Baseline

Distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of a Tropical Bay influenced by anthropogenic activities (Todos os Santos Bay, BA, Brazil)

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ABSTRACT

The present study aimed to evaluate the distribution and origin of 16 Priority PAHs in surficial sediment samples of Todos os Santos Bay (TSB, Brazil). Total PAHs concentrations ranged from below the method detection limit ($<$ DL) to 533 ng g^{-1} (dry weight). The toxic equivalent concentrations (TEQ^{carc}) of PAHs in the studied area ranged from 0 to 104 ng g^{-1} and were lower when compared to other contaminated bays in the world. Diagnostic ratios indicated that pyrogenic processes, such as pyrolysis of fossil fuel, biomass, and coal, were the main PAHs sources for sediments. Proximity of the sources, the hydrodynamics and geochemistry of the sediments were the factor influencing the distribution of PAHs along the studied area.

Polycyclic aromatic hydrocarbons (PAHs) are organic compost consisted by two or more condensed aromatic rings, which can be formed through biological synthesis, processes of thermal evolution of sedimentary organic matter and during the incomplete pyrolysis of fossil fuels, wood and crop residues (Tissot and Weste, 1984; Abdel-Shafy and Mansour, 2016). The main sources of PAHs released to the environment are anthropogenic activities, such as oil and by-product spills, maritime transport, releases of industrial and domestic effluents, wet and/or dry atmospheric deposition and urban runoff (Viñas et al., 2010; Ekpo et al., 2012; Le Bihanic et al., 2014). PAHs are environmentally persistent and toxic compounds with carcinogenic and mutagenic effects (IARC, 2010; Flores-Serrano et al., 2014; Li et al., 2014). Studies have also shown PAHs to be genotoxic for marine organisms exposed to high levels of contamination (Venier and Canova, 1996; Pisoni et al., 2004). Thus, there is a constant interest in studying these compounds in different environmental compartments.

The physicochemical properties of PAHs confer a hydrophobic and lipophilic character for them. When diffused in the marine environment, they tend to associate with suspended particulate matter that is deposited and accumulates in the sediments (USDHHS, 1995; Liu et al., 2009a). Sediments are considered one of the main sinks of PAHs in marine environments. Therefore, environmental studies have investigated this matrix to determine the distribution of PAHs in coastal ecosystems (Oros and Ross, 2004; Liu et al., 2009a; Wagener et al., 2010; Dauner et al., 2016).

Todos os Santos Bay (TSB, Fig. 1) is a region of ecological and social relevance for Brazil. It hosts different ecosystems, such as coral reefs and mangroves, and it is sources of livelihood for families living in its surroundings. Despite this, there are notable impacts caused by the anthropogenic activities developed in the region. Approximately 3.5 million people live in 14 districts around TSB, including the city of Salvador, which is considered the fourth most populous of Brazil (IBGE, 2016). The effluents generated at these sites reach the bay partially through the discharge systems (Wagener et al., 2010). The anthropogenic activities conducted in ports (Salvador and Aratu ports), shipyards, industrial centres (such as the Aratu Industrial Centre located in the northeast portion of the bay), and the petroleum industry (Landhulpho Alves de Mataripe Oil Refinery - RLAM) are also sources of PAHs (Venturini and Tommasi, 2004; Celino and Queiroz, 2006; Wagener et al., 2010; Nascimento et al., 2017). Most of the studies that
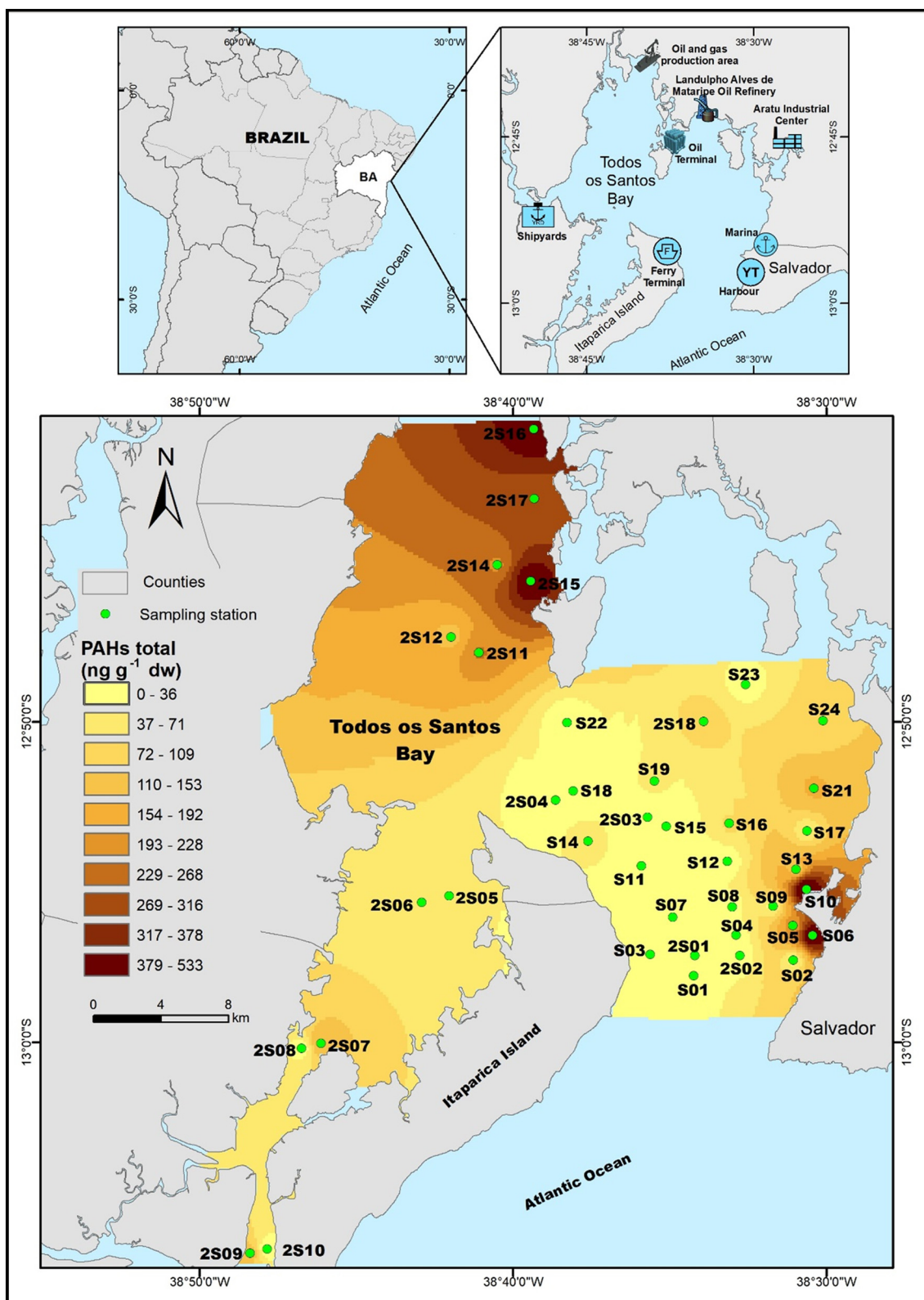
Fig. 1. Locations of sampling sites for surface sediments in the infralittoral zone of Todos os Santos Bay (Brazil), distribution of PAHs concentrations in the surface sediments and the main anthropogenic activities developed in the region.

