

DISTRIBUTION DYNAMICS AND POTENTIAL SOURCES OF POLYCYCLIC AROMATIC HYDROCARBONS FOR SURFACE SEDIMENTS AND BIVALVES FROM A HIGHLY ANTHROPIZED ESTUARY

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ABSTRACT

The Santos Estuarine System (SES), located in southwest Brazil, presents strategic economic importance for the country due to the presence of the biggest Brazilian Port and for being one of the most industrialized areas. On the other hand, this environment is adversely impacted by industrial and dredging activities, which can cause environment pollutants enrichment and potential hazard compound bioavailability. In this context, Polycyclic Aromatic Hydrocarbons (PAH) were assessed in fifteen sampling stations distributed along the estuary. Polycyclic aromatic hydrocarbon (PAH) concentrations were analyzed in surface sediment samples and two bivalve species' tissues (*Crassostrea rhizophorae* and *Perna Perna*). In addition, water column salinity, sediment organic matter, and grain size were analyzed to check their influence on the contaminant accumulation. Total PAH sediment concentrations ranged between N.D. and 1711.79 ng g⁻¹ dry weight (d.w.). Bivalve hydrocarbon levels varied between 88.38 and 988.76 ng g⁻¹ (d.w.). The calculated PAH ratios revealed that the PAH compounds found in the studied area has both petrogenic and pyrolytic origins. A comparison of the PAH concentrations found in this study with those listed in the sediment quality guidelines (SQGs) indicated that adverse biological effects on the biota are eventually expected.

Keywords: Polycyclic Aromatic Hydrocarbon; Contamination; Industrial Activities.

INTRODUCTION

Pollution levels in aquatic ecosystems are increasing rapidly due to the presence of human activities, such as residue discharges, industrial and commercial processes, and navigation activities (Lewis *et al.*, 2011). As a result, toxic compounds have been released into the ecosystem, leading to water and sediment contamination and, lastly, pollution transference through the trophic chain in such areas (Loureiro and Hepp, 2020).

Organic compounds such as Polycyclic Aromatic Hydrocarbons (PAH) are globally dispersed environmental pollutants (Slezakova *et al.*, 2013; Nakata *et al.*, 2014). The origin of these compounds in the coastal aquatic ecosystems can be pyrolytic (thermal decomposition of organic materials at elevated temperatures), petrogenic (associated with petroleum products or sources), or diagenetic (direct extrusion of the earth's crust) (Souza *et al.*, 2015). They may enter the marine environment through several ways, including atmospheric deposition, surface water and runoff, domestic and industrial outfalls, and direct spillage of petroleum or petroleum products (Maioli *et al.*, 2010). As a result of the rapid spread of PAH contamination, the study of these hazard compounds in the various ecosystems has been increased during the last 50 years (Maioli *et al.*, 2010).

PAHs are classified as toxic compounds with the potential to cause carcinogenic and mutagenic effects on biota (Rengarajan *et al.*, 2015; Devi *et al.*, 2016). These compounds are divided into two groups based on their weight: low (LMW) and high molecular weights (HMW). Although the first group is less carcinogenic than the second, it still offers toxic risks to many aquatic organisms (Brown and Peake, 2006). On the other hand, the HMW PAHs are more recalcitrant, presenting greater persistence in an aqueous ecosystem and thus tending to bioaccumulate in aquatic organisms such as fish and shrimp (Rocher *et al.*, 2004).

Due to the compounds hydrophobic character and resulting tendency to associate with suspended particles, PAHs can be incorporated by aquatic filtering organisms and concentrated in their fatty tissues (Olayinka *et al.*, 2019). In this sense, bivalve mollusks have been extensively used as sentinel organisms of pollution, mainly polycyclic aromatic hydrocarbons and other compounds (Baumard *et al.*, 1998a).

Therefore, it is fundamental to evaluate the processes that govern the behavior of these contaminants in aquatic systems to establish their potential toxic effects on water and biota. Previous studies have suggested that the PAHs' transference and fate patterns are strongly influenced by the circulation dynamics of inflowing particles in estuarine systems (McGroddy and Farrington, 1995; McGroddy *et al.*, 1996; Countway *et al.*, 2003; Shilla, 2011; Allan *et al.*, 2016;

Rügner *et al.*, 2019). Once inside the aquatic environment, hydrocarbons present a tendency to adsorb to particulate matter due to their hydrophobic nature and decant, accumulating in the bottom sediments (Tam *et al.*, 2001; Nogami *et al.*, 2002), which are globally considered potential reservoirs for such contaminants (Maioli *et al.*, 2010).

There is limited information regarding the current petroleum distribution and sources in the sediments and biota of the Santos Estuarine System (SES). The scarcity of studies related to tropical developing countries' coastal ecosystems, in general, is one of the incentives for the present research. In this context, this study aims to determine the distribution of the Polycyclic Aromatic Hydrocarbons (PAH) between the sediment/biological interface and the main influencing parameters involved in the contaminant pool's distribution in SES.

Study area

Santos Bay is situated in Brazil, in the central coastal area of southeastern São Paulo State (**Figure 1**), representing one of the most metropolitan and economically important areas in South America. The riverine and estuarine systems in this area have been severely contaminated since the 1950s (Martins *et al.*, 2011) when the activities of the largest industrial complex in Latin America were initiated around the city of Cubatão. Nowadays, this area represents one of the most industrialized sites in Brazil (Perina *et al.*, 2018). Additionally, as a consequence of intensive harbor activities, huge amounts of polluted sediment have been historically dredged up and discarded in the adjacent marine area (Lamparelli *et al.*, 2001; Torres *et al.*, 2009).

