shelf particles (40 m isobath) consists of gravel and those from the inner shelf

**Table 1** Sediment characteristics, total concentrations of LABs, AHs and PAHs including the diagnostic criteria for sediments collected in Mucuripe and Pecém harbors

Sites	Depth (m)	Mud (%)	CaCO <sub>3</sub> (%)	OM (%)	TOC (%)	Total LABs (ng/g)	Total AHs (μg/g)	Total <i>n</i> -alk (μg/g)	UCM (μg/g)	CPI	DP	LMW-PAH (ng/g)	HMW-PAH (ng/g)	Total PAHs (ng/g)	LMW/HMW
M1	7.4	24	18.4	5.6	0.9	<0.8	25.7	0.8	22.0	2.9	<i>n</i> -C <sub>30</sub>	18.0	59.9	77.9	0.3
M2	15.0	7.9	30.3	12.7	1.4	<0.8	19.1	0.6	16.0	2.9	<i>n</i> -C <sub>29</sub>	41.6	66.2	107.8	0.6
M3	15.4	22.7	25.0	6.0	0.9	<0.8	17.6	0.9	14.8	4.9	<i>n</i> -C <sub>29</sub>	15.7	44.0	59.7	0.4
M4	14.7	24.4	35.0	16.2	1.4	5.8	21.1	1.3	17.2	3.8	<i>n</i> -C <sub>29</sub>	34.0	53.9	87.9	0.6
M5	10.7	15.6	15.7	3.3	0.4	<0.8	1.1	0.2	NC	4.5	<i>n</i> -C <sub>17</sub>	3.5	24.4	28.0	0.1
M6	14.6	16.7	26.6	8.6	1.1	1.3	2.5	1.1	NC	4.6	<i>n</i> -C <sub>29</sub>	9.0	27.7	36.7	0.3
M7	9.6	5.4	22.2	12.2	0.8	<0.8	13.5	0.7	11.1	4.6	<i>n</i> -C <sub>31</sub>	5.9	37.5	43.4	0.2
M8	9.6	0.6	9.4	1.0	0.2	<0.8	1.0	0.1	NC	NC	<i>n</i> -C <sub>17</sub>	<1.00	<1.00	<1.0	NC
M9	11.9	0.1	5.7	0.5	0.2	<0.8	0.5	0.1	NC	NC	<i>n</i> -C <sub>24</sub>	<1.00	<1.00	<1.0	NC
M10	12.6	0.0	8.6	0.1	0.2	<0.8	0.3	0.1	NC	NC	<i>n</i> -C <sub>17</sub>	<1.00	<1.00	<1.0	NC
P1	16.7	4.4	37.0	14.9	1.3	3.2	14.8	0.7	12.6	2.1	<i>n</i> -C <sub>31</sub>	49.4	94.5	143.9	0.5
P2	16.4	10.9	33.8	12.2	1.1	2.9	19.5	0.9	16.7	2.8	<i>n</i> -C <sub>29</sub>	64.9	227.1	292.0	0.3
P3	17.5	8.2	29.0	14.7	1.4	4	17.4	1.0	14.7	1.8	<i>n</i> -C <sub>31</sub>	25.0	52.2	77.2	0.5
P4	17.2	14.3	26.5	7.7	0.8	1.6	1.5	0.7	NC	2.5	<i>n</i> -C <sub>29</sub>	10.2	21.8	31.9	0.5
P5	15.1	6.9	24.8	2.5	0.5	<0.8	1.1	0.4	NC	2.6	<i>n</i> -C <sub>29</sub>	68.3	114.6	182.9	0.6

*Total LABs* total linear alkylbenzenes, *Total n-alk* total *n*-alkanes, *Total AHs* total aliphatic hydrocarbons (*n*-C<sub>12</sub>–*n*-C<sub>34</sub>), *UCM* unresolved complex mixture, *CPI* carbon preference index (*n*-C<sub>25</sub>–*n*-C<sub>33</sub>), *DP* dominant peaks, *LMW-PAH* low molecular weight PAHs (sum of 2 and 3 rings PAHs), *HMW-PAHs* high molecular weight PAHs (sum of 4–6 rings PAHs), *NC* not calculated

(below the 20 m isobath) are composed of sand, biotrittic gravels and low amounts of mud (below 2.5 %).

