



PAHs in Water, Sediment and Biota in an Area with Port Activities

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Abstract

The study reports concentration of 16 PAHs in sediment, water, plankton and in muscle and liver of sampled fishes from Paranagua Bay in Southern Brazil. According to the range of PAHs concentration found in sediments (Σ PAHs 15.33–133.61 $\mu\text{g g}^{-1}$) and water (Σ PAHs 51.20–162.37 $\mu\text{g L}^{-1}$), the area was characterized as slightly polluted. In contrast, significant concentration of PAHs was found in fish and plankton, ranging from 26.52 to 2055.00 $\mu\text{g g}^{-1}$ and 175.41 to 2096.10 $\mu\text{g g}^{-1}$, respectively. The concentrations were 15 times more than in sediments. Even though the concentration of PAHs in water and sediments are low, the concentration in fish tissues are alarmingly. The hypothesis of bioaccumulation is not discharged. Accumulation levels of PAHs in the biota were used to calculate biota-sediment accumulation factor (BSAF) and bioaccumulation factor (BAF). For example, fish sampled from site 11 had a BAF of 49 and BSAF of 2.3, whereas for plankton the BAF was 16.3 and BSAF 0.7. Mean values of BAF and BSAF were higher in plankton samples. It is known that PAHs are enzymatically metabolized by organisms, thus the lower BSAF in fish might have resulted from biochemical transformation. Statistical analysis indicates no significant correlation between total PAHs concentration in fish tissues and total lipid content in fishes ($p > 0.1$).

Accumulation in tissues is controlled by lipid content, although factors, such as spatial distribution of compounds, trophic level, and behavior of each species in the environment, must be considered. Besides, size and nutritional conditions can affect both absorption as well as metabolic process and excretion. A positive and significant correlation was found between total PAHs and trophic positions obtained from FishBase data ($r^2 = 0.784$; $p < 0.05$). Thus, it seems that the area, with great influence of urban and industrial activities, and the bioaccumulation compounds, such as PAHs, depend on others factors, as well as resuspension of sediments and releasing of compounds for biota.

Among several groups of contaminants found in the marine environment, the polycyclic aromatic hydrocarbons (PAHs) are the most investigated in water, sediments, and suspended particles due to their carcinogenic properties and high level of resistance to microbiological degradation (Barakat et al. 2011; Guzzella et al. 2005). Although hundreds of PAHs compounds are known to exist in the environment, only 16 are considered as priority pollutants by US Environmental Protection Agency (USEPA). In aquatic bodies, sediment is the major sink for PAHs (Liu et al. 2012; Ranjan et al. 2012). In environment, PAHs are persistent, the degradation

occurs slowly, mainly due to their persistence and hydrophobic characteristic (Lei et al. 2005).

Various PAHs are potent mutagens and carcinogens to both aquatic and terrestrial animals, including humans (Dickhut et al. 2000; Duran and Cravo-Laureau 2016). From sediments, PAHs can be transferred to organisms by accumulation or through trophic chain (Bandowe et al. 2014; Jiao et al. 2014). However, most of the studies did not consider those aquatic organisms, even in low concentration in sediments and water, where could be accumulated. Few studies examined the presence of PAHs transferred from sediment to biota (Waszak and Dabrowska 2009; Soclo et al. 2000).

Generally, monitoring programs assess the concentration of total PAHs in sediments, and most of them do not consider or estimate influence on biota. PAHs effects on fish can be shown by some pathologies in the liver and gills, corroborated by biochemical disturbances and genetic damage by biomarkers (e.g., somatic index, chemical analysis of bile, biochemical, genetic and morphological parameters). These

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effects showed up even at concentrations below the threshold for PAHs in sediments (Ribeiro et al. 2013; Cappello et al. 2017; Maisano et al. 2016). PAHs bioaccumulation occurs when PAHs are present in water and/or sediments and are driven by lipid content of organisms (Soclo et al. 2008). Bioaccumulation can be assessed by methods that directly measure or predict it through mathematical models based on the lipid content in the organisms and compounds properties (Gobas 1993). Noxious effects of PAHs on biota are estimated or predicted by mathematical models based on routes of exposure, lipid content of species, diet composition, and dynamic process of pollutants (Torres et al. 2014). The main advantage of using models is the small number of analysis and the possibility to assess in a short time the extension of damage. From concentration in sediments, the extension of accumulation is determined by the bioaccumulation factor (BAF) and the biota-sediment accumulation factor (BSAF) models (Jiao et al. 2014; Soclo et al. 2008).

Estuarine areas are prone to receive large amounts of PAHs from drainage and deposition of suspended air particles (Ranjan et al. 2012). Sediments from coastal marine environments concentrate most of the PAHs. Port areas also suffer from constant discharges or accidental spills of crude oil and/or derivatives from boat/ship traffic (Guzzella et al. 2005; Stout et al. 2004). Previous studies have shown that Paranaguá Estuary surroundings (Southern Brazil) are suffering the impact due the socioeconomic development. In

addition, the port activities have increased as well as the vessels size and capacity (Rizzi et al. 2017; Abreu-Mota et al. 2014; Froehner et al. 2010).

In this work, the content and distribution of PAHs in sediments and biota from Paranaguá Bay, Southern Brazil (Fig. 1), were examined. The studied area is affected by local industry, port services, and soil occupation. The presence of PAHs in biota, i.e., plankton and fish (liver and muscle), were examined to understand the possible side effect, such as bioaccumulation. To understand the extension of bioaccumulation, BSAF and BAF deterministic models were used. Additionally, statistical analysis was performed in an attempt to investigate the relationship between PAHs in organisms, sediments, and among the subareas of the estuary.