Still, the region comprises the main tourist coastal area of São Paulo State (Muto *et al.*, 2014). The main beaches in the cities of São Vicente and Santos are major tourist spots during the summer (Braga *et al.*, 2000). Lastly, marine and estuarine fisheries represent another important economic activity. Due to its economic and ecological importance and the environmental pollution in the area, Santos Bay has been intensely studied (Hortellani *et al.*, 2008).

MATERIAL AND METHODS

Salinity is the predominant parameter impacting the PAH partition between aqueous and solid phases in freshwater, estuaries, and seawater (Cloern *et al.*, 2017) since it influences PAHs' adsorption behavior, changing the solubility of the compounds and the physicochemical properties of sediments (Wang *et al.*, 2014). On the other hand, environmental factors such as salinity can influence the toxic element depuration capacity of bivalves (El-Gamal, 2011). Therefore, the

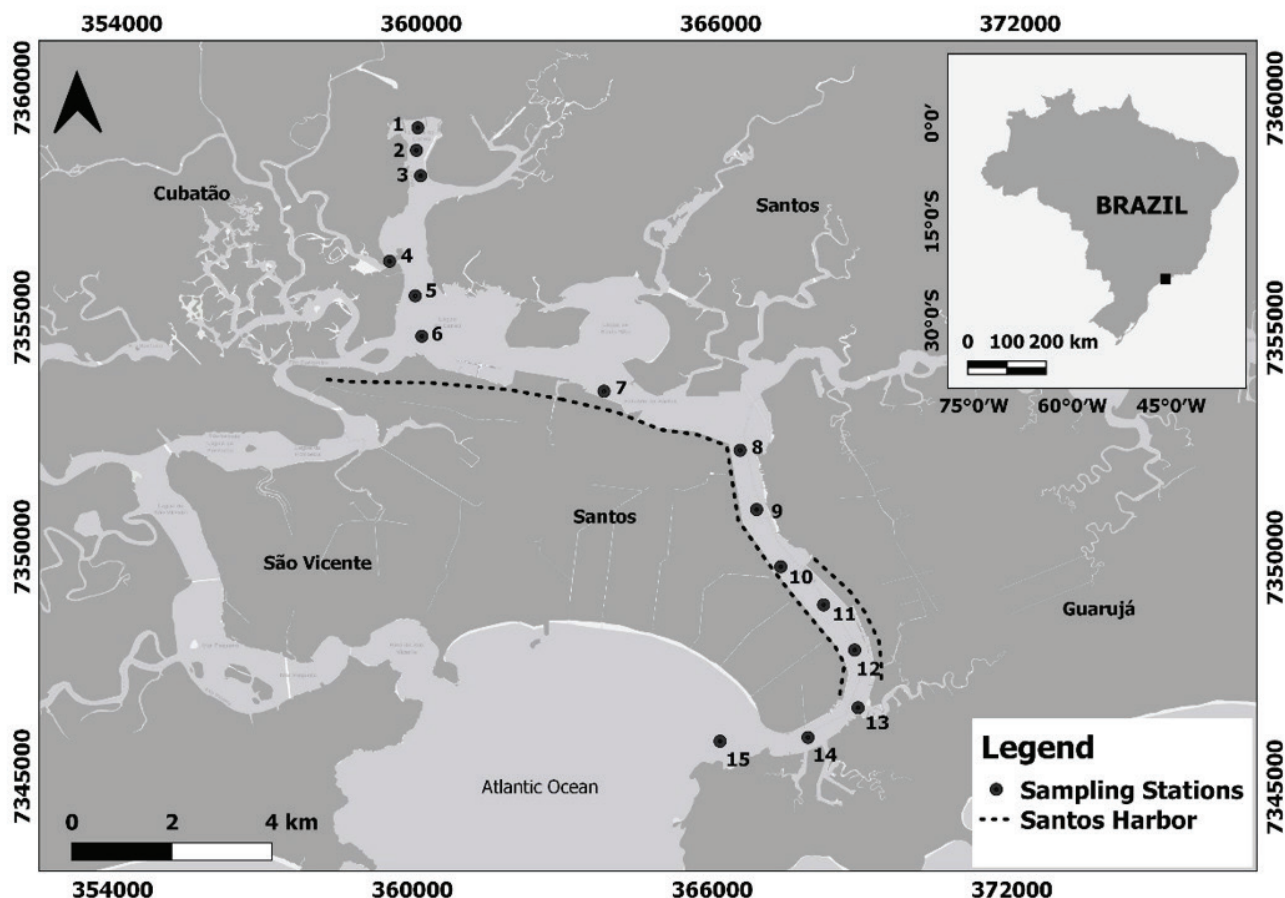


Figure 1. Santos estuarine complex and sampling stations

salinity data analyzed in this study were collected during a field campaign in September 2019. Salinity was evaluated at 15 sampling spots using a multiparameter Horiba U10 probe (Figure 1). Physico-chemical measurements were made at surface and bottom water depths during the ebb and flow tides. Past monitoring data were added to increase the accuracy of the physical analysis results; two other groups of data corresponding to measurements in January and March of the same year were used.

Sediment and bivalve specimens were sampled in the same spots. Sediment samples were collected at each site using a Van Veen grab to determine the sediment grain size, Total Organic Carbon (TOC) levels, and Polycyclic Aromatic Hydrocarbons (PAH) concentrations.

One gram of homogenized sediment samples was acidified with 0.1 mol L⁻¹ HCl solution to remove carbonates, rinsed with deionized water, and dried at 60 °C before determining the total organic carbon (TOC). TOC was evaluated through the utilization of an elemental analyzer (Carlo Erba EA 1110, Wigan, Reino Unido). On the other hand, the grain size was analyzed using the sieving method described by Suguio (1973).