evaluated the contamination by these compounds in TSB were conducted near contaminant sources mainly in the Northeast (Venturini and Tommasi, 2004; Nascimento et al., 2017) and North portion of the bay (Souza et al., 2017). TBS has 1112 km^2, which made it the second largest bay in Brazil (Hatje and Barros, 2012). In its western area, in the

limit of the Frades Island, depths are inferior to 10 m. In the eastern area, which includes the Salvador Channel, the depths vary between 10 and 50 m (Marta-Almeida et al., 2017). Considering the dimensions, the geomorphological and oceanographic characteristics of TSB, it is important to carry out studies that aim interpreting the distribution of

PAHs along all bay.

The objective of present study was to evaluate the spatial distribution and sources of PAHs in Todos os Santos Bay (TSB). A multivariate analysis considering data of PAHs concentrations, grain size and TOC of the sediments was made to understand, in an integrated way, the mechanisms that influence the spatial distribution of these contaminants in the surface sediments. It also aimed to evaluate the sources of PAHs and the toxicity based on sediment quality guidelines and the carcinogenic potential for groups of PAHs.

Surface sediment samples (0–3 cm deep) were collected at 40 sampling stations (Fig. 1) in TSB, Brazil. Sedimentation rate along the studied area varies from 3.8 to 10 mm y^{-1}, with a mean of 6.9 mm y^{-1} (Argollo, 2001). A Van Veen stainless steel grab sampler was used for sampling the bottom sediment in the bay. The samplings were conducted between July and August 2015 for samples S01 to S24 and in April 2016 for samples 2S01 to 2S18. Those distinct periods of collection happen because the sampling was done together with other research studies. Considering the sedimentation rate of TBS, a six-month interval is not relevant to change severely the PAHs accumulation between those two periods of collection. Samples were stored in precleaned and calcined glass containers. After sampling, the samples were transported to the laboratory where they were stored in a freezer at −20 °C. Subsequently, all sediment samples were freeze-dried and homogenized.

The determination of total organic carbon (TOC) was done as described in Souza et al. (2017), with modifications. Briefly, 2 g of homogenized sediments were treated with hydrochloric acid (HCl) to remove inorganic carbon and washed with distilled water to remove HCl. The sample was oven dried (50 °C), and the TOC content was determined in an elemental analyzer (LECO-CHN 628). For the determination of the particle size fractions of the sediments, 2 g of each sample was calcined (450 °C for 8 h), and then, hydrogen peroxide was added to remove residual organic content.

The particle size fractions were determined by sieving the material through stainless steel sieves for the size fractions larger than 500 μm. A particle analyzer with laser diffraction (model Cilas 1064) was used for the fractions smaller than 500 μm. The textural classification of the sediments was based on the relative percentage of the different size fractions: < 4 μm: clay; 4–63 μm: silt; 63–2000 μm: sand.

For analysis of PAHs in the collected samples, the compounds were extracted based on the United States Environmental Protection Agency (USEPA) 3546 microwave extraction method with modifications (USEPA, 2007). Approximately 10 g of sediment from each site was weighed and added to 50 μL of the surrogate standard (*p*-terphenyl-D_{14}, 2.0 ng μL^{-1}) and 25 mL of a mixture of *n*-hexane and acetone (1:1, V:V). The samples were then extracted using a microwave (Anton Paar, 16SOLV MF100). After extraction, the samples were filtered using anhydrous sodium sulphate (pre-calcined at 400 °C for 4 h). Activated copper was added to the extracts to remove the elemental sulphur, and each of the solutions was concentrated to an approximate volume of 500 μL. The extracts were transferred into vials where the volume of each extract was adjusted to 500 μL. The analysis of PAHs was performed using a gas chromatograph (Agilent 7890B) coupled to a mass spectrometer (Agilent 5977A) (GC–MS) in the single ion monitoring (SIM) mode. A silica capillary column (HP-5MS, 30 m × 250 μm i.d. × 0.25 μm film thickness) was used. The initial oven temperature was 100 °C, which was increased at a rate of 10 °C min^{-1} to 200 °C and kept at that temperature for 1.5 min, followed by an increase to 250 °C at a rate of 25 °C min^{-1}. A temperature of 250 °C was maintained for 2 min, with a final heating rate of 5 °C min^{-1} until reaching 300 °C. The temperature of the ion source was 230 °C, and that of the detector was 150 °C. High-purity helium was used as the carrier gas at a flow rate of 1 mL min^{-1}. A five-point internal calibration of the equipment for quantification of PAHs was performed using a mixture of the 16 priority PAHs (Naphthalene: Na; Acenaphthylene: Ayl; Acenaphthene: Aen; Fluorene: F; Phenanthrene: Pn; Anthracene: Ant; Fluoranthene: Fl;