Materials and Methods

Study area and Samples Preparation

Surface sediments, water, and phytoplankton samples were collected in April 2012 from 17 sample sites (Fig. 1). A statement was added to the sample sites to distinguish between sediments (S), water (W), and plankton (P). Considering our previous studies, the area was divided in two subareas. Subarea 1 (including points 1–12) corresponds to the East–West Axis. Within this subarea is located Paranaguá

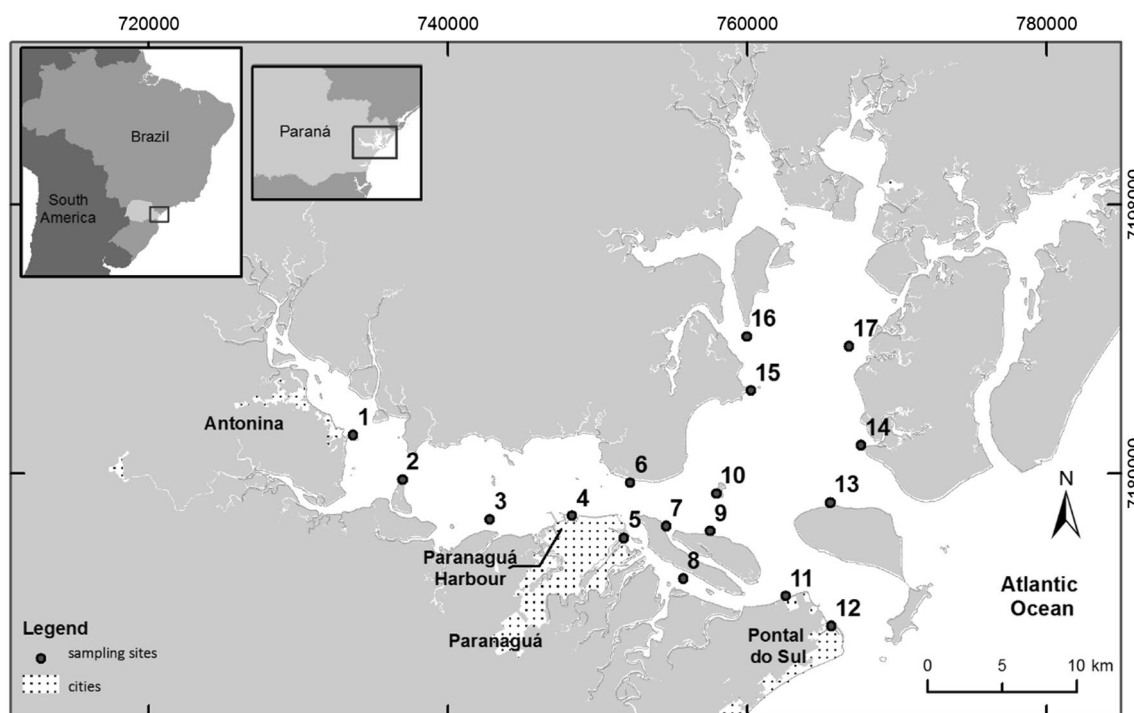


Fig. 1 Map of the study area showing the sampling sites of Paranaguá Bay. Sites 1–12 following to East–West axis (E–W) and sites 13–17 following to North–South axis (N–S)

Port, city of Paranaguá, and the Galheta channel (a channel of navigation). Subarea 2 corresponds to the North–South Axis and includes points 13–17, which are considered to have low human impact (Torres et al. 2014; Martins et al. 2010; Choueri et al. 2009).

The sediments were collected using a Van-Veen grab sampler. The samples were wrapped in aluminum foil and were kept at 4 °C. In the laboratory, they were frozen-dried before the extraction procedure. The plankton samples were only collected in subarea 1, using a fishing net of 20- μ m mesh. Finally, the filtered extract containing the plankton was frozen. For the PAHs content, the same procedure adopted to sediments was followed. Samples of fishes were collected using a different net. Table 1 contains the characteristics of fishes examined. To determine the PAHs level in fish, the liver and muscle were removed for analysis of compounds. Most PAHs were metabolized in the liver and muscles containing the unmetabolized compounds (Soclo et al. 2008). The removed tissues were kept at –15 °C until extraction and analysis.

Water samples were collected using a Van Dorn-type bottle and collected at a depth of 50 cm. Samples were kept at 4 °C in amber glass bottles. In the laboratory, the PAHs compounds were extracted with 60 mL of dichloromethane (twice), according the method 3510B proposed by EPA. Acenaphthylene-d8 was added as surrogate to monitor the quality of the extraction procedure. The recovery rate was higher than 76%. The extracts were combined, and the volume was reduced to approximately 1 mL in a rotatory evaporator and then dried under flux of nitrogen. The extracts were redissolved in 200 μ L of hexane for further quantification by CG-MS. The chromatographic conditions are described below.

Granulometric Composition of Sediments

The granulometric composition (sand, silt, and clay) was determined by an integrated technique (sieving and laser

diffraction). Briefly, samples were passed through a set of sieves with standardized mesh screens (mesh size 8, 14, 42, 80, 170, 250, 400, 500, and 635). The classification of sand, silt, and clay was obtained according the Wentworth granulometric scale (Besler and Ritter 2010). The fine grains were collected and examined with a laser analyzer, which measures the size by detecting angular diffractions from a light scanning after it has passed through the sample in an optical cell (Froehner and Martins 2008).

Total Organic Carbon

In the process of determination of total organic carbon (TOC), all samples were acid digested using 16% (v/v) hydrochloric acid to remove the carbonate fraction. Then, the organic carbon was converted to CO₂ and quantified by using a TOC analyzer (Shimadzu, TOC-VCPH).

