CUANTIFICACIÓN DE HAPs, FACTORES DE BIOACUMULACIÓN Y BIOTA-SEDIMENTO EN LAGUNA ADYACENTE A UN ÁREA DE PROTECCIÓN DE FLORA Y FAUNA

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Resumen

Se cuantificaron Hidrocarburos Aromáticos Policíclicos (HAPs) en sedimentos y peces comestibles (*Megalops atlanticus*) de la laguna Caleta (Laguna de Términos, México) para evaluar la toxicidad y factores de bioacumulación (BAF) y bioacumulación biota-sedimento (BSAF). Se colocaron un total de 15 estaciones de muestreo dividido en tres estratos (zona I, II y III) a lo largo de la laguna de Caleta. La parte intermedia (zona II) mostró mayor concentración de HAPs de 223.96 ng g^{-1} peso seco, mientras que las zonas I y III mostraron HAPs de alto peso molecular (HMW) (629.6 ng g^{-1} peso seco y 319.12 ng g^{-1} peso seco, respectivamente), lo que sugiere fuente petrogénica y pirolítica. La alta concentración de HAP de bajo peso molecular (LHW) (190.3 ng g^{-1} peso seco) en el tejido de los peces indica una mayor disponibilidad en la columna de agua. Los valores del cociente TEQ_{BaP}, MEQ_{BaP} y ERM mostraron un sedimento con baja probabilidad de ser tóxico. Mientras que los valores de BAF y BSAF sugieren una alta biodisponibilidad de HAPs de las zonas de intercambio entre el océano y las aguas residuales urbanas; contribuyendo los derrames accidentales, descarga de aguas residuales y quema de combustible por vehículos.

Palabras clave: Hidrocarburos aromáticos policíclicos, calidad de sedimentos, cociente de equivalencia tóxica, factor de bioacumulación, factor de acumulación biota-sedimento.

QUANTIFICATION OF PAHS, FACTORS OF BIOACCUMULATION AND BIOTA-SEDIMENT IN LAGOON ADJACENT TO A FLORA AND FAUNA PROTECTION AREA

Abstract

PAHs in sediment and edible fish (*Megalops atlanticus*) from Caleta lagoon (Lagoon of Terminos, Mexico) were quantified to evaluate the toxicity and bioaccumulation BSAF and biota-sediment BAF. A total of 15 sampling stations were placed in three strata (zone I, II and III) along the Caleta lagoon. The intermediate part (zone II) showed higher concentration PAHs (LMW) of 223.96 ng g^{-1} dw, while zone I and III showed PAHs-HMW (629.6 ng g^{-1} dw and 319.12 ng g^{-1} dw, respectively), suggesting petrogenic and pyrolytic source. The high

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PAHs concentration of LHW (190.3 ng g^{-1} dwt) in fish tissue indicates a greater availability from the water column. The TEQ_{BaP}, MEQ_{BaP}, and $ERM_{quotient}$ values showed a sediment with low probability of toxic. While the BAF and BSAF values suggest a high bioavailability of PAHs from the exchange zones between the ocean and urban wastewater; contributing accidental spills, wastewater discharge and fuel burning by vehicles.
Keywords: Polycyclic aromatic hydrocarbons, sediment quality, toxic equivalence quotient, bioaccumulation factor, biota-sediment accumulation factor.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one of the major organic pollutants found in the environment. A number of PAHs are classified as mutagenic and carcinogenic, therefore, a prolonged exposure of PAHs causes effects such as skin cancer, lungs, and bladder in humans (Li et al. 2016). The PAHs have high hydrophobicity and therefore can be strongly absorbed into organic matter or fine particles, which are eventually deposited at the bottom of the sediment, increasing their concentration because they are resistant to microbial degradation. Many of these compounds deposited in the sediment are transferred to benthic organisms causing a risk to ecosystems and human health. This results in a long-term threat in those ecosystems that contain PAHs due to the effects of bioaccumulation and biomagnification when entering the food chain (Tu et al. 2018). Therefore studies have focused on determining the distribution of PAHs in the environment and the probable ecological risk and human health (Zhang et al. 2016). Methodologies have been implemented to evaluate the possible impacts on ecosystems and some are based on the study of the origin and source of PAHs according to the analysis of the rate of certain PAHs in aquatic sediments (Yunker et al. 2002; Qiao et al. 2016; Franco et al. 2017). Others are based according to the one established by the National Oceanic and Atmpospheric Administration (NOAA) evaluating the effects range-low (ERL) and effects range-median (ERM) in aquatic sediments and evaluate the adverse biological effects of PAHs (MacDonald et al. 2000; Long 2006). The impacts of PAHs on an ecological system can also be evaluated using toxic equivalence quotient (TEQ) of potentially carcinogenic PAHs mixture. TEQ is an aggregate measure of toxicity based on each chemical compound sharing a common mechanism of action. Each contributing PAHs is assigned a weighting factor, the toxic equivalency factor (TEF) relative to the most toxic component benzo (a) pyrene. Similarly, the sediment quality guidelines (SQGs) have been development for sediments quality evaluation. SQGs have been used for historical data interpretation, sediment quality assessments, monitoring programs design and sediment quality remediation objectives development, quality of prospective dredged materials assessment, and remedial investigations and ecological risk assessments (Tu el al. 2018). Generally, the evaluation methods available and commonly used in monitoring programs have as main objective to determine the total concentration of PAHs, however they do not consider or estimate the influence of PAHs on the biota. PAHs effects on fish can be observed by some pathologies in the liver and gills and bioaccumulate in muscle tissue. PAHs bioaccumulation occurs when PAHs are present in water and sediments and are driven by lipid content of organisms (Froehner et al. 2018). Bioaccumulation can be assessed by methods that directly