In the case of the bivalve samples, 10 g of bivalve tissue (wet weight) was treated with 30 g of sodium anhydrous sulfate, with the resulting mixture blended at high speed for five minutes. The resulting matrix was extracted with a Soxhlet extractor with 200 ml of methanol for eight hours (UNEP/IOC/IAEA, 1981). After that, 0.7 M KOH (20 ml) and distilled water (30 ml) were inserted into the flask and the reflux continued for two hours to saponify the lipids. The content of the extraction flask was extracted in a separatory funnel with 80 ml/3 hexane combined, finally dried with Na₂SO₄, and filtered through glass wool. The hexane fraction was concentrated with a rotary evaporator down to approximately 15 ml at 30 °C, followed by a concentration with a nitrogen gas stream down to a 1 ml volume.

A standard PAH mixture contained acenaphthene, acenaphthylene, anthracene, benz[a]anthracene, benz[a]pyrene, benz[b]fluoranthene, benz[g,h,i]perylene, benz[k]fluoranthene, chrysene, dibenz[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3,cd]pyrene, naphthalene, phenanthrene, and pyrene, each one at 2.0 mg mL⁻¹ in dichloromethane: benzene, was obtained from AccuStandard (New Haven, CT, USA).

In order to investigate the presence and distribution of PAH in sediment samples, 5 g of sediments were extracted in triplicate through ultrasonication for 30 min into 15 mL of a mixture of dichloromethane:methanol (2:1).

The PAH was analyzed by GC-MS using Helium as the carrier gas. Quality assurance procedures included analytical curves for the quantification of PAH in the sediment samples.

A Spearman correlation test was applied using SPSS Statistics 17.0 to evaluate the potential relationship between sediment matrixes and PAH levels in sediment and bivalve samples. Posteriorly, PAH's diagnostic ratios were a tool to identify and assess pollution emission sources.

The transfer factor (BAF) in biota tissues from the aquatic ecosystem, including water and sediments, was calculated according to Kalfakour and Akrida-Demertzi (2000) and Rashed (2001) as follows:

$$BAF = \frac{\text{PAH concentration in aquatic animal}}{\text{PAH concentration in sediment}}$$

Lastly, to investigate the potential adverse health effects risk resulting from the ingestion of the bivalve tissues by local community, the PAH4 sum was calculated through the summation of benz[a]anthracene, chrysene, benz[b]fluoranthene, and benz[a]pyrene (Tongo *et al.*, 2018). Then, the obtained results in the organisms' samples were compared with regulatory limits to evaluate the possible risk of bivalve consumption.

RESULTS AND DISCUSSION

Due to the typical salinity gradients, estuaries act as biogeochemical receptors, trapping a fraction of the continental material, especially suspended particles containing anthropogenic organic substances such as PAH (Chen *et al.*, 2020). As a result, estuarine ecosystems tend to accumulate PAH in the sediment to a level greater than nearby ecosystems (Chizhova *et al.*, 2020). In the present study, the increase in salinity values toward the sea became clear, and the stratification of the water column suggests the significant influence of marine waters within the estuarine system. Ocean water's influence on deeper strata became evident even in the interior (Figure 2).

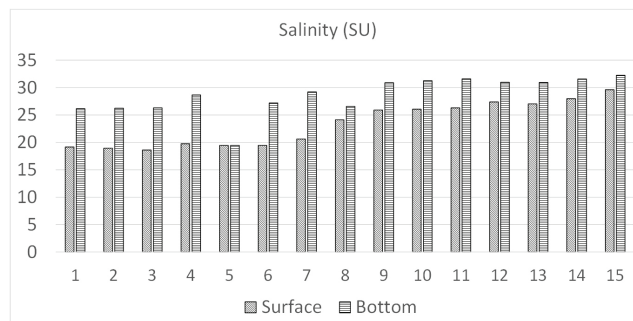


Figure 2. Salinity values recorded in Santos Estuarine System

The grain size distribution varied significantly between sampling stations, with the silt fraction predominantly located in the innermost region of the estuarine system. The sandy fraction, in turn, became more represented in the outermost sampling stations located in the Santos channel (Figure 3). Clay, silt, and sand fractions varied between 5.17 and 34.34%, 4.64 and 84.05%, and 6.43 and 87.25%, respectively. Then, in general, except for the stations located in the outermost sector, the sampling area appears to be a depositional environment, with a predominance of silt and clay fractions. Dredging activities along the Santos channel may be responsible for the sandy character of the sediments in this area. Sousa *et al.* (2007) reported very similar results in the same area.