Extraction, Clean Up, and Analysis of PAHs

The extraction and analysis of PAHs in all samples were performed according to the procedure described in the existing literature (Jiao et al. 2014; Liu et al. 2012; Zakaria et al. 2002; Yunker et al. 2002). Briefly, bulk sediment (10 g) was extracted by using an accelerated solvent extractor (ASE, Dionex) in 5-min static cycles (100 °C, 4 MPa) with a mixture of dichloromethane (DCM) and acetone (1:1). Sulfur was removed from the extracts using activated copper, which was added directly after the extraction. The PAHs in the total lipid extract (TLE) was separated from other compounds by elution with hexane in columns filled with silica (3 \times 4 mL). The volumes were combined and reduced to approximately 0.5 mL and completely dried under a gentle flow of nitrogen before the internal standard. The extract was redissolved with 200 μ L of hexane for injection and analysis. A solution containing 16 PAHs (USEPA priority pollutants) (AccuStandard PAH Mix Z-014G) was used as a standard solution to obtain a calibration curve for quantification. The standard mixture was composed

Table 1 Characteristics of fishes collected in Paranaguá Bay

Station	Sample	Species	TL	St_d	PL	St_d	TW	St_d	n. individuos
1	F1Dr	<i>Diapterus rhombeus</i>	77.0	10.2	54.6	6.2	6.2	2.1	5
1	F1Br	<i>Bardiela ranchus</i>	92.0	2.4	77.0	2.2	9.8	0.5	3
3	F3Ip	<i>Isopisthus parvipinnis</i>	13.0	0.0	11.5	0.0	24.4	0.0	1
3	F3Cs	<i>Cathorops spixii</i>	14.0	1.7	11.7	1.5	32.6	13.3	11
6	F6Cs	<i>Cathorops spixii</i>	15.2	1.4	12.72	1.1	37.5	8.0	12
7	F7 Ma	<i>Menticirrhus americanus</i>	18	2.11	14.64	1.8	62.52	21.3	7
10	F10Gg	<i>Genidens genidens</i>	30.3	0.2	25.4	1.0	320.7	33.0	5
11	F11Cl	<i>Cynoscion leiarchus</i>	21.0	0.0	17.5	0.0	107.5	0.0	1
11	F11Ea	<i>Eucinostomus argenteus</i>	12.2	1.2	9.2	0.9	24.8	5.5	2

TL total length, PL partial length, TW total weight, n number of organisms in each sample to get ~1 g of dry tissue to analysis

by anthracene (ANT), acenaphthylene (ANP), acenaphthene (AEN), phenanthrene (PHE), fluorene (FLU), pyrene (PYR), indene[1,2,3-*cd*]pyrene (IcP), benzo[*a*]pyrene (BaP), benzo[*k*]fluoranthene (BkF), benzo[*b*]fluoranthene (BbF), chrysene (CHR), dibenzo[*a,h*]anthracene (DhA), benzo[*ghi*]perylene (BgP), benzo[*a*]anthracene (BaA), fluoranthene (FLA), indene (IND), and naphthalene (NAP). Before the analysis, deuterated fluorine-d10 was added to each sample as an internal standard, whereas acenaphthylene-d8 was added before the extraction as surrogate to monitor the efficiency of the analytical protocol. The recovery rates were higher than 75% for most of all samples. All solvents were HPLC grade; silica gel was treated with DCM (24 h) and activated in an oven for (400 °C; 4 h). The PAHs were identified and quantified by chromatograph gas coupled to mass spectrometer with electron-impact ionization (GC–MS Varian model 450). The GC was equipped with a factor four VF 5MS fused silica capillary column (60 m, 0.25 mm i.e., 0.25- μm film thickness) and helium as a carrier gas with a constant flow of 1.2 mL min⁻¹. The GC oven was programmed to increase from 40 to 120 °C (at 30 °C min⁻¹), with an initial hold of 1 min at 40 °C and a final hold of 16 min at 280 °C. Both full scan and selected ion monitoring (SIM) modes were applied. PAHs were identified by comparing retention time with those of the appropriate authentic standards and published spectra. Quantitative analysis was performed using internal and external calibration methods.

Liver and muscle of fish and phytoplankton were lyophilized and then extracted following the same procedure described above for sediments. The amount used for extraction varied from 0.5 to 3.0 g.

Lipid proportion was determined following the procedure described by Tölgyessy and Miháliková (2015). Briefly, approximately 5 g of tissue fish was extracted with acetone/ethylacetate mixture (6:4) using vigorous shaking, and then inorganic salt (2 g MgSO₄ and 0.5 g NaCl) was added and agitated. The organic phase was separated by centrifugation. An aliquot of the organic phase was air-dried and then oven-dried, and the lipid content of the fish homogenate was determined gravimetrically on a wet weight basis.

Bioaccumulation Models

To better understand the possible extension of contaminants in the trophic chain, bioaccumulation factors models were used. For this purpose, the bioaccumulation factor (BAF) and biota sediment factor accumulation (BSAF) were applied (Kwok et al. 2013). To measure the uptake of PAHs from sediments to biota, the bioaccumulation factor (BAF) was calculated. The BAF is represented by Eq. (1):

$$\text{BAF} = \frac{C_f}{C_s} \quad (1)$$

where C_f is the concentration in organisms and C_s the concentration in sediments (in ng g⁻¹ dw).

The extension of bioaccumulation also was tested considering the lipid content of each organism. For this, a BSAF model was used according Eq. (2):

$$\text{BSAF} = \frac{C_f/L}{C_s/C} \quad (2)$$

where C_f is the concentration of compound in organism (ng g⁻¹), L is the lipid proportion in the biological tissue in %, C_s is the concentration of compound in sediment (ng g⁻¹), and C is the organic compound in the sediment in %.

Statistical Analysis

Analysis of variance (ANOVA) was performed for the data obtained. To evaluate the significant differences between the two designated subareas of the estuary, the least significant difference (LSD) was determined by the Tukey test, at 5% level of probability. Additionally, the Tukey test was performed by ANOVA (NESTED) to check any LSD difference between environment matrices (water, sediment, and fish plankton) and PAHs groups (di, bi, tetra, penta, and hexa-aromatics rings). Normality was assessed using the Shapiro–Wilk test. Statistical correlation coefficients between total PAHs and physical–chemical characteristics of the sediments, i.e., grain size TOC and total PAHs in fish tissues and biological characteristics, i.e., percentage of lipids, total length, total weight, and trophic level, were calculated to evaluate the influence of each parameter at accumulation of PAHs. Analyses were performed using the program XLSTAT Version 2015.4.01.20116.