measure or predict it through mathematical models based on lipid content in the organisms and compounds properties (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. The extension of accumulation in lakes or estuaries is determined by the bioaccumulation factor (BAF) and the biota-sediment bioaccumulation factor (BSAF) models (Jiao et al. 2014; Guzzella et al. 2005). In the present study, the content and distribution of PAHs in sediment and fish (muscle) from a lagoon adjacent to the Lagoon de Terminos Protected Natural Area were examined to understand the possible side effect, such as bioaccumulation and to evaluate the extent of bioaccumulation using BSAF models and BAF deterministic models.

Materials and methods

Study area, sampling and chemical analysis

The study area, Caleta lagoon is located at the western extreme of Isla of Carmen, it measures 7 km long, and average depth of 1.5 m. The system has an area of 140 000 m^2 and a volume of 210 000 m^3, that communicates at the west with Terminos lagoon and the ocean (**Figure 1**). Oil companies, fisheries and urban development's surround this area discharge 613 260 m^3 of wastewater every year, affecting negatively the ecosystem (Ruiz-Marin et al. 2014). A common practice is the fishing of Atlantic tarpon *(Megalops atlanticus)* from Caleta lagoon and marketed for local consumption. Therefore, it is important to evaluate concentrations of PAHs in sediment and fish (muscle) to evaluate the extension of bioaccumulation.

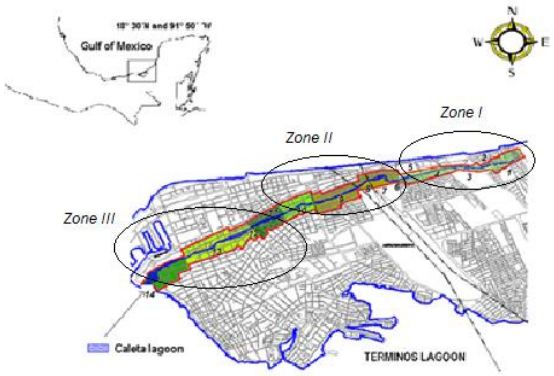

Figure 1. Location of the study area and strata (zone I, II, III) within Caleta lagoon

A total of 15 sampling stations were placed in three strata (zone I, II and III) along the Caleta lagoon (5 sampling stations each zone). For each station 5 cm of surface sediment was collected in triplicate with a Van Veen dredge. The samples of sediment were dried in drying oven at 40±5 °C for 48 h or until completed dried, homogenized and divides in triplicated of 20 g (Salgado et al. 2019). Dry sediment was homogenized and sieved by 250 μm mesh size sieve and stored until extraction. The procedure for sediment sample processing has been described by Canedo-Lopez et al. (2020). Internal standards (3,6-dimethylphenanthrene and 2,2'-binaphthylene) were added to samples prior to instrumental analysis. Fishes were caught with cast net. The species was grouped into size groups according to length, weight and lipid percent of the individuals. The tissue extraction method for the identification of

PAHs compounds was as described by El-Deeb et al. (2007).