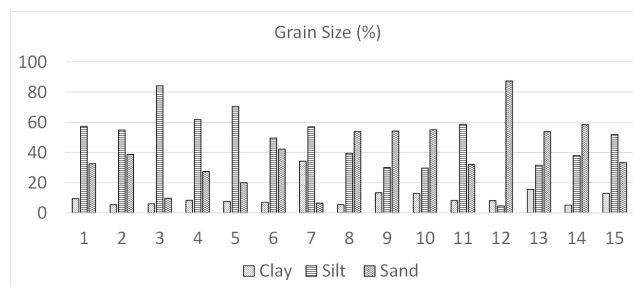


Figure 3. Grain Size results along the Santos Estuarine System

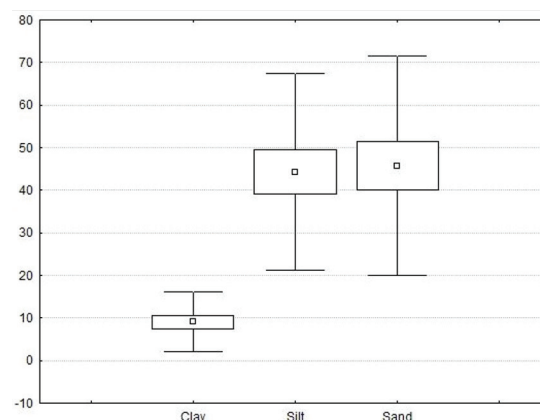


Figure 4. Grain Size descriptive statistics

TOC levels represent the part of organic matter that did not complete the remineralization process during decantation. This parameter is impacted by biomass initial production and the subsequent degradation degree. The Total Organic Carbon (TOC) percentages, which are an essential proxy for describing the abundance of organic matter in sediments (Barcellos *et al.*, 2018), ranged from 0.74% (station 14) to 5.06% (station 15). Regarding TOC percentage results, they agree with studies previously reported for the same region (between 0.9 and 8.6%) (Perina *et al.*, 2018).

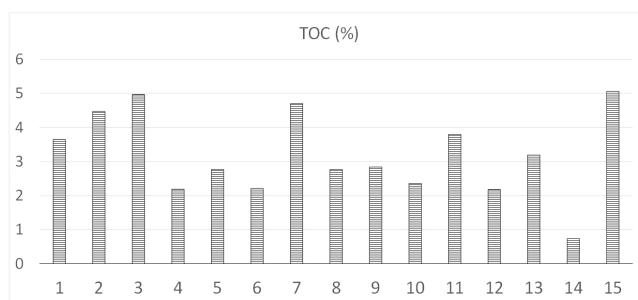


Figure 5. Total Organic Carbon percentages

The total PAH levels in sediments expressed as the sum of the 16 priority compounds ranged from N.D. (Not Detected) to 1,711.79 ng g⁻¹ d.w. (Figure 5). The highest concentrations were observed at stations 1, 2, and 3, located in the estuarine innermost sampling stations, with total PAH levels higher than 500 ng.g⁻¹. According to some authors (Notar *et al.*, 2001), concentrations higher than 500ng g⁻¹ can classify the area as relatively highly contaminated. Baumard *et al.* (1998b) suggested another PAH classification pattern to characterize sediment quality in terms of the contamination level as low, moderate, high, or very high (0-100, 100-1000, 1000-5000, and > 5000 ng.g⁻¹, respectively). Regarding this classification and based on the 16 PAH summary, the contamination level of stations 7 to 15 can be classified as low, station 5 as moderate, and stations 1 to 3 as high. According to this study, port activities no longer represent the largest source of hydrocarbons in the area.

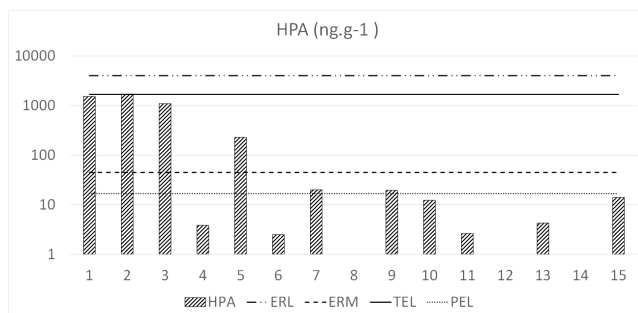


Figure 6. PAH total concentrations in the SES sediments

By comparing PAH levels to grain size and COT percentage results, the direct influence of the sediment features on the contaminant concentrations can be pointed out. Apparently, the higher fine sediment content and the greater organic matter percentages are turning those sampling stations into effective pollution deposits. The Spearman test did not confirm this hypothesis, since the correlations did not show high significance (Table 1). Another explanation may be the proximity to the potential contaminant sources. The sampling stations with high hydrocarbon concentrations were found in the vicinity of the contributing basin. Therefore, the present records suggest that the PAH accumulation in the study area is related to the source proximity rather than to grain size or organic matter levels. This hypothesis is supported by the positive correlation between sediment and bivalve HPA concentrations (Table 1).

Table 1. Spearman test results

	HPA organism	HPA sediment	Fine grain	Surface Water Salinity	Bottom Water Salinity	Organic Matter
HPA organism	1					
HPA sediment	0,556	1				
Fine grain	0,383	0,315	1			
Surface Water Salinity	-0,509	-0,573	-0,611	1		
Bottom Water Salinity	-0,455	-0,607	-0,399	0,896	1	
Organic Matter	0,192	0,459	0,617	-0,222	-0,170	1

Another way to evaluate PAH concentrations in sediments is to compare them to the international sediment quality guidelines (SQGs), which is a useful approach to assess the pollution in marine and estuarine sediments (McDonald *et al.*, 2000). In this research, two quality guidelines (the effects range-low value (ERL), effects range-median value (ERM), the probable effects level (PEL), and the threshold effects level (TEL) values) were applied to assess the potential PAH ecotoxicological risks existent in SES (Figure 7). Results of this study suggested that adverse effects on the local benthic communities are expected to occur in the innermost area of the estuarine system (Figures 5, 6, and 7). The probable effect level (PEL) and the effect range-median (ERM) were exceeded at the innermost points of the estuary (sampling stations 1, 2, 3, and 5) (Figure 5). The evaluation of the priority PAH detected a similar pattern (Figures 6 and 7).