Results and Discussion

Granulometric Composition of Sediments

To better understand the influence of anthropogenic activities, the area was segmented in two parts: subarea 1 and subarea 2. The granulometric composition of sediments clearly showed two different areas. The inner part of estuary (sites 1, 2, and 3, subarea 1; Fig. 1) was mostly muddy, with high silt content, ranged from 41 to 46%. In contrast, sediments from the other segment (subarea 2) is composed by fine and medium sand (500–62 μm). As expected, inner parts of the estuary presented the highest content of organic carbon. In sites 1, 2, and 3 (subarea 1) varied from 85 to 69 mgC g_{sed}⁻¹ and in site 17 (subarea 2) 70 mgC g_{sed}⁻¹. In general, fine and medium sand (63–500 μm) and silt (4–63 μm) fractions dominated the most samples composition, whereas clay particles (< 4 μm) were absent. The sediment samples

from sites 11 and 15 presented the highest content of coarse sand (2000–500 μm), ranging from 12 to 22%, with lower TOC, 4.96 $\text{mgC g}_{\text{sed}}^{-1}$ minimum.

The level of TOC in sediments is crucial to define the fate and transport of pollutants; in addition, the TOC content is usually higher for fine particles. Furthermore, a positive and strong correlation was found for TOC and silt ($r^2=0.730$, $p<0.001$), whereas a negative correlation was found for samples with high content of sand ($r^2=-0.507$, $p<0.05$). Previous study in this area showed that currents and tidal are responsible for organic matter accumulation (Herrling 2003).

Distribution Levels of PAHs in Water and Sediments Samples

PAHs present very low water solubility (2–260 $\mu\text{g L}^{-1}$). In this research, the level of total concentration of PAHs (ΣPAHs) in water samples was found low, the concentration ranged from 51.2 to 162.4 ng L^{-1} (Table 2), with predominance of low molecular weight compounds (naphthalene, anthracene, and fluoranthene). Water samples from sites 3 and 16 presented the highest concentration of total PAHs. Site 3 is influenced by the intense traffic of commercial ships, offloading and loading activities. Water sample from site 16 (W16) also showed ΣPAHs concentration in the same level for W3. Such high concentration is accounted for the intense traffic of small boats, including those used for local transportation driven by diesel fuel. This observation is supported by low molecular weight (LMW)/high molecular weight (HMW) PAHs ratio higher than 1, indicating petrogenic source of PAHs in water (Yunker et al. 2002).

As expected HMW PAHs are absorbed by suspended particles, whereas LMW PAHs can be present in the water in significant concentration (ASTDR 1995) HMW PAHs, i.e., chrysene, benzo(bk)fluorantene, benzo(a)pyrene, indene, dibenzo(ah)anthracene, and benzo(ghi)perylene, were found in concentrations (14.96–146.50 ug L^{-1}). With the help of previous literature, one can say that bioaccumulation can occur even at small concentration in water (Silva et al. 2007; Gobas 1993).

The presence of PAHs in rivers and estuarine waters have become common; for instance, in the Mississippi River there were ΣPAHs ranging from 62.9 to 144.7 ng L^{-1} (Zhang et al. 2007), Venice was reported to have the total PAHs concentration ranging from 12.4 to 266.8 ng L^{-1} (Manodori et al. 2006). The results found in this work are similar with both studies mentioned. The ΣPAHs values, found in Paranaguá Bay, showed a distinct range compared with other areas regarding to pollution, such as Daya Bay (4228–29,325 ng L^{-1}) (Zhou and Maskouei 2003) and Guanabara Bay (1592 ng L^{-1}) (Silva et al. 2007).

Presence and abundance of PAHs in sediments are frequently used to classify an area as polluted or not (Barakat, et al. 2011; Baumard et al. 1998). Sediments with ΣPAHs ranged from 0 to 100 ng g^{-1} are considered as unpolluted or with minimum pollution. Sediments with concentration ranges from 100 to 1000 ng g^{-1} are classified as moderated polluted, whilst values higher than 5000 ng g^{-1} represent areas extremely polluted. In this work, most of sites were classified as unpolluted, except sites 3 (133.61 ug g^{-1}), 13 (107.5 ug g^{-1}), and 15 (132.42 ug g^{-1}) that were considered as moderately polluted, according the abundance of total PAHs.

The concentration of PAHs in sediment samples ranged from 15.5 to 133.6 ng g^{-1} . However, the distribution was quite different (Table 2). As expected, the results showed distinct areas among sediment samples, high polluted and almost pristine ones. Site 3, near the port, presented the highest concentration of PAHs. On the other hand, site 9, close to Cotinga Island and Galheta navigation channel, presented the lower concentrations followed by sites 16 (36.9 ng g^{-1}) and 17 (37.3 ng g^{-1}), both located in subarea 2. Those results are in same level of magnitude in accordance with previous studies in some parts of Brazilian coast. For example, in the Patos Lagoon, Southern Brazil, PAHs were found ranging from 4.7 to 112.5 ng g^{-1} (Luz et al. 2010). The Patos Lagoon suffers influence from anthropogenic activities, especially fishing. The estuarine system of Mandau-Manguaba, Northeastern Brazil, showed PAHs ranging from 29.2 to 222.7 ng g^{-1} (Silva et al. 2013).