The PAHs analysis was performed by a gas chromatographer (Agilent Technology, model 7890) equipped with a flame ionization detector, and a 30 m x 0.32 mm capillary column (silica phenyl methyl silicone) with a 0.25 µm thick layer. The transport gas (nitrogen) was injected at a rate of 1.5 mL min^{-1}. Injector temperature was 350 °C and detector temperature was 360 °C. The oven heating program was 50 °C for 4 min; followed by 10 °C min^{-1} increments until 300 °C for 15 min. Analyses were run for sixteen PAHs congeners: acenaphthene, 2-methylnaphthalene, anthracene, acenapthylene, phenanthrene, fluorene, fluoranthene, pyrene, chrysene, dibenzo[a]anthracene, benzo[a]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno [1,2,3-cd]pyrene, benzo[g,h,i]perylene, and dibenzo[a,h]anthracene. PAHs analytical procedures were implemented under strict quality assurance and quality control protocols (QA/QC). One procedural blank was prepared for each set of samples to monitor potential contamination resulting from laboratory procedures. Internal standard reference compounds were also validated for recovery and analytical response variability. The recoveries of the surrogate standard in all sediment samples were 91 ± 5%, and 87 ± 6% in fish tissue samples. Limits of detection (LOD) were determined by spiking blank samples with a standard solution (5 ng μL^{-1}) of the determined PAHs, and calculated considering the ratio S/N >2. LOD in the case of PAHs were between 0.5 and 1.0 ng g^{-1}. In addition to PAHs quantification, the organic matter content (OM) and organic carbon (OC) in dry sediment was measured using the method explained by Briggs (1977). Dry sediment (2 g) from each station was placed in a clean preweighed porcelain dish and heated in a furnace at 550°C for 4h. The percentage of OM was calculated based on the mass ratio of sediment weight in the porcelain dish before and after heating.

Sediment quality evaluation

The PAHs potential toxicity evaluation methods and, the sediment quality guidelines (SQGs), were used to evaluate the level of contamination of the sediment described by Tu et al. (2018). The ERM and ERL reference values developed for aquatic environments (MacDonald et al. 2000; NOAA 2000) were used to evaluate the ecotoxicity of PAHs concentrations (ERM quotient) in sediment. The ERM quotient value was calculated using the following equation:

$$ERM\ quotient = \sum \frac{Ci\ /ERMx}{n}$$

Where C_i is the measured concentration of the examined component (x) in sediment, ERMx is the ERM for PAHx (**Table 1**), and n is the numbers of PAHs. When the mean ERM quotient value of a sediment sample is below 0.11, it has a 9% probability of being toxic. However, sediments that reach values of 21, 49 and 76% probability, can be toxic if they reach a quotient ERM of 0.11-0.5, 0.51 - 1.5, and greater than 1.5, respectively (Long et al. 2000). On the other hand, the toxic carcinogenic equivalents (TEQ) and mutagenic equivalents (MEQ) can be calculated using the Toxic Equivalent Factor (TEF) and Mutagenic Equivalent Factor (MEF) for PAHs (**Table 1**) using the following equations.

$$TEQ = \sum Ci\ x\ TEF_i$$

$$MEQ = \sum Ci\ x\ MEF_i$$

Where C_i is the concentration of PAHs components in the sediment, TEF_i and MEF_i

represent the toxic and mutagenic equivalence factor, respectively, for PAHs relative to benzo (a) pyrene (BaP) (Nisbet and LaGoy 1992; Durant et al. 1996; Balgobin and Ramrrop 2019).

On the other hand, for a comprehensive evaluation, when sediments have PAHs concentrations lower than the SQC sediment quality criterion value (SQC-Low), the sediment has no adverse effects on the ecosystem. When the concentration of PAHs in sediment has concentrations higher than the SQC (SQC-Up), the sediments need to be remediated after a risk assessment process (**Table 1**). However, if the sediments have concentrations between the two criteria, the sediments require frequent monitoring (Tu et al. 2018).

Table 1. Toxic equivalency factor (TEF) and mutagenic equivalency factor (MEF) for PAHs (Nisbet and LaGoy 1992; Durant et al. 1996) and sediment quality criterion value (SQC).