Pyrene: Py; Benz[*a*]anthracene: BaA; Chrysene: Ch; Benzo[*b*]fluoranthene: BbF; Benzo[*k*]fluoranthene: BkF; Benzo[*a*]pyrene: BaP; Indeno[123, *cd*]pyrene: IP; Benzo[*ghi*]perylene: Bghi; Dibenz[*a,h*]anthracene: DhA) at concentrations ranging from 10 to 2000 μg L^{-1}. The accepted correlation coefficient for these curves was 0.995. The recovery rate of the surrogate in the samples ranged from 60% to 112% (78 ± 14%). To calculate the method detection limit (DL), seven replicates (10 g each) were fortified with a mixture of the 16 priority PAHs. The DL was calculated by multiplying the Student's *t*-test value (nc = 99%; n − 1 = 3.1417) by the standard deviation (S) of the concentration reported for each analyzed compound (DL = t_{n-1} x S) (Wade and Cantillo, 1994). The calculated DL ranged from 9.40 to 39.6 μg L^{-1} (dry weight) (Supplementary material Table S1). During the analysis, the extraction of a sediment sample was performed in duplicate (S22.1 and S22.2) and spiked with a standard containing the 16 PAHs. The percentage differences between each compound in the duplicate sample were < 16% (Supplementary material Table S1). To investigate possible laboratory contamination, a procedural blank was used for each batch of nine samples. The blank was subjected to the same analytical procedure used for the real samples, and the set of samples whose PAHs concentrations in the blank were below the DL were considered free of laboratory contamination.

A sediment quality assessment was performed using the toxicological carcinogenic potential (toxic equivalent concentration; TEQ^{carc}) for the PAHs. The calculation was made using the group of PAHs that includes BaA, Ch, BbF, BkF, BaP, IP and DhA (Peters et al., 1999; Li et al., 2014). Based on toxicological data collected from other studies, benzo[*a*]pyrene (BaP) is considered to be one of the most potent carcinogenic agents in this group of PAHs (Peters et al., 1999; Li et al., 2014). The toxic equivalency factor (TEF$_i$) values for the group of PAHs are shown in Table 1 (Nisbet and Lagoy, 1992; Durant et al., 1996). The equation for the calculation of TEQ^{carc} (Eq. (1)) is shown below:

$$TEQ^{carc} = \sum_{i=1}^{n} C_{HPAi} * TEF_i \tag{1}$$

where C_{HPAi} is the concentration (ng g^{-1} (dry weight)) and TEF$_i$ is the toxic equivalency factor (Nisbet and Lagoy, 1992; Qiao et al., 2006; Chen and Chen, 2011; Dong et al., 2014; Li et al., 2014).

Descriptive statistical analyses were performed using the statistical package BioEstat 5.3, and comparisons were made at a significance level of $\alpha = 0.05$. The data sets did not present a normal distribution ($p < 0.05$); thus, the variables analyzed were log-transformed for the subsequent analyses. Multivariate analysis was performed by principal component analysis (PCA) using the Canoco for Windows statistical package version 4.5 (Ter Braak and Smilauer, 1998). The Spearman correlation analysis was performed to identify the relationships among PAHs, TOC and particle size (mud).

The results for the individual concentrations of PAHs, the sum of low molecular weight PAHs (compounds with 2–3 aromatic rings) and

Table 1
Toxic equivalency factor (TEF) values used in calculations that express the carcinogenic potential of polycyclic aromatic hydrocarbons (PAHs) in sediments.

PAH	IARC class	TEF[a]
BaA	2B	0.10
Ch	2B	0.01
BbF	2B	0.10
BkF	2B	0.10
BaP	1	1.00
IP	2B	0.10
DhA	2A	1.00[b]

1 - carcinogen; 2A - probable carcinogenic; 2B - possible carcinogen.
[a] Data from Nisbet and Lagoy, 1992.
[b] Data from USEPA, 1993.

high molecular weight PAHs (compounds with 4–6 rings), and concentrations of TOC, mud and sand determined for each sample are included as supplementary material (Supplementary material Tables S2 and S3).

Sand fraction was predominant (content of sand > 50%) in 85% of the samples (Table S3). The highest contents occurred in the Southeast of the bay, in the Salvador channel. This shows that this area is under higher energy conditions (Fig. S1, Flemming, 2000). Concentration of TOC ranged from 0.0% to 1.9% (average 0.7 ± 0.7%). TOC levels showed significant correlation with mud contents (silt + clay) (Spearman's Rho = 0.75, $p < 0.0001$). This was already found in previous studies conducted in TBS (Souza et al., 2017; Nascimento et al., 2017) and is a commonly found in aquatic environments (Gireeshkumar et al., 2013). It happens because finer particles have higher surficial area, increasing the capacity to absorb the OM compared to larger materials (Yuan et al., 2017).

The total PAHs concentrations (Σ_{16}PAHs) in the surface sediments of TSB ranged from below the method detection limit (< DL) to 533 ng g^{-1} (dry weight), with a mean value of 106 ± 147 ng g^{-1} (dry weight). When compared to previous studies made in TBS, the present levels of PAHs are relatively lower. Venturini and Tommasi (2004), for example, reported a maximum concentration of 4163 ng g^{-1} (dry weight) for total PAHs in TSB. These authors evaluated more compounds (23 PAHs), and the region that they studied was located closer to an oil refinery and urban centers in the northeast portion of the TSB. Wagener et al. (2010) reported a total PAHS (16 priority PAHs) concentration of 2226 ng g^{-1} (dry weight) close to the port and industrial area of the bay. This study included some sampling sites similar to the present one. A comparison between these sites revealed no significant differences between the concentrations of PAHs in the sediments reported by both studies (tcalculated = 1844, $p > 0.05$) (Table 2). This indicates that the levels of contamination have varied little between when Wagener et al. (2010) sampled the sediments and the present evaluation period. Both studies demonstrate that higher concentrations of PAHs are found on the bay's margins where the primary potential sources of PAHs are found.