Paranaguá Bay has some analogous activities with the most polluted coastal areas in Brazil, i.e., Guanabara Bay and Santos Bay, economic activities and sewage input are similar (da Silva et al. 2007). However, in those places the activity is quite intense which reflected in the level of pollution. At Guanabara Bay, there was a record of ΣPAHs values in the sediments ranging from 77 to 7751 ng g^{-1} and in Santos Bay concentrations higher than 15,300 ng g^{-1} . Previous studies in the Paranaguá estuary observed ΣPAHs ranging from 3.85 to 89.5 ng g^{-1} at North–south axis (subarea 2) of Paranaguá Bay (Martins et al. 2012). In Hugli, a highly industrialized estuarine area in India, the concentration of PAHs varied from 2.5 to 1081 ng g^{-1} (Guzzella et al. 2005). In addition, concentration of total PAHs in sediments from Mediterranean Sea was higher than 21,600 ng g^{-1} (Barakat et al. 2011). The values of PAHs found in the present research confirmed an area quite preserved compared with the threshold values labeled as polluted. The PAHs content in sediments are lower than those concentrations assumed to trigger deleterious effects on biota according to sediment quality guidelines (SQG) (NOAA 1999). Table 3 shows the PAHs values for each sample and the values used as guidelines. The results are lower than the values of Effects Range-Low

Table 2 Polycyclic aromatic hydrocarbons (PAHs) concentrations in water, sediment, plankton, and fish samples from Paranaguá Bay (in ng g⁻¹ dw)

Matrix	Id	Station	NAP	ANP	AEN	FLU	PHE	ANT	FLA	PYR	BaA	Chr	BbKF	BaP	Ind	DahA	BghiP	ΣPAHs	
Water	W1	1	2.46	2.53	2.60	5.14	0.53	4.56	1.64	3.87	16.77	40.15	<DL	<DL	5.13	0.42	<DL	85.82	
	W3	3	1.47	<LD	2.38	5.94	0.65	<DL	5.35	<DL	66.23	49.00	14.28	<DL	13.40	2.13	1.46	162.31	
	W11	11	2.50	1.78	1.23	6.60	7.81	12.42	3.90	<DL	<DL	<DL	<DL	5.50	1.70	<DL	<DL	51.20	
	W16	16	1.83	2.69	2.67	19.56	1.69	1.61	16.19	<DL	68.81	35.49	11.64	<DL	<DL	<DL	0.20	162.37	
	Sediment	S1	1	0.13	0.63	0.12	0.17	0.81	0.36	0.55	0.58	0.64	6.56	4.43	12.42	14.50	<DL	32.07	73.98
		S2	2	4.90	0.92	0.63	0.41	0.60	0.57	0.53	0.75	0.39	4.50	1.02	0.87	1.22	0.09	23.74	41.14
		S3	3	45.74	5.99	1.11	0.85	1.31	0.22	1.30	1.65	1.13	2.80	2.21	1.48	2.27	<DL	65.56	133.61
		S4	4	3.79	0.21	0.16	0.16	1.46	0.23	0.96	1.22	0.65	0.65	0.58	0.11	58.38	0.75	0.41	69.71
		S5	5	0.44	0.35	0.68	0.29	1.14	1.08	0.63	0.35	1.22	1.75	0.92	1.24	0.97	<DL	78.08	89.14
		S6	6	0.38	0.17	0.30	0.08	0.66	0.18	0.58	0.81	0.81	1.28	1.15	2.96	6.56	0.38	37.49	53.79
		S7	7	1.02	0.33	0.15	0.14	0.66	0.10	0.49	0.11	0.32	0.08	0.18	0.41	15.10	<DL	64.02	83.11
		S8	8	21.46	0.91	0.53	0.37	0.78	0.08	0.64	0.95	0.62	2.14	1.03	0.70	15.32	<DL	25.23	70.78
		S9	9	4.28	0.44	0.19	0.19	0.26	0.09	0.43	0.20	<DL	0.39	0.40	0.58	0.38	<DL	7.70	15.53
		S10	10	4.07	0.26	0.17	0.16	0.78	0.46	0.35	0.21	0.21	0.08	0.72	0.38	0.93	<DL	65.10	73.88
	S11	11	5.89	0.38	0.24	0.17	0.35	<DL	0.43	0.43	0.03	0.47	0.57	1.60	9.34	<DL	22.05	41.93	
	S12	12	7.48	0.56	0.19	0.16	0.85	0.35	0.49	1.17	0.29	2.18	0.54	1.16	6.48	<DL	28.58	50.47	
S13	13	5.40	0.48	0.17	0.16	0.46	0.40	0.31	0.29	0.14	0.33	0.41	0.98	65.25	<DL	32.72	107.50		
S14	14	<DL	0.16	<DL	<DL	0.31	0.13	0.35	0.13	0.59	0.10	0.44	0.88	12.68	<DL	32.55	48.31		
S15	15	7.12	0.36	0.56	0.29	0.52	0.13	0.79	0.49	<DL	7.40	0.71	1.04	25.16	<DL	87.84	132.42		
S16	16	0.17	0.08	<DL	<DL	0.14	<DL	<DL	<DL	0.14	0.29	0.94	2.13	5.10	<DL	27.93	36.92		
S17	17	3.66	0.45	0.19	0.14	0.69	0.40	0.61	0.34	0.36	1.18	0.29	0.55	0.05	0.10	28.28	37.27		
Plankton	P3	3	0.60	2.36	0.28	3.22	11.51	1.02	14.19	1.73	194.13	<DL	10.83	4.01	1144.6	<DL	707.58	2096.1	
	P6	6	1.48	10.33	2.25	1.36	13.48	6.00	33.47	31.07	9.54	12.56	9.86	17.37	12.96	13.65	0.04	175.41	
	P11	11	3.70	7.11	3.73	2.36	7.60	3.16	42.46	17.11	6.41	25.27	9.85	157.74	140.66	<DL	257.71	684.88	
Fish (muscle)	F1Dr	1	2.63	1.75	1.63	0.90	4.31	4.11	2.96	3.03	9.72	<DL	2.02	<DL	0.06	23.52	1.78	58.42	
	F1Br	1	50.22	5.50	4.92	2.29	10.54	5.24	15.16	12.87	9.70	4.52	2.68	14.22	29.09	<DL	546.36	713.30	
	F31p	3	97.51	15.48	6.30	4.44	4.63	6.81	20.53	7.99	4.30	4.71	12.94	14.08	23.56	<DL	1330.6	1553.9	
	F3Cs	3	17.05	2.06	2.71	9.31	10.16	3.75	4.28	5.35	3.62	16.23	28.96	49.89	4.93	0.63	141.19	300.11	
	F6Cs	6	35.10	4.41	4.70	6.93	9.25	2.50	3.19	8.64	10.22	0.74	11.52	46.22	<DL	<DL	579.96	723.39	
	F7Ma	7	2.08	0.91	0.27	0.03	3.77	1.99	1.13	1.35	3.66	0.03	0.69	6.39	0.83	3.07	0.33	26.52	
	F10G	10	76.09	22.18	9.78	5.07	51.44	33.63	25.08	18.42	30.78	3.69	22.44	136.64	22.03	19.96	3.11	480.33	
	F11Cl	11	6.16	13.61	6.98	0.06	125.57	41.89	34.89	101.87	314.40	0.90	62.73	132.97	5.80	<DL	1207.2	2055.0	
	F11Ea	11	26.40	6.17	3.33	1.97	4.74	8.52	23.76	16.29	7.15	4.97	4.02	7.58	4.62	3.22	102.90	225.66	