A comparison of the total PAH concentrations in the Santos Estuarine System with other estuarine and coastal environments along the Brazilian coast and worldwide can be found in Table 2. Exposed data suggests that the PAH concentrations obtained in this study are lower than those reported for the same estuary, as recorded by Martins *et al.* (2011). The present paper also presented values lower than the other estuaries along the Brazilian coast, except for the Itajaí-Açu estuarine system and the Patos Lagoon, both environments in southern Brazil. Con-

cerning other areas around the globe, the values found in the literature were extremely variable, making it difficult to establish comparative standards with the present study (Table 2).

As previously mentioned, there are three main PAH sources in estuaries: pyrolytic, petrogenic, and natural sources (Yunker *et al.*, 2002). The PAH compound profile is caused by the reactions during PAH production (Manoli *et al.*, 2004). As a result of low temperature processes, such as wood burning, low molecular weight PAHs are normally produced. Moreover, at high temperatures, higher molecular weight PAH compounds are released (Mostert *et al.*, 2010). Several ratios have been proposed as an approach to identify potential sources of PAH in marine sediments. Table 3 presents the PAH ratios applied to evaluate the sediment.

Ratios between low and high molecular weight PAH and those from their specific isomers have often been used to identify sources, such as petrogenic or pyrolytic (Tobiszewski and Namieśnik (2012). According to Zhang *et al.* (2008), results derived from the ratio of Low Molecu-

lar Weight (LMW) / High Molecular Weight (HMW) under one suggest pyrogenic origin. Values over one, in turn, indicate petrogenic sources (Soclo *et al.*, 2000) (Table 3). In this study, most results indicated petrogenic sources (Figure 10).

With the aim of decreasing the influence of particular compound characteristics (for example, differences in volatility, water solubility, and adsorption), the ratio between isomer pairs, such as phenanthrene and anthracene (Pies *et al.*, 2008) and fluoranthene and pyrene, can be applied (De La Torre-Roche *et al.*, 2009).

In the particular case of anthracene to phenanthrene (Ant/Phe + Ant) ratio, values under 0.10 normally indicate petrogenic sources. Values over 0.10, on the other hand, suggest a pyrolytic origin (Pies *et al.*, 2008). Although the (Ant/Phe + Ant) ratio could not be calculated for most stations due to the absence of one or both compounds, all stations where the ratio application was possible presented values over 0.10, suggesting pyrolytic sources as opposed to the first applied ratio.

Table 2. Polycyclic Aromatic Hydrocarbons along Brazilian coast and around the world

Area	PAH levels (ng/g)	Authors
Santos Estuarine System, Brazil	N.D. - 1711.79	Present study
Santos Estuarine System, Brazil	60 - 8680	Martins <i>et al.</i> , 2011
Todos os Santos Bay - Brazil	6.9 - 2226	Wagener <i>et al.</i> , 2010
Todos os Santos Bay - Brazil	8.29 - 4163	Venturini <i>et al.</i> , 2008
Guanabara Bay - Brazil	96 - 135000	Wagener <i>et al.</i> , 2012
Itajaí-Açu estuarine system, Brazil	63.9 - 1459.0	Frena <i>et al.</i> , 2016
Mundaú-Manguaba estuarine-lagoon system and Paraíba do Sul River, Brazil	2.9 - 9344.3	Maioli <i>et al.</i> , 2010
Patos Lagoon, Brazil	7.3 - 92.8	Sanches Filho <i>et al.</i> , 2012
Mediterranean Sea	3.40 - 14100	Barakat <i>et al.</i> , 2011
Santander Bay - Spain	20 - 25800	Viguri <i>et al.</i> , 2002
Daya Bay - China	42 - 158	Yan <i>et al.</i> , 2009
Kaohsiung Harbor - Taiwan	1460 - 15,743	Chen <i>et al.</i> , 2011
Estuary Yangtze - China	107 - 663	Hui <i>et al.</i> , 2008
Arabian Gulf - Qatar	2.6 - 1025.6	Soliman <i>et al.</i> , 2014
Hadhramount - Yemen	2.1 - 199	Mostafa <i>et al.</i> , 2009