Table 3 shows a comparison of the concentrations of PAHs detected in the sediments of the present study with those of other marine coastal environments in America and wordwilde, and also presents a classification of PAHs contamination at four levels: low (0–100 ng g^{-1}), moderate (100–1000 ng g^{-1}), high (1000–5000 ng g^{-1}) and very high (> 5000 ng g^{-1}) (Baumard et al., 1998). Concentrations of Total PAHs in TBS were higher than those reported in pristine areas such as Camamu Bay (Northeast of Brazil, 1.17 to 313 ng g^{-1}, Pedreira et al., 2017), Paranaguá Estuarine System, (South of Brazil, < DL to 14.41 ng g^{-1}, Bet et al., 2015) or remote areas such as He-Ping Harbor/He-Ping Estuary (Taiwan, 8 to 312 ng g^{-1}, Kuo et al., 2012) and Prydz Bay (Antarctica, 12.95 to 30.93 ng g^{-1}, Xue et al., 2016). In other hand, concentrations found in TBS were lower than other regions that have experienced comparable impacts of multiple anthropogenic activities

over the years such as Guanabara Bay (Southeast of Brazil, 5 to 78,523 ng g^{-1}, Wagener et al., 2012) and Bahía Blanca Estuary (Argentina, 19.7–30,055 ng g^{-1}, Oliva et al., 2015). TSB sediments presented low to moderate levels of contamination, with Total PAHs concentrations close to those reported for Todos Santos Bay of Mexico (Macías-Zamora et al., 2002), Abu Qir Bay in Egypt (Barakat et al., 2011), Leizhou Bay in China (Huang et al., 2012) and the Beibu Gulf, Qinzhou Bay and Sannian Bay in China (Li et al., 2015a). All these environments have experienced the impacts of multiple anthropogenic activities over the years, which are related to sediment contamination by PAHs.

In general, the concentrations of Σ16PAHs increased towards the margins of the bay (Fig. 1). Sites S10, S06, 2S15, 2S16, 2S17, 2S11, 2S14, S05, S21, 2S07, 2S09, 2S12 and S13 showed the highest concentrations of Σ_{16}PAHs. Some of these sites (2S15, 2S16, 2S17, 2S11, 2S14 and 2S12) are located in the north-western portion of the bay near an oil terminal, the urban center of São Francisco do Conde (oil and gas production site), and the mouth of the Subaé river, with several anthropogenic activities occurring along its sub-basin, such as industrial activities, domestic effluent discharge, pesticide use in crops and inadequate solid waste discharge (Barros et al., 2009). Sites 2S07 and 2S09, located between Itaparica Island and the mainland in the western portion of the bay, are close to urbanized regions and the mouth of the Jaguaripe River. In addition, there are several anthropogenic activities along the drainage area of this river, such inadequate disposal of sanitary sewage and solid waste, and the indiscriminate use of pesticides and soil amendments (Barros et al., 2009). It is also noted that the samples 2S08 and 2S10, located close to these stations (2S07 and 2S09), have lower concentrations of PAHs and higher ratios of sand, which characterizes them as representative of an environment of higher hydrodynamics according to Flemming's classification (2000). Samples 2S07 and 2S09 have higher ratios of mud and reflect sediment deposition in a regime of lower hydrodynamics. The PAHs present in that area indicate a greater tendency for adsorption to the finer fractions of the sediment (Oros and Ross, 2004).

Samples collected at stations S10, S06, S05, S21 and S13 are close to the marinas, the port regions, the Ferry Boat terminal and the urban center of Salvador. It is also worth noting that station S14, located in front of the Ferry Boat terminal on Itaparica Island, has a higher concentration than the surrounding sites, indicating that activities associated with the ferry terminal are a potential source of PAHs in the region.

Studies conducted in impacted regions have also reported higher concentrations of PAHs in areas close to large urban centers, where multiple anthropogenic activities are developed. Barakat et al. (2011), studying PAHs in the sediments of the Mediterranean coastal environment in Egypt, reported higher PAHs concentrations at sites under anthropic influence, such as docks, shipyards and industrial and urban areas. Neira et al. (2017) reported high concentrations of PAHs in the marine areas of San Diego Bay, California, USA. Masood et al. (2016) associated the higher concentrations of PAHs in the estuarine areas and the Selangor River in Malaysia with intensive industrial activities, urban densification and domestic effluent discharge.

The composition patterns of compounds with two to six aromatic rings found in the surface sediments of TSB are shown in Fig. 2. The high-molecular-weight PAHs (ΣHPAHs, four to six rings) corresponded on average to 95% of the total composition of PAHs in the sediments of the bay, while the low-molecular-weight (ΣLPAHs, two to three rings) corresponded to an average proportion of 5%. In 94% of the sampled sites, the four- to six-ring PAHs accounted for > 79% of the total composition. On average, five- to six-ring PAHs indicated a greater relative abundance (32.8%, 31.7%, respectively), followed by four-ring (26.0%), three-ring (9.2%) and two-ring PAHs (0.3%). A higher contribution of four- to five-ring PAHs (pyrogenic) than those with two- to three-ring PAHs (petrogenic) is indicative of higher contributions of PAHs from pyrogenic sources to the environment (Zhang et al., 2008;

Table 2

Comparative analysis at similar samplings sites in the study by Wagener et al. (2010) and the present study at Todos os Santos Bay.