Table 3 Sediment quality guidelines (SQG) and average and maximum concentrations of superficial sediments of Paranagua Bay *Source:* Buchman (2008) and Froehner et al. (2010)

PAH	ERL	ERM	TEL	PEL	Average	Maximum
ANP	16	500	6.71	88.9	0.75	5.99
AEN	44	640	5.87	128	0.32	1.11
ANT	85.3	1100	46.9	245	0.28	1.08
FLU	19	540	21.2	144	0.22	0.37
NAP	160	2100	34.5	391	6.82	45.74
PHE	240	1500	86.7	544	0.69	1.46
BaA	261	1600	74.8	693	0.44	1.22
BaP	430	1600	88.8	763	1.74	12.42
CHR	384	2800	108	846	1.89	7.4
DahA	63.4	260	6.22	135	0.08	0.75
FLA	600	5100	113	1494	0.55	1.3
PYR	665	2600	153	1398	0.57	1.65

Values in ng g^{-1} of sediments (dw)

(ERL), Effects Range-Median (ERM), Threshold-Effects Level (TEL), and Probable-Effects Level (PEL) (Buchman 2008). According to these results, the area can be considered as unpolluted; nevertheless, histopathological studies had demonstrated mutagenic effects on some fishes collected at this estuary (Ribeiro et al. 2013).

The granulometric composition of sediment controls its content of PAHs. Besides, in marine environments physical and chemical process, water circulation and currents affect the PAHs distribution (Yunker et al. 2002; Kowalewska et al. 2003). There was a positive correlation found among PAHs and granulometric composition. PAHs showed strong positive correlation with sediments rich in silt ($r^2 = 0.417$; $p < 0.1$) and negative correlation with sediments rich in medium sand ($r^2 = -0.445$; $p < 0.1$). Differences in sorption of compounds are accounted for organic carbon referenced sorption coefficient ($\log K_{oc}$), however pH and ionizable capacity of soils and sediments also affect the efficiency of sorption. Thus, PAHs with high molecular weight seems to be strongly absorbed by sediments, as consequence, their mobility will be lower (Liu et al. 2012). A typical example of this behavior is the result found in site 11, composed predominantly by sand and 1.55% of TOC. The Σ PAHs for this site was only 15.5 ng g^{-1} , even the site is located near a pollution outfall.

To distinguish the source of PAHs, the compounds were subset in LMW ($< 202 \text{ g mol}^{-1}$) and HMW ($> 202 \text{ g mol}^{-1}$). Thus, a HMW/LMW ratio lower than 1 indicates a petrogenic source of PAHs (Barakat et al. 2011; Baumard et al. 1998). The ratio values obtained indicate a mixture of sources (pyrogenic and petrogenic), except for S3 (1.4) and S9 (1.7) sites, which PAHs are mostly from pyrogenic source. In general, LMW PAHs are associated with oil. Considering the area and its activities, it was not a surprise that among 16 PAHs, lower molecular weight were predominant compounds, indicating oil spill. Such observations were in

accordance with previous studies in this area (Martins et al. 2012; Froehner et al. 2010).

Because PAHs are released and reach the environment, microorganisms can modify the distribution of PAHs, especially those with low molecular weight. To decipher the source of PAHs in sediments, different ratios among PAHs were applied, according to the ratios proposed by Yunker et al. (2002). These ratios were used: FLA/(FLA + PYR), ANT/(ANT + PHE), and BaA/(BaA + CHR). Sediments from sites 1, 2, 3, 4, 6, 8, and 12 showed contamination by oil derivatives; however, according to the results, it is more appropriate to assume a mixture of contribution (Fig. 2). For sediments collected near the port, it was already identified as influences of urban sewage (Martins et al. 2010). All samples located in the North–South of the estuary (S13, S14, S15, and S17) showed contamination associated mainly from pyrogenic and mixed sources.

Concentrations of PAHs in Plankton and Samples of Fish

Samples of plankton were collected in three different sites: P3, P6, and P11 (P denotes plankton samples and the number the location of sample site). In general, samples were constituted by phytoplankton and small fraction of zooplankton. Fish samples were collected in sites F1, F2, F3, F6, F10, and F11 (where F denotes fish samples and the number the location of sample site). In fish samples, the presence of PAHs was examined in the muscle (M) and liver (L). The Σ PAHs in plankton and fish samples were higher than those found in sediments. The Σ PAHs varied from 26.52 to $2096.08 \text{ ng g}^{-1}$ in dry weight. The highest values was found in phytoplankton from site 3, and the values of total PAHs was 1569% higher than concentration in sediment of this site. This site also presented the highest value of PAHs in the water and sediment. Among fishes, samples from sites