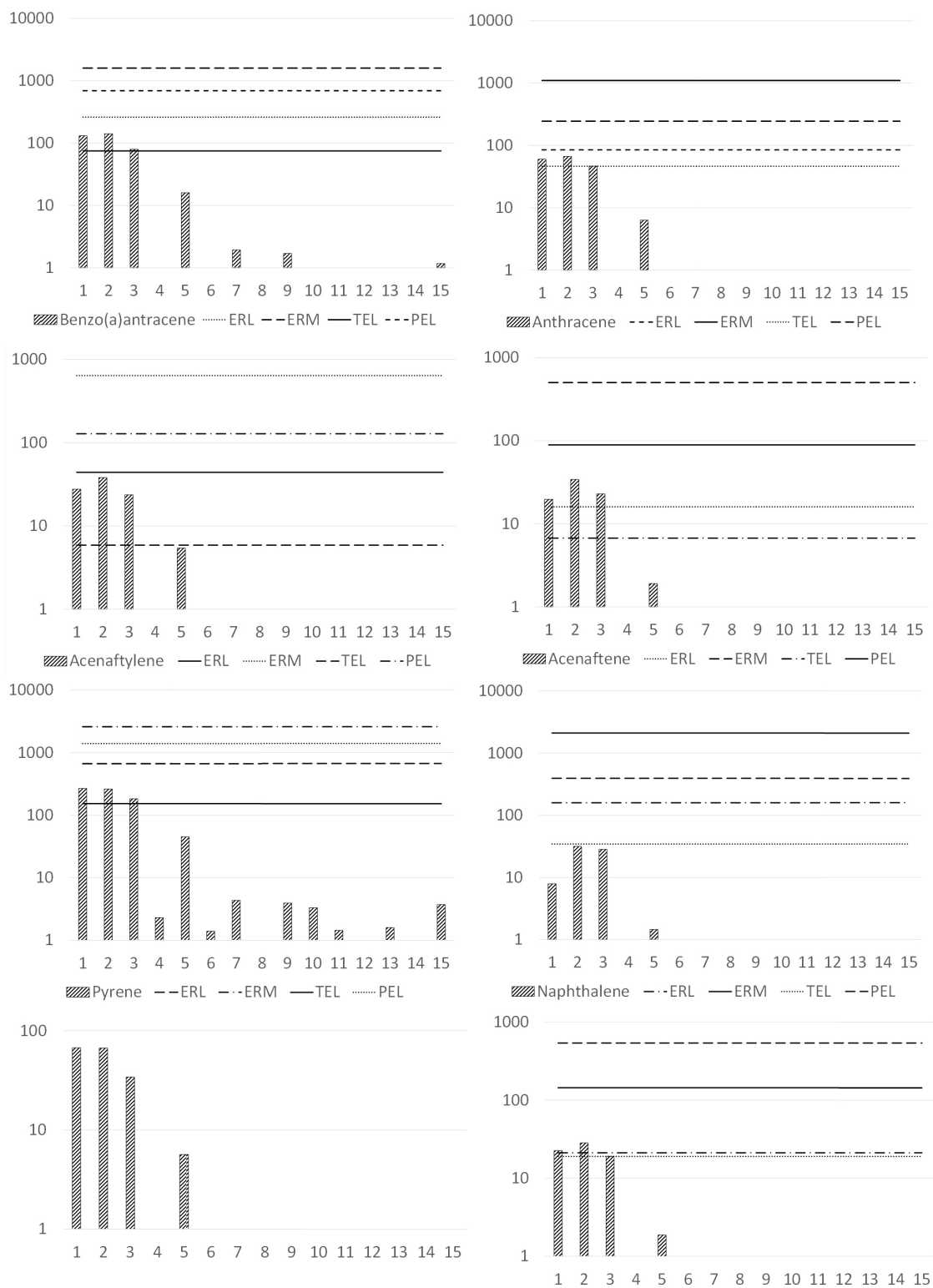


Figure 7. Eight PAH priority compound values recorded in ESSE sediments (ng/g) (Benzo(a) anthracene, Anthracene, Acenaftylene, Acenaftene, Pyrene, Naphthalene, Indene(1,2,3-cd)pyrene, and Fluorene)