Total concentrations of LABs are given in Table 1. In both areas only C<sub>13</sub>-LABs (tridecylbenzene) were detected. Moreover, concentration of LABs was found to be very low compared with other polluted places (Wei et al. 2014); in the most samples, values were below detection limits. In Mucuripe, LABs were found only in M4 and M6 (1.3 and 5.8 ng/g, respectively), while, in Pecém, they were found in P1–P4, ranging from 1.6 to 4 ng/g. The main source of sewage in Mucuripe harbor can be attributed to discharge of drainage channels of urban pluvial water system, which also receives inputs of illegal sewage. In Pecém, the potential source of sewage is the Oceanic Outfall System that was designed to release industrial and domestic sewage effluents from the harbor

facilities. For both harbors, the contribution of such source seems to be small.

According to Raymundo and Preston (1992) compositions of most commercial detergents presented LABs with 11 and 12 carbons atoms in the alkyl chain (C<sub>11</sub>-LABs and C<sub>12</sub>-LABs) in their formulations. However, the only compounds detected in both harbors were the C<sub>13</sub>-LABs. The presence of C<sub>13</sub>-LABs can be explained by their low solubility in water and high affinity for organic matter, which were assessed by octanol–water partition coefficient (Kow) by Sherblom et al. (1992). These values can be considered as baseline for samples collected in harbors and nearby areas.

Total concentrations of the AHs, including *n*-alkanes (from C<sub>12</sub> to C<sub>35</sub>), unresolved complex mixture (UCM), carbon preference index (CPI) and dominant peaks are also

presented in Table 1. The concentrations in samples ranged from 0.3 to 25.7  $\mu\text{g/g}$  in Mucuripe and 1.1 to 19.5  $\mu\text{g/g}$  in Pecém. Total *n*-alkanes concentrations ranged from 0.1 to 1.3  $\mu\text{g/g}$  in Mucuripe and 0.4 to 1.0  $\mu\text{g/g}$  in Pecém. Values above 50  $\mu\text{g/g}$  of these hydrocarbons can be related to polluted samples, while concentrations below 10  $\mu\text{g/g}$  are normally from biogenic source and unpolluted sediments (Volkman et al. 1992). Based on these results, it can be suggested a natural input of these hydrocarbons for both areas.

Dominant hydrocarbons ranged from *n*-C<sub>17</sub> to *n*-C<sub>31</sub> in Mucuripe, while *n*-C<sub>29</sub> and *n*-C<sub>31</sub> predominated in sediment samples from Pecém. The alkanes *n*-C<sub>29</sub> (M2, M3, M4, M6, P2, P4 and P5) and *n*-C<sub>31</sub> (M7 and P1) were found in sediments with high % of fines and OM (depositional zones). In these sites, such molecules are related to inputs from terrestrial higher plants, as they are commonly found in environments situated close to land due to the composition of epicuticular waxes from leaves of mangrove trees (Shaw and Johns 1985). The metropolitan region of Fortaleza has 14.1 km<sup>2</sup> of mangrove area with 60 % distributed in urban zones (Cavalcante et al. 2009). Considering the direction of currents of sediment transport, the outflows from Pacoti and Cocó rivers are located upstream of the Mucuripe harbor, while Pecém is located downstream of both rivers, and also to Ceará river (Fig. 1), which explains the distribution of these compounds.

Moreover, *n*-alkanes with low molecular weight, such as *n*-C<sub>17</sub>, are related to phytoplankton origin, also indicating a biogenic source from marine primary production in M5, M8 and M10 (Requejo and Quinn 1983; Volkman et al. 1992).

Carbon preference index (CPI) is used to characterize the contribution of terrestrial plant waxes that have high CPI value (>3) (NRC NRC, National Research Council 1985), and petroleum contribution that has CPI generally values around 1.0 (Wang et al. 1999). In this study, samples from most stations (except M9 and M10) presented values above 1.2, and sediments from M3, M5, M6 and M7 presented CPI values higher than 4, corroborating a biogenic contribution to the sediments.

The UCM can be defined as a raised baseline hump that is often observed in gas chromatograms of petroleum, which are related to the majority of molecules present in the total AHs that cannot be resolved by capillary GC columns (Volkman et al. 1992). The UCM is also a common feature in chromatograms of biodegraded oils and its presence can be used as an indicator of oil pollution (Fryzinger et al. 2003). Even with low concentration, some samples presented signs of petroleum residues. The contents of UCM ranged from 80 to 85 % of total hydrocarbons in the samples with near the effluent discharge from

oil refinery in Mucuripe (M1–M4 and M7) and the sheltered sites of Pecém (P1–P3). Both these areas are shadowed by their respective jetties, which decreases the material-carrying capacity of waves and currents and therefore, the dispersion of compounds in the water column.