PAHs	Abbreviation	TEF_i	MEF_i	SQC-Low	SQC-Up	NOAA-ERL	NOAA-ERM
Naphthalene	Nap	0.001		70	550	260	2100
Acenaphthene	Ace	0.001		40	270	16	500
Anthracene	Ant	0.01		80	800	85	1100
Acenaphthylene	Acy	0.001		40	420	44	640
Fluorene	Fl			40	260	19	540
Phenanthrene	Phen	0.001		150	1120	240	1500
Chrysene	Chr	0.01	0.017	190	1730	-	-
Fluoranthene	Flu	0.001		290	2860	290	600
Pyrene	Pyr	0.001		290	2410	670	2600
Benzo(a)anthracene	BaA	0.1	0.082	140	1210	261	1600
Benzo(b)fluoranthrene	BbF	0.1	0.25	320	3030	-	-
Benzo(k)fluoranthrene	BkF	0.1	0.11	160	1400	-	-
Benzo(a)pyrene	BaP	1	1	160	1340	430	1600
Dibenzo(a,h)anthracene	DhA	1	0.29	40	260	63	260
Benzo(ghi)perylene	BgP	0.01	0.19	150	1280	-	-
Indeno(1,2,3-cd)pyrene	InP	0.1	0.31	160	1230	-	-

Bioaccumulation Models

The bioaccumulation factor (BAF) and biota-sediment bioaccumulation factor (BSAF) were applied (Froehner et al. 2018) and calculated by equation (1).

$$BAF = \frac{C_f}{C_s} \qquad \text{(ec. 1)}$$

Where C_f is the concentration of PAHs in organisms and C_s the concentration in sediments (ng g^{-1} dw). Bioaccumulation was also evaluated considering the lipid content of each organism. The bioaccumulation factor (BSAF) was calculated according to equation (2).

$$BSAF = \frac{C_f/_L}{C_s/_C} \qquad \text{(ec. 2)}$$

Where C_f is the concentration of PAHs in organisms (ng g^{-1} dw), L is the proportion of lipids in biological tissue (%), C_s is the concentration of PAHs in sediment (ng g^{-1} dw), and C is the component organic carbon in sediment (%).

The predominant pathway in which PAHs reach humans occurs from sediment

to organisms for human consumption (seafood). Therefore, the concentration of PAHs accumulated via the food chain can be represented by the following equation (Balgobin and Ramrrop, 2019).

$$C_{biota}=\frac{CS\ x\ f_{lipid}\ x\ BSAFi}{OC_{sediment}} \quad \text{(ec. 3)}$$

Where C_{biota} represents the concentration of PAHs accumulated in the food chain, f_{lipid} is the fraction of lipids in fish, C_S is the concentration of PAHs in sediment and $OC_{sediment}$ is the fraction of organic carbon in sediment of the study area, $BSAF_i$ is the indvidual PAH biota-sediment accumulation factors (Balgobin and Ramrrop, 2019; US-EPA, 2004).

Statistical Analysis

The Kolmogorov-Smirnov normality test and the Bartlett homogeneity test preceded data analyses (p=0.05). Analysis of variance (ANOVA, $p \leq 0.05$) was applied using STATISTICA 7.0 software to evaluate the concentration of PAHs for each sampling station, as well as, in fish tissue. Tukey's test of honestly significant difference (HSD) was applied when results exhibited significant differences. In addition, data analysis was done on the Pearson correlation coefficient matrix for PAHs individual and principal components analysis.

Results and discussions

Source and origin evaluation

According to Balgobin and Ramroop (2019), the ways in which PAHs reach marine environments can occur by atmospheric deposition, river discharges into coastal waters or by direct discharges from anthropogenic activities. Once in aquatic environments, PAHs combine with dissolved phase (DP), suspending particulate matter (SPM), and sediment based on their individual PAHs octanol-water coeffients (K_{ow}). In the present study, the intermediate part of the lagoon (zone II) there is an important exchange between marine waters from zone III and the wastewater discharged from zone I, which probably contributes to zone II having a higher concentration of low molecular weight PAHs (LMW) of 223.96 ng g^{-1} dw, unlike zone I and zone III, which present a higher concentration of high molecular weight PAHs-HMW (629.6 ng g^{-1} dw and 319.12 ng g^{-1} dw, respectively). The analyzes Pearson correlation coefficient between individual PAHs between zone I and III (r = 0.8); suggests that these two areas show an increase in PAHs of a similar proportion, which was related to the transit of boats and the port area, as well as the discharge of wastewater in these areas.