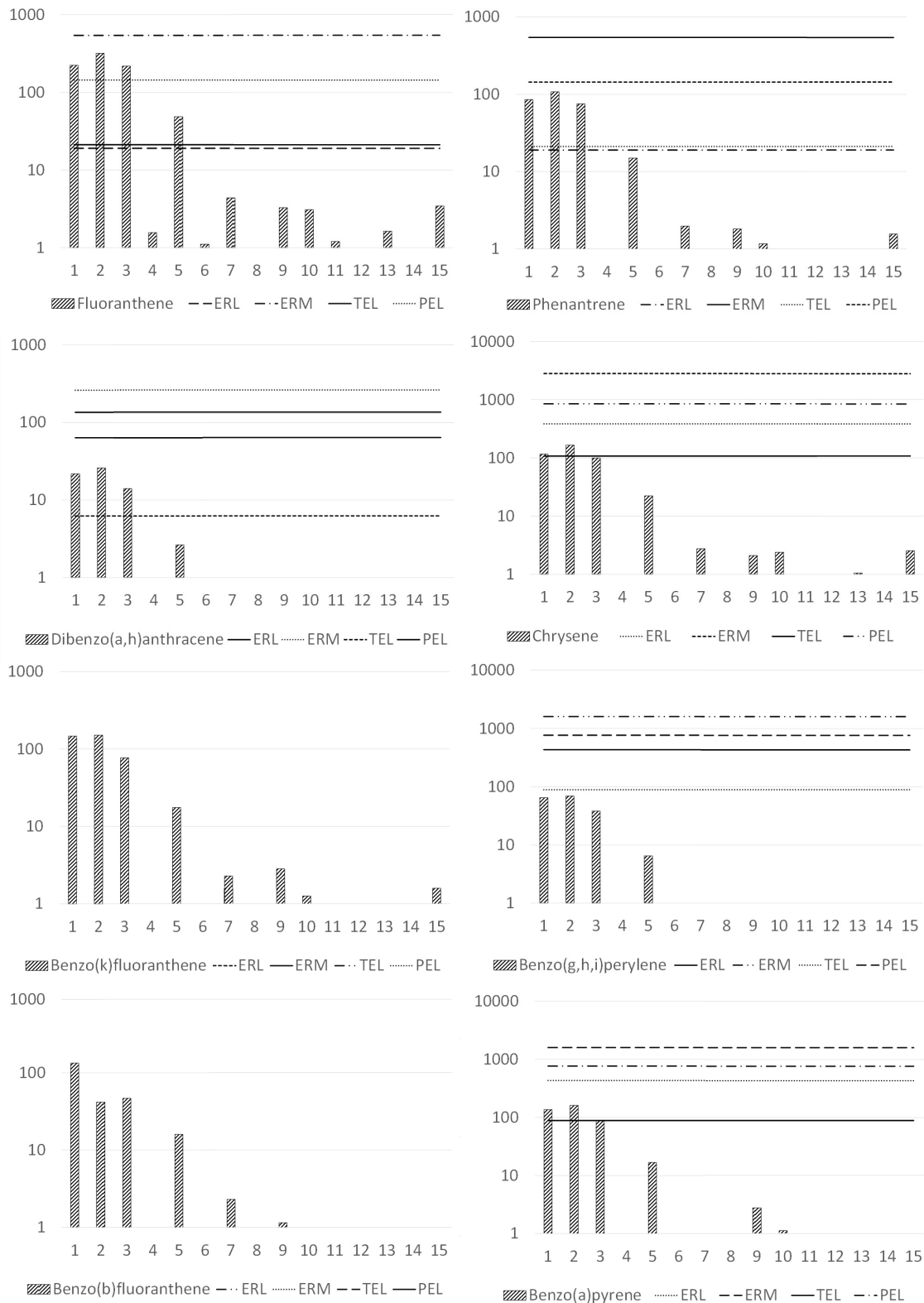


Figure 8. Eight PAH priority compound values recorded in ESSE sediments (ng/g) (Fluoranthene, Phenanthrene, Dibenzo(a,h)anthracene, Chrysene, Benzo(k)fluoranthene, Benzo(g,h,i)perylene, Benzo(b)perylene, and Benzo(a)pyrene)

Table 3. PAH's diagnostic ratios used applied to evaluate the sediment

PAH ratio	Value range	Source	Reference
$\sum \text{LMW} / \sum \text{HMW}$	< 1 > 1	Pyrogenic Petrogenic	Zhang et al., 2008
$\frac{\text{Anthracene}}{\text{Anthracene} + \text{Phenanthrene}}$	< 0.1	Petrogenic	Pies et al., 2008
	> 0.1	Pyrogenic	
$\frac{\text{Fluoranthene}}{\text{Fluoranthene} + \text{Pyrene}}$	< 0.4	Petrogenic	De La Torre-Roche et al., 2009
	0.4 - 0.5	Fossil fuel combustion	
	> 0.5	Grass, wood, coal combustion	

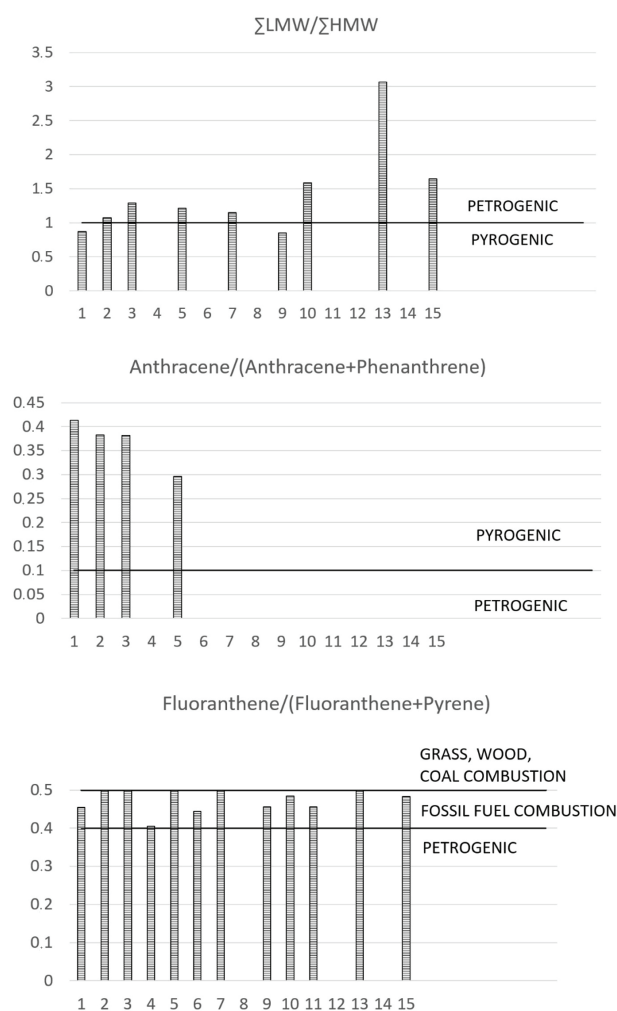


Figure 9. HPA's Ratios

The third used ratio in this study was fluoranthene to fluoranthene plus pyrene (Fluo/Fluo + Pyr). According to De La Torre-Roche *et al.* (2009), values greater than 0.5 suggest grass, wood, or coal combustion. Values under 0.4 indicate

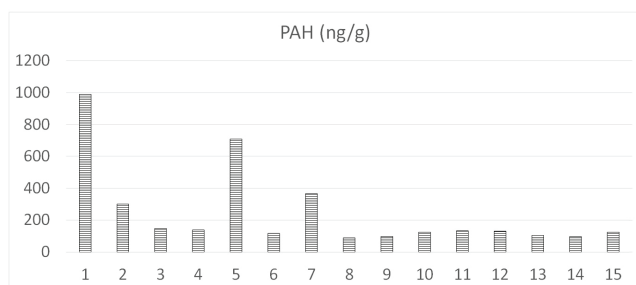
petrogenic sources. Finally, ratio results between 0.4 and 0.5 are suggestive of liquid fossil fuel combustion. As shown in **Figure 10**, the results for this ratio were between 0.4 and 0.5 at all stations, suggesting that the PAH sources in the present study area are mainly from liquid fossil fuel combustion, reinforcing the Fluo/Fluo + Pyr ratio results. The fact that contradictory results were achieved with different diagnostic ratios does not indicate that the results are wrong, once light PAHs are released from different sources compared to heavy ones (Tobiszewski and Namiesnik, 2012). According to Martis *et al.* (2011), the isomer pair ratios applied in the same estuary showed that PAHs derive primarily from combustion and not petroleum. Conversely, the same authors concluded that the hydrocarbon sources varied along with the area's historic evolution.