Total concentrations and diagnostic ratios for the identification of PAH origins are presented in Table 1. In sediments from Mucuripe and Pecém, total respective PAH levels ranged from 36.7 to 107 ng/g and from 31.9 to 292 ng/g. These concentrations are low and presented a similar distribution to that found for AHs, with higher levels in sediments from sheltered zones of both areas, associated with fines sediments and organic matter.

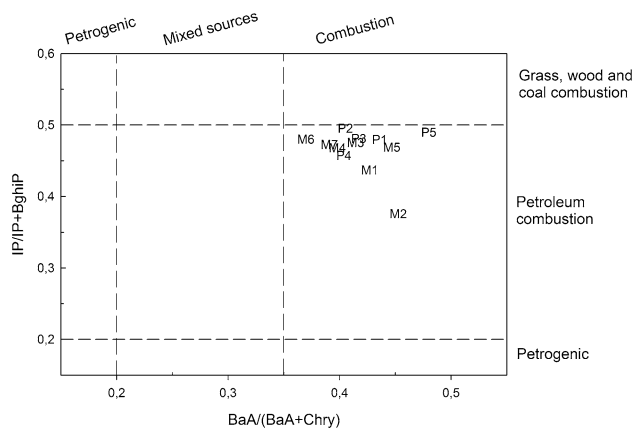
The main sources of PAHs to the environment are anthropogenic and related to direct input of oil effluents or the incomplete combustion of fossil fuels (Readman et al. 2002). The main approaches for discrimination these sources includes the use of molecular markers and PAH diagnostic ratios (Tobiszewski and Namieśnik 2012). Aiming to identify the origin of PAH, the following diagnostic ratios were calculated and the values indicate their respective sources: (1)  $\sum\text{LMW}/\sum\text{HMW} < 1$  pyrogenic source and  $>1$  petrogenic source (Zhang et al. 2008); (2)  $\text{IP}/(\text{IP} + \text{BghiP}) < 0.2$  indicate dominance of petrogenic, 0.2–0.5 petroleum combustion and  $>0.5$  grass, wood and coal combustion (Yunker et al. 2002); and (3)  $\text{BaA}/(\text{BaA} + \text{Chry}) < 0.2$  petrogenic, 0.2–0.35 coal combustion and  $>0.35$  combustion (Yunker et al. 2002).

Hydrocarbons of low molecular weight (LMW) includes petrogenic hydrocarbons with 2 and 3 rings originated from non-combusted or low-temperature combusted PAHs, such as crude oil and refined products, whereas the hydrocarbons with high molecular weight (HMW) represents pyrogenic compounds with 4, 5 and 6 rings that are derived from combustion sources, such as vehicle exhaust, coal and forest fires (Bai et al. 2014; Ünlü et al. 2010). The ratios of  $\sum\text{LMW}/\sum\text{HMW}$  varied from 0.1 to 0.6 in Mucuripe and from 0.3 to 0.6 in Pecém (Table 1), and these results suggest the contribution of pyrogenic processes to PAHs in sediments from both areas.

The cross plots of the ratios  $\text{IP}/(\text{IP} + \text{BghiP})$  versus  $\text{BaA}/(\text{BaA} + \text{Chry})$  (Fig. 2) indicated that the sediments of sheltered areas in Mucuripe and Pecém are affected by PAH from oil combustion which typically occurs in harbor areas, originated by the traffic of fishing boats, commercial and industrial ships. Such emissions are associated with regions under influence of diffuse sources including not only harbor, but also industrial activities, combustion of fuel from motor vehicles, atmospheric inputs and urban runoff (Liu et al. 2005).

According to Cavalcante et al. (2012), the metropolitan region of Fortaleza has a considerable





**Fig. 2** PAH cross plots for the ratios: IP/(IP + BghiP) versus BaA/(BaA + Chry) for the sediments collected in Mucuripe and Pecém harbors. IP indeno[1,2,3-c,d]pyrene, BghiP benzo(ghi)perylene, BaA benzo[a]anthracene, Chry chrysene

volume of vehicular emissions of PAHs, but still lower than those found in industrial and urban areas of developed countries. Moreover, the author pointed that the region is also surrounded by two industrial areas, a refinery at the northeast, located in the Mucuripe Harbor

area, and other industries in the southwest, in the Maracanaú city. These data are in agreement with the study of Cavalcante et al. (2009), which also identified pyrogenic processes among the main sources of PAHs in sediments from the mangroves in Fortaleza, and stated that these PAHs are introduced in the aquatic environment by atmospheric deposition combined with the stormwater drain system.