Wagener et al. (2010)		Present study	
Sampling station	ng g^{-1}	Sampling station	ng g^{-1}
1	351	S06	480.5
2	7.6	S13	129.1
14	838.7	2S16	448.50
20	244.2	2S12–2S11	184.6 ± 66.3
29	31.7	2S06–2S05	52.9 ± 1.2
30	Nd	2S10–2S09	70.4 ± 96.4
35	39.4	S23–2S18	59.0 ± 54.9

Nd = Not detected.

Table 3

Comparison of the sum of the concentrations of 16 priority PAHs (Σ_{16}PAHs) according to the United States Environmental Protection Agency (USEPA) in surface sediments collected in different coastal regions worldwide and current study (ng g^{-1}; dry weight).

Location	Range	Mean	Contamination levels	Reference
Todos os Santos Bay (northeast Brazil)	< DL to 533	105	L to M	This study
Todos os Santos Bay (northeast Brazil)	12.3 to 511	141	L to M	Souza et al. (2017)
São Paulo river Estuary, Todos os Santos Bay (northeast Brazil)	11.5 to 1825	–	L to H	Nascimento et al. (2017)
Todos os Santos Bay (northeast Brazil)	nd to 2226	283	L to H	Wagener et al. (2010)
Camamu Bay (northeast Brazil)	1.17 to 313[B]	–	L to M	Pedreira et al. (2017)
Paranaguá Estuarine System (South Brazil)	< DL[a] to 14.4	–	L	Bet et al. (2015)
Amazon River Estuary (northwest Brazil)	22.2 to 159	49.4	L to M	Rodrigues et al. (2018)
Guanabara Bay (Southeast Brazil)	184 to 3653	–	M to H	Meniconi (2007)
Guanabara Bay (Southeast Brazil)	5 to 78,523	–	L to VH	Wagener et al. (2012)
Bahía Blanca Estuary (Argentina)	19.7 to 30,055	1799	L to VH	Oliva et al. (2015)
Todos os Santos Bay (Mexico)	7.6 to 813	96	L to M	Macías-Zamora et al. (2002)
Helter Island Yacht Basin (USA)	246 to 3452	1059	L to H	Neira et al. (2017)
West Harbor Island (USA)	389 to 1448	785	L to H	
East Harbor Island (USA)	606 to 19,967	3736	VH	
Prydz Bay (Antarctica)	12.95 to 30.93	17.99 ± 5.57	L	Xue et al. (2016)
Eastern Harbor of Alexandria (Egypt)	180 to 14,100	4851	L to VH	Barakat et al. (2011)
Abu Qir Bay (Egypt)	3.51 to 483	155.2	L to M	
El-Max Bay (Egypt)	925 to 2010	1467	L to H	
Zhanjiang Bay (China)	41.96 to 933.9	–	L to M	Huang et al. (2012)
Leizhou Bay (China)	21.72 to 319.6	–	L to M	
Beibu Gulf, Qinzhou Bay and Sannian Bay (China)	3.01 to 388[A]	–	L to M	Li et al. (2015a)
Jinhae Bay (Korea)	2.4 to 2430	208	L to H	Yim et al. (2014)
He-Ping Harbor and He-Ping Estuary (Taiwan)	8 to 312	–	L to M	Kuo et al. (2012)

A = Sum of 15 PAHs; < DL = below the method detection limit; B = Sum of 38 PAHs; < DL[a] ≤0.01 μg g^{-1}, nd = not detected. Contamination levels according to Baumard et al. (1998): low (L) (0–100 ng g^{-1}), moderate (M) (100–1000 ng g^{-1}), high (H) (1000–5000 ng g^{-1}) and very high (VH) (> 5000 ng g^{-1}).

Yancheshmeh et al., 2014). Pyrogenic PAHs are formed during the pyrolysis of organic substances, such as fossil fuels and biomass, under high-temperature conditions (generally 350 °C to 1200 °C) and low or no oxygen content. These conditions favour the formation of high-molecular-weight PAHs, in which the molecules are more stable, with higher carbon: hydrogen ratios (Lopes and Andrade, 1996; Abdel-Shafy and Mansour, 2016).

The high-molecular-weight PAHs (four to six rings, ΣHPAHs) deposited in the TSB surface sediments showed a strong significant correlation with TOC (Spearman's Rho = 0.73, $p < 0.0001$). The low-molecular-weight PAHs (two to three rings, ΣLPAHs) showed moderate significant correlation with TOC (Spearman's Rho = 0.63, $p < 0.0001$). High-molecular-weight PAHs typically have a higher tendency of adsorption to organic carbon than low-molecular-weight PAHs. This behavior of the PAHs is influenced by their organic carbon partition coefficient (log K_{oc}). The log K_{oc} measures the ratio between the concentrations of PAHs adsorbed to the organic carbon of the sediments and to the aqueous phase (USDHHS, 1995). In general, the

PAHs have a hydrophobic and lipophilic character defined by the octanol-water partition coefficient (log K_{ow}). The higher the log K_{ow}, the more liposoluble the PAHs is, and this characteristic increases with the increase in its molecular weight (USDHHS, 1995). PAHs tend to adsorb to suspended particulate matter and are deposited and accumulate in sediments (Oros and Ross, 2004; Liu et al., 2009a). The particle-size distribution of the sediments indicate significant correlations with the PAHs distribution. Mud showed moderate significant correlation with high-molecular-weight (Spearman's Rho = 0.63, $p < 0.001$) and low-molecular-weight (Spearman's Rho = 0.55, $p < 0.001$) PAHs. The finer sediment fractions, such as clay minerals, have high specific surface area and cation exchange capacity, which facilitates the adsorption of PAHs (Zhang et al., 2011).