Marine biota can incorporate hydrocarbons from sub-aquatic sediments and suspended particulate material into the water column and food sources (De Mora *et al.*, 2010). Organism assimilation capacity depends not exclusively on the presence of pollutant compounds but also on several physiologic and environmental parameters (filtration rate, metabolism, water column physic-chemistry, etc.) (Neff, 2002; Hussein *et al.*, 2016). Thus, biomonitoring represents an effective approach to contamination evaluation. In this study, two mollusk species (*Perna perna* and *Crassostrea rhizophorae*) were used to evaluate PAH presence and bioavailability. This approach implies that the quantitative comparison between the sampling stations is limited due to physiological differences between both species. The PAH assimilation dynamics are influenced by the hydrophobic character of these compounds. Its tendency to associate with other floating particles present in the water column favors their accumulation in floating particles and the lipid tissue of organisms (Rubio-Clemente *et al.* 2014). As mussels are less selective in their filtration process, they would be more prone to assimilating polycyclic aromatic hydrocarbons (Kehrig *et al.*, 2006). Even so, the results were important since the presence of PAH was detected in both species at all sampling

stations, suggesting PAH's bioavailability in the water column. The PAH accumulation values ranged between 88.38 and 133.62 ng.g^{-1} in oysters, and between 97.68 and 988.76 ng.g^{-1} in mussels, presenting relatively concordant levels compared to the available literature (Table 4).

Table 4. Total PAHs in bivalves reported by other studies around the world.

Bivalve species	Total PAH (d.w.)	Reference
<i>Crassostrea rhizophorae</i>	88.38 – 133.62 ng.g^{-1}	Present Study
<i>Perna perna</i>	97.68 – 988.76 ng.g^{-1}	Present Study
<i>Crassostrea sp</i>	300 – 1400 ($\mu\text{g.kg}^{-1}$)	Cortazar et al., 2008
<i>Saccostrea cucullata</i>	6,600 (ng.g^{-1})	Tolosa et al., 2005
<i>Barbatia helblingii</i>	129.5 – 634.7 (ng.g^{-1})	Safahieh et al., 2011
<i>Arca senilis</i>	3.0-16.0 (ng.g^{-1})	Moslen et al., 2019
<i>Crassostrea brasiliiana</i>	671.0 – 1928.7 (ng.g^{-1})	Fontenelle et al., 2019



Values of BAF are shown in Figure 12. The Calculated Bioaccumulation Factors (BAF) ranged between 0.0 and 50.5. Results obtained by Shilla and Routh (2018) found similar values ranging between 0.20 and 69.5, considered low by the authors. Hence, additional comparative studies, whereby PAH levels in animals, sediments, and SPM samples from the same sites need to be correlated and compared with other sites in the Santos estuarine system throughout the year to confirm this hypothesis.

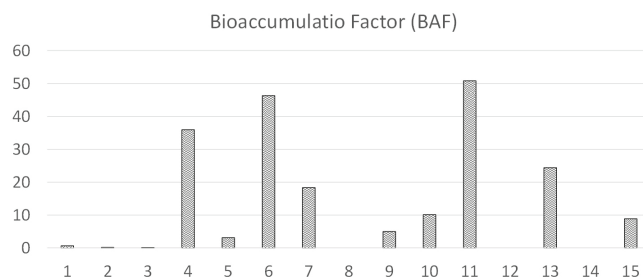


Figure 11. BAF results obtained for SES

The sum of PAH4 was demonstrated graphically in Figure 13. The d.w. concentration data were converted into wet weight and compared to the limit values established by international regulatory agencies. This conversion was made by dividing the value obtained in d.w. by 6.8, which

is the indicated for the species *Crassostrea* (Wright et al., 1985). PAH4 varied from 4.9 ng.Kg^{-1} to 58.12 ng.Kg^{-1} . Values reached in this study were inferior to those from the EU regulatory limits of maximum levels of 30 $\mu\text{g.Kg}^{-1}$ (Commission Regulation-EU / No. 835/2011).

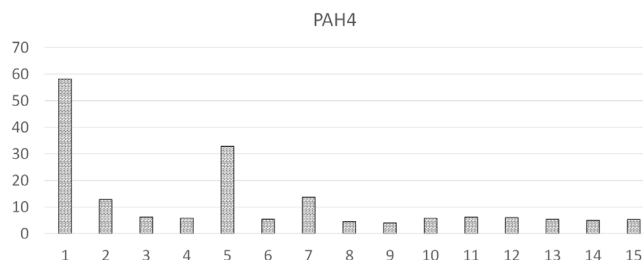


Figure 12. BAF results obtained for SES

CONCLUSIONS

The present research provided data on the polycyclic aromatic hydrocarbon concentrations in the surface sediments and bivalves of the Santos Estuarine System. The recorded data suggested that the innermost region was the most contaminated by HPAs and was classified as highly contaminated. According to this paper, port activities no longer represent the largest source of hydrocarbons in the area.

The SQG values available in the literature suggest that adverse biological effects on the living biota are expected to occur occasionally. On the other hand, the Bioaccumulation Factor calculated results did not replicate the pollution transference to the local biota.

The calculated PAH ratios characterized the sediment PAH levels as composed of a mixture of petrogenic and pyrolytic sources. Results obtained in this study represent a useful data collection related to hydrocarbon concentrations, sources, and bio-assimilation dynamics in the Santos Estuarine System, which represents a significant economic area in Brazil. Local environmental management is fundamental to maintaining the ecosystem's health, and periodic biotic and abiotic monitoring is essential for the government's decision-making processes.

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