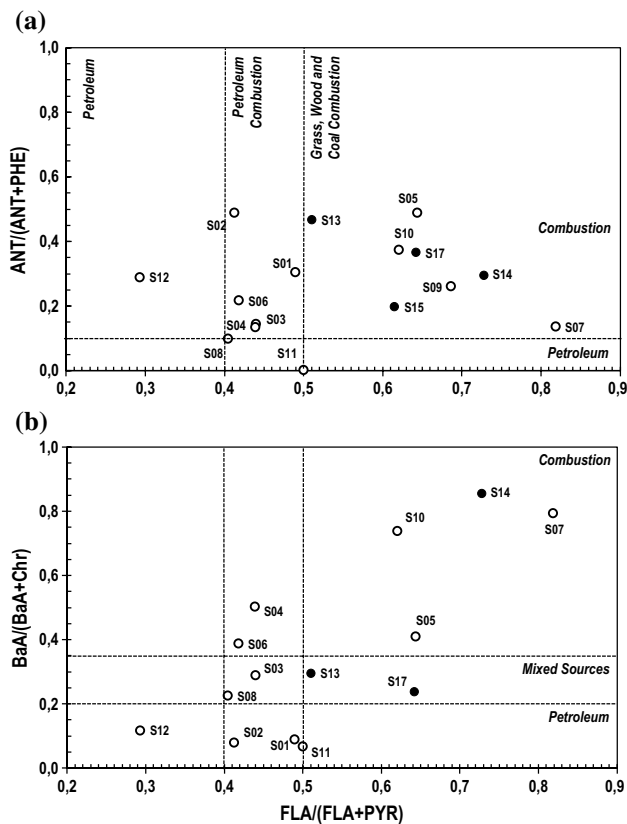


Fig. 2 PAHs cross plot for the ratios of **a** FLA/(FLA + PYR) versus ANT/(ANT + PHE), **b** FLA/(FLA + PYR) versus BaA/(BaA + CHR) of sediments from Paranaguá Bay

3 and 11 (near the port activities) had the most significant level of PAHs amount in their bodies. The level of PAHs in biological tissue resulted from transfer from water, sediment, and diet. The lipid content in organisms controls the accumulation of organic compounds (Bandowe et al. 2014; Baumard et al. 1998).

Hydrophobic compounds can accumulate in organisms for long period of time (Kwok et al. 2013); the concentration in the organism is due to the environment activities and diet of each specie. Organisms that have poor biotransformation capacity (e.g., plankton) can accumulate high amounts of PAHs and other compounds (Perugini et al. 2007). Recently, samples of plankton from Seine Estuary presented 3866 ng g⁻¹ as maximum concentration (Cailleaud et al. 2007). While in fish muscle from Ghana, the total PAHs was up to 481 ng g⁻¹ (Bandowe et al. 2014). Muscle fishes from Hong Kong presented lower concentrations (184–194 ng g⁻¹ dw). The presence of poly aromatic compounds in biological samples imply the existence of contaminated sites transferred through diet. The accumulation of compounds can happen even when sediments has low amount of pollutants. Different levels of concentration of PAHs can be observed in species in the same trophic chain, such difference might

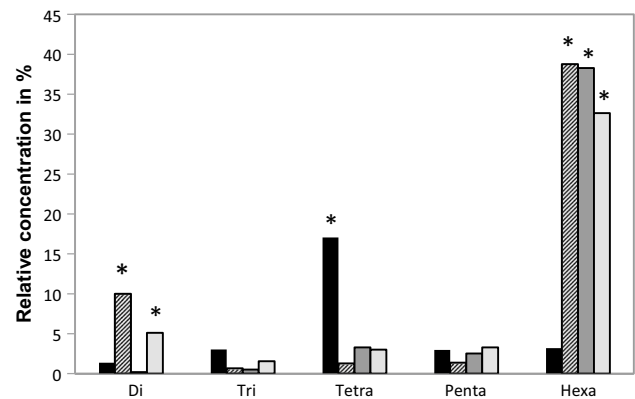


Fig. 3 Relative concentration of PAHs per group of aromaticity (tri-, tetra-, penta- and hexa aromatics) in waters (■), sediments (▨), plankton (▩) and fish (□) sampled at Paranaguá Bay. The highest means significantly different were with the asterisk symbol (*)

be attributed to the lipid content of each organism. In fish, compounds can be metabolized by biochemistry and enzymatic mechanism in response to reduce the concentration in the body (Beyer et al. 2010). Even some organisms are able to metabolize PAHs, the accumulation in the tissue with more lipids content is significant (Gobas 1993; Taniguchi et al. 2009; Maisano et al. 2016).

In this study, the highest concentration of PAHs was found in *Cynoscion leiarchus* (Cl) species (smooth weakfish), collected in site 11 (F11Cl), and the lower concentration was identified in muscle of *Menticirrhus americanus* (Ma) from site 7. Age, diet, habitat, and habits are essential to explain and understand the concentration of PAHs in fish. Smooth weakfish (*C. leiarchus*) is easily found in muddy habitats as well as in sand bottoms of estuarine areas (FishBase 2015). Smooth weakfish is a piscivorous species, however, macro- and micro-plankton, crustaceans, and mollusks, also form part of its diet (Chaves and Umbria 2003). Among the collected species, smooth weakfish is in the highest trophic position (TP) (4.0 ± 0.7). Trophic position indicates the trophic level occupied by animal, based on its diet, according to FishBase data (2015). The highest concentration might be a result of a biogmanification process. Southern king croaker (*M. americanus*) is quite common in the Brazilian coast, found in sediments (sand and mud), feeding benthonic organisms (Rondineli et al. 2007), and it has trophic position (TP) of 3.5 ± 0.0.

The distribution of PAHs showed a distinct pattern for each matrix examined (Fig. 3). Such differences can be attributed as organic carbon content in each compartment and lipophilicity of each compound. For example, PAHs up to four benzene rings tend to be in water (17% of the total PAHs); in contrast, those PAHs with five benzene rings or more tend to be bind by sediments (39%). In biota, the accumulation is associated to the level in the trophic chain and

lipid content; plankton presented 39% and fishes 38% of the total PAHs. All species analyzed were benthonic and the contact with muds is intrinsic of their habits. The bioaccumulation process is initiated by the contact with contaminated sediments. Thus, the HMW PAHs found in tissue of fish might have originated from contaminated sediments (Baumard et al. 1998). In port areas, dredging procedures often are conducted in an attempt to improve the navigation conditions. Such procedure could promote resuspension of contaminants. Usually, low molecular weight PAHs are degraded faster than high molecular weight. Thus, some of the PAH compounds are bioavailable (Perugini et al. 2007).