A principal component analysis (PCA) was performed considering the concentrations of the 16 individual PAHs (Na, Ayl, Aen, F, Pn, Ant, Fl, Py, BaA, Ch, BbF, BkF, BaP, IP, Bghi, DhA), the TOC contents, the mud levels and at the 40 sediment sampling sites in the bay. The PCA plot showed that the first and second components explained 78% of the
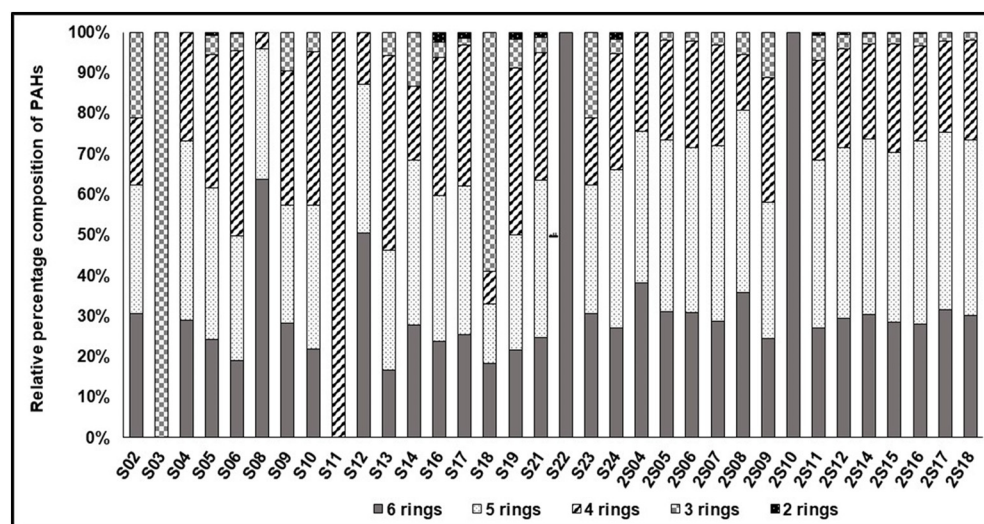

Fig. 2. Distribution pattern of 2- to 6-ring polycyclic aromatic hydrocarbons (PAHs) found in the surface sediments of Todos os Santos Bay, except for sampling stations S01, S07, S15, 2S01, 2S02, 2S02 and 2S03, which were not included in the distribution because their PAHs concentrations were below the method detection limit.
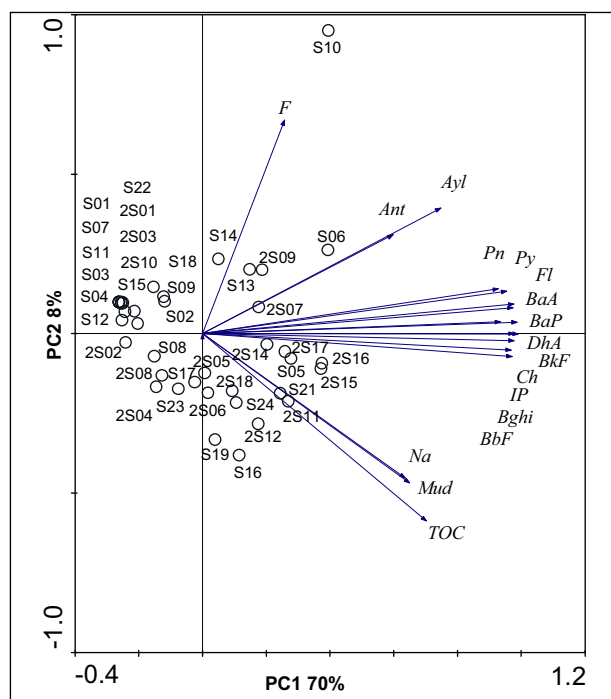
Fig. 3. PCA biplot for relationships between PAHs, TOC and Mud (TOC = Total Organic Carbon; Mud = Clay + Silt).

Table 4
Diagnostic ratios, with their ranges for identification of the sources of polycyclic aromatic hydrocarbons (PAHs) in the sediments of TSB.

Ratio	Range	Source	This study	Reference
$\dfrac{Ant}{178}$	< 0.1	Petrogenic	0.04–0.97	Yunker et al.
	> 0.1	Pyrogenic	(n = 26)	(2002); Chen and Chen (2011)
$\dfrac{Fl}{Fl + Py}$	< 0.4	Petrogenic	0.36–0.86	Yunker et al.
	0.4–0.5	Pyrogenic: petroleum combustion	(n = 35)	(2002); Chen and Chen (2011)
	> 0.5	Pyrogenic: Grass, wood and coal combustion		
$\dfrac{BaA}{228}$	0.2–0.35	Mixed sources	0.14–0.49	Yunker et al.
	< 0.2	Petrogenic	(n = 35)	(2002)
	> 0.35	Combustion (vehicle emissions)		
$\dfrac{IP}{IP + Bghi}$	< 0.2	Petrogenic	0.24–0.78	Yunker et al.
	0.2–0.5	Petroleum combustion	(n = 36)	(2002)
	> 0.5	Grass, wood and coal combustion		
	> 1	Petrogenic		

Ant/178: Anthracene / (Anthracene + Phenanthrene); Fl/(Fl + Py): Fluoranthene / (Fluoranthene + Pyrene); BaA / (228): Benzo[*a*]Anthracene / (Benzo[*a*]Anthracene + Chrysene); IP/(IP + Bghi): Indeno[1,2,3-*cd*]Pyrene / (Indeno[1,2,3-*cd*]Pyrene + Benzo[*ghi*]Perylene).

data variability (Fig. 3). The first component (PC1) explained 70% and the second component (PC2) explained 8%.