In order to observe associations between the hydrocarbon distribution and sediment characteristics, Spearman's correlation coefficients were calculated assuming that the data do not present a Gaussian distribution. The results showed significant correlations ( $p < 0.05$ ) for the fine sediments with AHs and also for all hydrocarbons with calcium carbonates and organic matter (Table 2). Hydrocarbons are compounds known for their ability to adsorb on organic or inorganic particles and precipitate onto the superficial sediments surface (Chiou et al. 1998). The data suggest that the depositional zones created by jetties in the sheltered areas of both harbors promote the sedimentation of fines particles and organic matter, including biogenic carbonates, controlling thus the occurrence and distribution of these compounds.

**Table 2** Matrix of Spearman's correlation coefficients for hydrocarbons and characteristics of sediments from Mucuripe and Pecém harbors

	Depth	Fines	CaCO <sub>3</sub>	OM	TOC	Total LABs	Total AHs	Total PAH
Depth								
Coefficient	1.00	–	–	–	–	–	–	–
p value	–	–	–	–	–	–	–	–
Fines								
Coefficient	0.03	1.00	–	–	–	–	–	–
p value	0.92	–	–	–	–	–	–	–
CaCO <sub>3</sub>								
Coefficient	<b>0.68</b>	0.41	1.00	–	–	–	–	–
p value	<b>0.01</b>	0.13	–	–	–	–	–	–
OM								
Coefficient	0.50	0.29	<b>0.88</b>	1.00	–	–	–	–
p value	0.06	0.29	<b>0.00</b>	–	–	–	–	–
TOC								
Coefficient	<b>0.53</b>	0.46	<b>0.91</b>	<b>0.93</b>	1.00	–	–	–
p value	<b>0.04</b>	0.08	<b>0.00</b>	<b>0.00</b>	–	–	–	–
Total LABs								
Coefficient	0.48	0.28	<b>0.70</b>	<b>0.78</b>	0.67	1.00	–	–
p value	0.07	0.31	<b>0.00</b>	<b>0.00</b>	0.01	–	–	–
Total AHs								
Coefficient	0.08	<b>0.51</b>	<b>0.60</b>	<b>0.70</b>	0.77	0.47	1.00	–
p value	0.77	<b>0.04</b>	<b>0.02</b>	<b>0.00</b>	0.00	0.08	–	–
Total PAH								
Coefficient	0.45	0.11	<b>0.67</b>	0.45	0.48	0.39	0.46	1.00
p value	0.09	0.71	<b>0.01</b>	0.09	0.07	0.15	0.08	–

Significant correlations are marked in bold

**Table 3** Compilation of hydrocarbons in marine and coastal sediments from northeast, southeast and South of Brazil and Sediment Quality Guidelines

Location	State	Samples	% Mud	% TOC	Total LABs (ng/g)	Total AHs (µg/g)	Total PAH (ng/g)	Author
Northeast								
Todos os Santos bay	Bahia	30 sites	0–99	0.1–5.4	–	–	42–4187	A
Mundaú–Manguaba	Alagoas	4 cores and 46 samples	–	1.9–3.3	–	29–139	29–223	B
Potiguar basin	Rio Grande do Norte	26 sites	–	0.6–0.8	–	0.1–5	0.5–10	C
Estuary of Ceará river	Ceará	3 cores/sites and 19 samples	–	0.01–1	–	–	3–2235	D
Estuary of Cocó river	Ceará	3 cores/sites and 26 samples	–	0.01–1.6	–	–	3–1859	D
Mucuripe harbor	Ceará	10 sites	0.1–24.4	0.2–1.4	1.3–5.8	0.3–25	28–108	E
Pecém harbor	Ceará	5 sites	4.4–14.3	0.5–1.4	1.6–4	1–19	31–292	E
Southeast and South								
Patos lagoon	Rio Grande do Sul	10 sites	–	–	3–1602	1–129	38–11,780	F
Guaratuba bay	Paraná	2 cores/sites and 43 samples	–	–	–	–	10–349	G
Laranjeiras bay	Paraná	10 sites	–	–	–	0.3–8.2	4–89	H
Santos estuarine system	São Paulo	26 sites	0.3–81	–	16–430	0.2–2508	22–68,130	I, J
São Sebastião	São Paulo	47 sites	0.2–100	–	13–28	0.1–8.53	3–370	K, L
Guanabara Bay	Rio de Janeiro	35 sites	–	0.04–12	–	0.8–21,260.4	96–153,316	M
Sediment Quality guidelines (SQGs)						–	4000 <sup>b</sup>	N
Site specific SQGs for Santos						–	163 <sup>a</sup> –950 <sup>b</sup>	O