Statistical analysis indicates no significant correlation between total PAHs concentration in fish tissues and total lipid content in fishes ($p > 0.1$).

Accumulation in tissues are controlled by lipid content, although factors, such as spatial distribution of compound, trophic level, and behavior of each species in the environment, must be considered. Besides, size and nutritional conditions can affect both absorption as well as metabolic process and excretion. A positive and significant correlation was found between total PAHs and trophic positions obtained from FishBase data ($r^2 = 0.784$; $p < 0.05$).

The BAF values obtained ranged from 0.3 (site S7) to 49 (site S11; Table 4). The TOC in sediments might support such variation together with granulometric composition (Baumard et al. 1998). The result is not surprising, because the more hydrophobic the compound is, the more tightly it will bind to the sediments containing higher organic matter, resulting in less partition from sediment to water and therefore lower bioavailability to accumulation by organisms. Site 11, which presented the highest BAF value for sample F11Cl, is composed predominately of sand (55%) and lower TOC (0.5%). The high value of BAF also suggests that PAHs are more available to be taken by organism than

other sites. In contrast, site 1, which had presented the highest percentage of silt and fine grain, showed the lowest BAF value (0.8). Biological characteristics of each species can be determinant in accumulation of organic compounds; the species *Cynoscion leiarchus* (F11C1M) is the top selected trophic chain and has a diet extremely piscivorous. For plankton, the BAF was 16.3.

The capacity of accumulation by organisms also was examined considering the lipid content of each species. The BSAF varied from 0.1 (F1Ma) to 13.5 (P3). Mean values of BAF and BSAF were higher in plankton samples (Fig. 4). It is known that PAHs are enzymatically metabolized by organisms. Thus, the lower BSAF in fish might have resulted from biochemical transformation.

To exclude variation due to different behaviors among species, such as feeding habits, the results of BAF and BSAF were determined to *C. spixii* sampled in sites 3 and 6, wherein the individuals presented similar characteristics of size and weight. It was observed that bioaccumulation

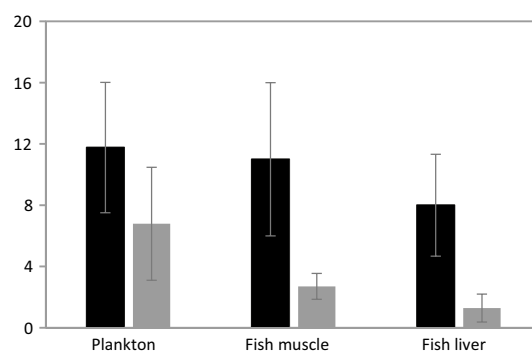


Fig. 4 Biaccumulation factors (■ BAFs) and Biota and sediment accumulation factors (■ BSAFs) of plankton, fish muscle and fish liver. Values are mean \pm SEM ($n = 2-8$)

Table 4 Bioaccumulation factors (BAFs) and biota-sediment accumulation factors (BSAFs) for the samples of Paranaguá Bay

ID	Station	Σ PAH	%Lip	Σ PAH _{sed}	%TOC	BAF	BSAF
P3	3	2096.08	8.1	133.61	6.9	15.7	13.5
P6	6	175.41	3.4	53.79	6.5	3.3	6.2
P11	11	684.88	11.3	41.94	0.5	16.3	0.7
F1Dr	1	58.42	15.1	73.98	8.5	0.8	0.4
F1Br	1	713.30	12.7	73.98	8.5	9.6	6.5
F3Ip	3	1553.88	17.4	133.61	6.9	11.6	4.6
F3Cs	3	300.11	21.9	133.61	6.9	2.2	0.7
F6Cs	6	723.39	14.3	53.79	6.5	13.4	6.1
F7 Ma	7	26.52	10.0	83.11	2.6	0.3	0.1
F10Gg	10	480.33	9.4	73.88	4.8	6.5	3.3
F11Cl	11	2055.00	10.4	41.94	0.5	49.0	2.3
F11Ea	11	225.66	9.6	41.94	0.5	5.4	0.3
F3CsL	3	1512.77	35.7	133.61	6.9	11.3	2.2
F7MaL	7	388.61	31.8	83.11	2.6	4.7	0.4

factors from site 6 (F6Cs) were higher than values from site 3 (F3Cs), (BAFs = 2.2 and 0.71 and BSAFs = 13.4 and 6.09, respectively). The hydrodynamic characteristics (tidal and eddy current) are the major difference between these sites. While station 3 is in a more protected area, station 6 is located in a region with more intense tidal currents near to the port shipping channel where dredging activities occur frequently. Thus, it seems that the area with greatest influence of urban and industrial activities, as station 3, bioaccumulation compounds, such as PAHs, depend on others factors as well as resuspension of sediments and releasing of compounds for biota.

Conclusions

PAHs pollution levels in water, sediment, and biota were investigated. The levels of total PAHs of water and sediments represent a slightly contaminated area; the concentrations found in plankton and in fish tissues were much higher. The concentration of PAHs in sediments were proportional to TOC.

There was no significant difference between the subareas (1 and 2) of the estuary respect to total concentration. However, PAHs distribution in sediments near to Paranagua Harbour and to the navigation channel were related with mixed combustion and petrogenic sources, showing the influence of this activity at the estuary, whereas the sites located at North–South axis of the estuary showed more influence of pyrogenic sources.

Plankton and benthic fishes exhibited preference in accumulate penta and hexa-aromatic rings compounds in their tissues, and they were the most abundant compounds in sediments. The mathematical models used to examine the extension of contaminants in biota showed bioaccumulation of PAHs in some species. Values obtained in organisms were more than 1000% higher than in sediments, clearly representing a potential bioaccumulation process. Even the concentration of contaminant in water and sediments label the area as unpolluted. The values of BAF and BSAF showed that the bioaccumulation of PAHs is evident at the estuary, and the sediments could represent the main source of contamination.

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