Half of the sampling sites plotted in PCA is in the negative PC1 axis, opposite to the vectors of PAHs, TOC and mud. Those samples are in areas of high hydrodynamic energy (i.e., low mud content), low TOC levels and low concentrations of PAHs. Projected samples on negative PC1 axis (50%) are characterized by low hydrodynamic energy (i.e., high mud content), high TOC levels and higher concentrations of PAHs. The distribution of the samples on this axis was mainly influenced by the vectors of pyrogenic PAHs (Ch, BbF, Bghi, BkF, BaP, IP, Fl, BaA, Py and DhA), petrogenic PAHs (Pn and Ayl), TOC and Mud. It is also observed that these PAHs are highly correlated with each other, showing a common source for these compounds in the sediments of the bay. The samples projected on the positive PC2 axis have the same pattern of negative PC1 axis, representing environments of high hydrodynamic energy and lower concentrations of PAHs. The negative PC2 axis shows a condition of lower hydrodynamic energy where the distribution of PAHs is influenced according to sediment geochemistry (TOC and mud contents).

Some samples projected on PCA showed a distinct distribution pattern. An example is the sample group formed by S06, S10, S13, 2S11, 2S14 and 2S16 projected in the positive PC1 axis. These samples have the highest concentrations of PAHs and low mud contents in the sediment composition. PAHs associated with suspended particulate matter tend to be deposited in low hydrodynamic environments (i.e. with higher ratio of mud). Therefore, it was expected that these samples would exhibit lower concentrations of PAHs compared to those with higher ratios of mud. This can be partly explained by the fact that these sites are close to anthropogenic activities identified in the bay (Fig. 1).

Diagnostic ratios of PAHs isomers can be used to distinguish the probable sources of these hydrocarbons in the marine environment (Yunker et al., 2002; Chen and Chen, 2011; He et al., 2014). Table 4 summarizes some of these ratios with their range and the minimum and maximum variations of the values reported in the present study. Fig. 4 shows the distribution of PAHs sources in the TSB using cross-plots of the following diagnostic ratios: Ant/(178) versus Fl/(Fl + Py); BaA/(228) versus Fl/(Fl + Py); and IP/(IP + Bghi) versus Fl/(Fl + Py).

When compounds concentrations used in these ratios were lower than DL, the samples were not considered.

The Ant / 178 versus Fl/(Fl + Py), BaA / (228) versus Fl / (Fl + Py) and IP / (IP + Bghi) versus Fl / (Fl + Py) diagnostic ratios indicate that the processes involving the burning of fossil fuels and combustion of grass, coal and wood (mixed source) were the main sources of PAHs for most sampled sites (Fig. 4A, B and C). Sampling stations located in Southwest (Itaparica Channel), Northwest (near RLAM and the shipyards) and in Northeast (near Aratu Industrial Center) of TBS have shown two distinct sources of PAHs (petroleum combustion; and grass, wood and coal combustion). Stations located in the Southeast (Salvador Channel and the area near the Harbor, marinas, Salvador City) have shown tree distinct sources of PAHs (petroleum; petroleum combustion; and grass, wood and coal combustion). These sites are located in the coastal area of the bay, near the large urban centre of Salvador, which has a fleet of approximately 850 thousand vehicles (DENATRAN, 2016). This suggests that the pyrogenic PAHs that originated from these emissions can be an important source of PAHs for the bay. The activities of the Aratu-Candeias port/Salvador are responsible for an annual flow of > 10 million tons of products transported by approximately 1200 cargo ships that circulated inside the bay (CODEBA, 2016). Both vehicles and ships are considered important sources of PAHs in the environment because of their use of fossil fuels as energy sources. In port regions, atmospheric emissions from ships and other vessels are considered important sources of PAHs (Martínez-Lladó et al., 2007). When the PAHs are released to the atmosphere, they can be adsorbed by suspended particulate matter. They are subsequently transported through the atmosphere and can be deposited and leached to the aquatic environment in wet or dry states through land drainage (Viñas et al., 2010; Chen and Chen, 2011; Le Bihanic et al., 2014). The sources of petrogenic PAHs identified in this study may be related to oil and by-product spills from anthropogenic activities developed in the bay. Some noteworthy accidents already reported within the TSB include an accident with a tanker ship that spilled 48,000 L of crude oil into mangroves northeast of the bay in 1992 (Orge et al., 2000), the spill of approximately 2500 L of oil in 2009 (Hatje and Andrade, 2009) and an explosion on the Golden Miller ship at Aratu Port, which caused the spillage of tons of fuel oil into the bay in 2013 (CODEBA, 2013).

The evaluation of sediment quality is an important tool because several PAHs are known for their deleterious effects on benthic
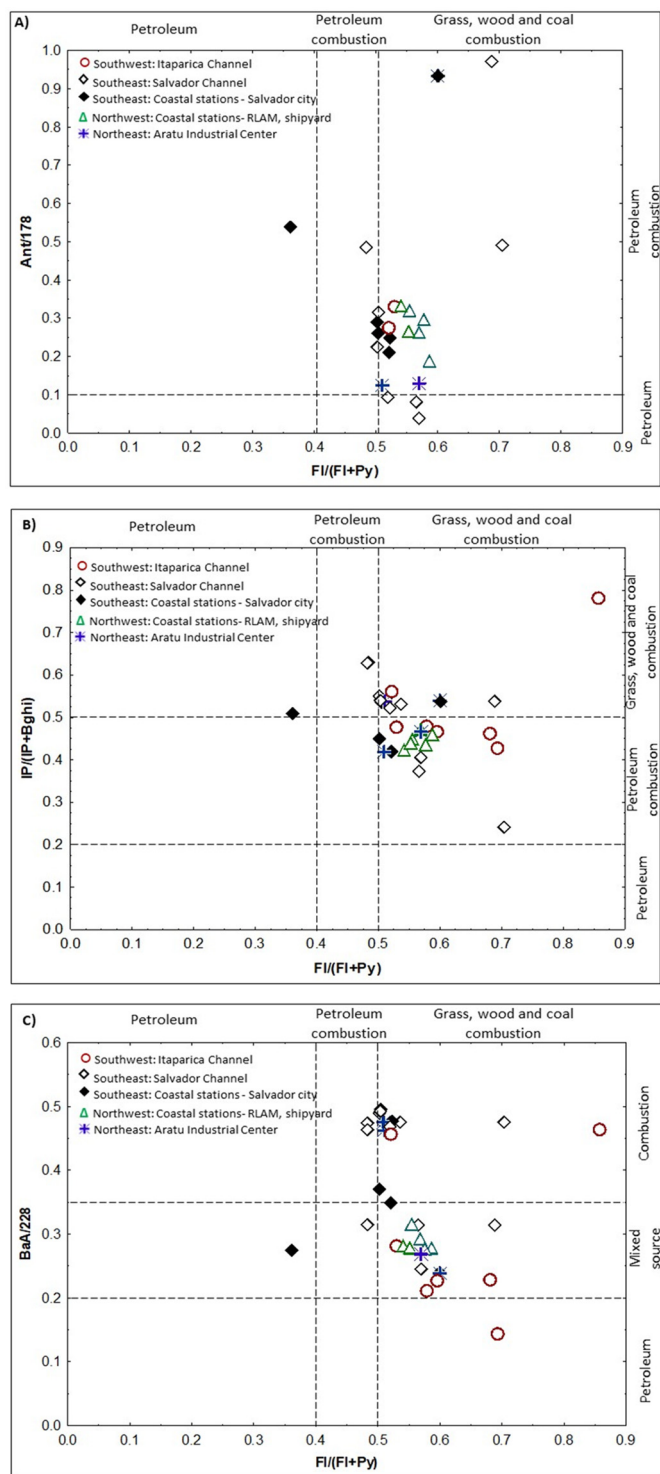
Fig. 4. Distribution of the PAHs sources in TSB according to diagnostic ratios: A) Ant/178 versus Fl/(Fl + Py); B) BaA/228 versus Fl/(Fl + Py); and C) IP/(IP + Bghi) versus Fl/(Fl + Py).