A Wagener et al. (2010), B Silva et al. (2013), C Wagener et al. (2011), D Cavalcante et al. (2009), E This study, F Medeiros et al. (2005), G Pietzsch et al. (2010), H Martins et al. (2012), I Medeiros and Bicego (2004a), J Bicego et al. (2006), K Medeiros and Bicego (2004b), L Silva and Bicego (2010), M Wagener et al. (2012), N Brasil (2012), O Choueri et al. (2009)

<sup>a</sup> Threshold effects level

<sup>b</sup> Probable effects level

A brief compilation of recent available data on hydrocarbon concentrations in coastal regions of Northeast (Tropical), Southeast and South (Subtropical) of the Brazilian coast is presented in Table 3. As mentioned before, the concentrations found in the northeast areas are lower than those found in industrialized areas such as Patos lagoon, Santos estuarine system, São Sebastião channel, Guanabara bay and Todos os Santos bay.

By comparing both harbors, levels of AHs and LABs were similar, and for PAHs the concentrations found in Pecém were higher than Mucuripe. The LABs concentrations were similar to those found in São Sebastião channel, a region with higher hydrodynamics (Medeiros and Bicego 2004b) and where the São Sebastião port and an oil terminal are installed. Also, these concentrations may indicate a low impact of sewage effluents.

Levels of AHs and PAHs reported in the present study were similar to those reported for Mundaú-Manguaba, a low-impacted estuarine lagoon system (Silva et al. 2013), and high compared to levels of Potiguar basin, which were considered as reference levels for monitoring of shore oil exploration that occurs in the northeast coast (Wagener et al. 2011).

The occurrence of hydrocarbons in the environment especially in sediments may result in negative effects on aquatic organisms. For example, molecular weight of PAHs ranging from 128 to 300 g/mol (naphthalene to coronene, respectively) and such group of compounds tend to be more soluble, which increases their potential bioavailability and mobility within the environmental compartments (Arfsten et al. 1996) and thus, their toxicity. Regarding detergents, data available are related to the toxicity of LAS and since the concentrations of LABs are used as a marker of LAS, the

relationship between levels of LABs and their potential toxicity may not be easily estimated.

It is commonly accepted that AHs have a lower toxicity potential than PAHs, but they have received special attention because they are the major chemical class in modern oil-base drilling muds (Payne et al. 1995). These authors also investigated chronic effects of AH-rich sediments on winter flounder *Pleuronectes americanus*. Such effect involved the analysis of organ and body condition indices, energy reserves, detoxification enzymes, blood parameters, and histopathology and they found no effects or dose–response relationships at exposure levels similar to those found in our study (6–21 µg/g of AHs). However, Thomas et al. (1995) pointed that an oxidation of AHs resulted in the formation of products with a greater solubility, and increased in two times the toxic effects on the feeding rate of mussel *Mytilus edulis*.

As mentioned, PAHs are toxic and some of these compounds are mutagenic and genotoxic, threatening thus the marine biota through chronic exposure (Oros et al. 2007). The toxicological concerns of PAHs are focused on metabolic activation of these compounds to metabolites more toxic than their parent compound (Mekenyan et al. 1994) and one well know process that act in such activation is the exposure of UV radiation. Arfsten et al. (1996) presented a review containing evidences that PAHs may become toxic or substantially more toxic upon coexposure to UV light. According to Nikolaou et al. (2009) toxic effects from some individual PAHs are documented, but in the presence of complex mixtures (e.g., superficial sediments) dose–response relationship for PAHs is difficult to identify.

Considering the potential toxicity of these substances, a chemical-specific criterion was applied by comparing the concentrations of PAHs with SQGs. Comparison with Brazilian SQGs revealed that the highest concentrations of total PAH found in Mucuripe and Pecém sediments were lower than probable effects level. However, when these concentrations were compared with site-specific values developed for Santos Estuarine System (Choueri et al. 2009), where the major Brazilian port is situated, the upper levels observed in Pecém (P2 and P5) were already higher than the threshold effect level. These results suggest that even the exposure of benthic organisms to low concentrations of contaminants may be associated with toxic effects. Thus, based on these results further investigations should be carried out in order to assess the potential of toxicity of the sediments in Northeastern coast of Brazil, especially in harbor areas.

## Conclusions

In general, hydrocarbon levels in sediments from some tropical areas of Brazil were low when compared with other industrialized areas. Analysis of *n*-alkanes revealed the input

of biogenic compounds and according to diagnostic ratios, PAHs in both harbors originated from fuel combustion, possibly from shipping. PAH concentrations were low and below threshold levels established by the SQGs. Data presented in this study can also assist the monitoring of harbor areas and the management of dredged material by providing information on two of the main ports of northeast region of Brazil, which lacks of data on sediment quality, especially regarding the distribution of hydrocarbons.

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