Because the Caleta lagoon is only connected to the Terminos lagoon and ocean (west mouth), it has a greater influence by the tides from zone III. Probably the exchange or mixing flows cause a higher concentration of suspended solids, distributing pollutants from the marine environment along the lagoon. The transport of suspended particulate matter (SPM) and dissolved particles (DP) along the lagoon, allowing that low molecular weight (LMW) 2 to 3 ring PAHs have higher solubility in the DP, while high molecular weight (HMW) 4 to 6 ring PAHs are more associated with SPM and sediment in the marine environment (Nielsen et al. 2015; Balgobin and Ramroop, 2019). It is a fact that the occurrence of PHAs in the environment can be due to natural or anthropogenic sources, although the presence of PAHs in sediment is dominated by the latter. This means that the main origin of these emissions can be pyrogenic, due to the incomplete combustion of organic matter, or petrogenic due to hydrocarbon spills (Yunker et al. 2002; Salgado et al. 2019).

In the present study, the ΣLWM / ΣHWM rate for zone II was greater than 1, indicating a petrogenic source, in contrast to zones I and III with significant correlation (r = 0.8) (**Table 2**), indicating a pyrolytic source. In general, the ΣPAHs concentration in sediment from the Caleta lagoon indicates a mixture of both sources, contributing accidental spills from small boats, wastewater discharge and fuel burning by vehicles, activities that directly influence the lagoon and are routes of transport of PAHs within the ecosystem; similar results were reported by Canedo-Lopez et al. (2020). Based on the Pearson correlation coefficient between individual PAHs (**Table 3**), it is possible to identify PAHs from the same source. Significant correlation was observed in the present study between BaA, Acy, Fl and Pyr (r = 0.9) and between BkF, Flu and BbF (r = 0.86), as well as between DhA and Fl, Flu, Pyr (r = 0.9), asi como BgP (r=0.9); this means that the compounds BaA, Acy, Fl, Pyr , BkF, Flu, BbF, BgP and DhA (r = 0.9), present in sediment have the same origin, which agrees with the persistence of compounds of high molecular weight from sediment of the Caleta lagoon. The sediment quality evaluation criteria show that zone I, which receives the contribution of sewage and waste, showed an ERM quotient value of 0.11, which indicates a probability of 21% that the sediments could become toxic to organisms; while for zone II and III the ERM quotient values were less than 0.11 with a 9% probability of being toxic (**Table 2**).

Table 2. Concentration of PAHs components (ng g^{-1} wt) for the three zones in the study area and sediment quality criterion value.

PAHs	abbreviation	Zone I		Zone II		Zone III	
		Media ±DS	ΣPAH[a]	Media ±DS	ΣPAH[b]	Media ±DS	ΣPAH[a]
Acenapthylene	Acy	16.22±6.3	129.7	11.05±6.1	110.5	0	0
Fluorene	Fl	5.14±3.1	41.1	3±2.1	30.0	2.69±1.1	26.9
Phenanthrene	Phen	0	0	2.98±1.3	30.0	0	0
Chrysene	Chr	2.91±1.0	23.2	3.71±2.1	37.0	3.68±3.4	36.8
Fluoranthene	Flu	3.75±2.4	26.2	0.31±0.6	3.1	1.72±1.6	17.2
Pyrene	Pyr	3.11±2.9	24.8	1.31±1.1	13.1	0.91±1.3	9.1
benzo (a) Anthracene	BaA	4.69±2.6	37.5	2.55±2.0	25.5	1.05±0.35	10.5
Benzo (b) Fluoranthene	BbF	4.22±2.6	33.7	1.85±1.1	18.4	5±0.39	50
Benzo (k) Fluoranthene	BkF	2.16±1.1	17.2	0.25±0.1	2.5	1.99±1.6	19.9
Benzo (a) Pyrene	BaP	2.20±1.8	17.5	2.12±1.4	21.1	3.50±2.8	35.0
Dibenz (a, h) Anthracene	DhA	12.13±10.3	97.0	4.7±3.3	47.0	5.75±3.5	57.5
Benzo (g, h, i) Perylene	BgP	48.94±17.2	391.5	3.65±4.1	36.4	12.07±6.3	120.7
Indeno (1,2,3 - cd) Pyrene	InP	4.36±2.0	34.9	1.03±1.0	5.1	2.54±1.6	25.4
ΣPAHs			874.8		380.2		409.2
ΣLMW (3-4 anillos)			245.2		223.9		90.1
ΣHMW (5-6 anillos)			629.6		156.2		319.1
LMW/HMW			0.39		1.4		0.28