Table 5
Class interval of the carcinogenic potential (TEQ^carc) of PAHs in the surface sediments of Todos os Santos Bay.

Class internal of TEQ^carc (ng g^{-1}, dry weight)	Xi	Fi	Percentage
0.00 |— 17.43	8.71	26	65.00%
17.43 |— 34.85	26.14	6	15.00%
34.85 |— 52.28	43.56	3	7.50%
52.28 |— 69.70	60.99	1	2.50%
69.70 |— 87.13	78.41	1	2.50%
87.13 |— 104.55	95.84	3	7.50%
Minimum TEQ^carc	0 ng g^{-1}		
Maximum TEQ^carc	104.45 ng g^{-1}		

Fi = frequency of occurrence; Xi = Mean value.

potential risk of adverse effects. With regard to the individual PAHs levels, only DhA had concentrations higher than the TEL in 25% of sampling sites (S06, S10, 2S07, 2S11, 2S12, 2S14, 2S15, 2S16, 2S17 and 2S18). These samples, however, did not have concentrations above the probable effect level (PEL). DhA is a class 1 PAHs with sufficient evidence of carcinogenicity in humans and animals (IARC, 2010).

The TEQ^Carc calculated for TSB varied between 0 and 104 ng g^{-1} (dry weight), with a median of 6.71 ng g^{-1} (dry weight) and a mean of 20.4 ± 28.4 ng g^{-1} (dry weight). According to Canadian soil quality standards for human health protection, values of TEQ^carc up to 600 ng g^{-1} are considered safe (CCME, 2010). Most of the sampled sites (65%) indicated a TEQ^carc ranging from 0 to 17.5 ng g^{-1} (dry weight), and only 7.5% were above 87.1 ng g^{-1} (dry weight) (Table 5). The risks to the marine biota in TSB from contamination by PAHs are smaller when compared to TEQ^carc values of other coastal marine environments of Brazil, such as Babitonga Bay (TEQ^carc from < DL to 757.7 ng g^{-1}, Dauner et al., 2018), and eight harbors in Southeast Brazil (TEQ^carc ranged an average from ≈10 to ≈330 ng g^{-1}, Pinheiro et al., 2017). The values reported in the present study are close to those of other places in worldwide e.g. Bohai Sea and the northern part of the Yellow Sea, China, (TEQ^carc from 5.95 to 68.80 ng g^{-1}, Li et al., 2015b) and is smaller than Meiliang Bay, China (TEQ^carc from 94 to 845 ng g^{-1}, Qiao et al., 2006), and San Diego Bay marinas in California, USA (Mean TEQ^carc values of 193 to 363 ng g^{-1}, Neira et al., 2017). In general, the carcinogenic potential calculated for TBS sediments compared to other bays indicates a low potential risk for the biota.

The levels of PAHs contamination in TSB were classified as low to moderate. The main sources of these compounds detected in TSB sediments are pyrogenic processes such as the combustion of oil and biomass. The levels of total PAHs in sediments, expressed as toxic equivalents (TEQ^carc), are relatively low compared to those reported for contaminated sediments in other bays in the world. The sites sampled in the present study did not present a risk of adverse effects to the biota. The highest concentrations of PAHs were recorded in sediment samples collected near the city of Salvador, where the Port of Salvador, the marinas and the ferry terminal are located. Higher concentrations are also observed in the vicinity of oil-related activities such as the oil refinery, oil terminal and oil and gas production areas between the northeast and northwest parts of the bay. Therefore, the main factor that influences the distribution of PAHs is the proximity of the sources of contamination. However, the hydrodynamics and geochemistry of the sediments also have an effect.

organisms (Liu et al., 2009b). Thus, sediment quality guidelines (SQGs) have been proposed to regulate their potential effects on marine ecosystems.

The maximum values of ΣLPAHs, ΣHPAHs and Σ16PAHs in the sediment samples collected in TSB were 26.2, 507 and 533 ng g^{-1}, respectively. These concentrations are below the TEL (312, 655 and 1684 ng g^{-1}, respectively) (Macdonald et al., 1996). This indicates that the concentrations of PAHs in these sampled sediments do not present a

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2018.10.040.

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