ERM quotient	0.11	0.064	0.047

*Different letters mean significant differences (Tukey P≤0.05)

This suggests that the sediment in the lagoon, although it does not require immediate restoration or bioremediation attention, it is important to note that zone I, which has a greater contribution of wastewater, could be minimized impacts with an adequate environmental program and protection of the ecosystem, in such a way to control a possible increase in the toxicity of the sediments and consequently help to protect the spices in the ecosystem. This was consistent with the SQC values analyzed (**Table 1; Table 2**); when the sediments have PAH concentrations below the sediment quality criteria (SQC-Low), the sediment has no adverse effects on the ecosystem, while if the concentration is above the SQC-Up, the sediment needs to be remediated after a risk assessment. However, if the sediments have concentrations of PAHs between both criteria (SQC), it suggests frequent monitoring. An analysis by PAHs components for the three study zones suggests that the sediments do not have adverse effects on the organisms (**Table 2**), which is consistent with the low toxicity levels (ERM quotient), suggesting that the ecosystem offers an adequate level of protection.

Table 3. Pearson correlation coefficient matrix of PAHs in sediments of Caleta lagoon

	Acy	*Fl*	*Phen*	*Chr*	*Flu*	*Pyr*	*BaA*	*BbF*	*BkF*	*BaP*	*DhA*	*BgP*	*InP*
Acy	1.00												
Fl	0.76	1.00											
Phen	0.38	-0.31	1.00										
Chr	-0.60	-0.97	0.51	1.00									
Flu	0.01	0.65	-0.92	-0.80	1.00								
Pyr	0.79	1.00	-0.27	-0.96	0.62	1.00							
BaA	0.95	0.93	0.06	-0.82	0.33	0.94	1.00						
BbF	-0.80	-0.23	-0.86	0.00	0.59	-0.27	-0.57	1.00					
BkF	-0.50	0.17	-0.99	-0.39	0.86	0.13	-0.20	0.92	1.00				
BaP	-1.00	-0.80	-0.32	0.65	-0.07	-0.83	-0.96	0.77	0.46	1.00			
DhA	0.44	0.92	-0.66	-0.98	0.90	0.90	0.71	0.18	0.55	-0.49	1.00		
BgP	0.42	0.91	-0.68	-0.98	0.91	0.89	0.69	0.21	0.57	-0.47	1.00	1.00	
InP	-0.07	0.59	-0.95	-0.76	1.00	0.55	0.25	0.65	0.90	0.01	0.86	0.88	1.00

Based on the Toxic carcinogenic equivalents (TEQ_{BaP}) and mutagenic equivalents (MEQ_{BaP}) analysis (**Table 1**); It is possible to observe that the high molecular weight PAHs components contribute to the increase of carcinogenic and mutagenic in humans based on the MEF and TEF factors. Zone I showed the highest TEQ_{BaP} value (12.13 ng g^{-1}) for dibenzo (a, h) anthracene and with a mutagenic equivalent (MEQ_{BaP}) of 3.52 ng g^{-1}. The TEQ_{BaP} and MEQ_{BaP} range for zone I was 0.0031-12.3 ng g^{-1} and 0.049-9.29 ng g^{-1}, respectively. While the TEQ_{BaP} range for zones II and III were estimated from 4.70 - 5.75 ng g^{-1}, respectively and with MEQ_{BaP}

values from 1.36 to 1.67 ng g^{-1}, respectively; some of these compounds that were present with high values were Benzo (b) fluoranthrene, Benzo (a) Pyrene, dibenzo (a, h) anthracene and Benzo (ghi) perylene for the different study areas. These values obtained in the present study were lower than those reported by Balgobin and Ramroop (2018) with TEQ_{BaP} ranges from 3.01 µg kg^{-1} to 22.37 µg kg^{-1} and MEQ_{BaP} ranges from 3.98 µg kg^{-1} to 38.61 µg kg^{-1}, concluding that those sites where PAHs of 4 to 6 rings are present and that may generate a greater risk of carcinogenic and mutagenic to human health were low.

It is a fact that anthropogenic activities around the study area may increase the carcinogenic and mutagenic risk to human health. However, in the present study the low probability of sediment toxicity is consistent with the low toxic carcinogenic equivalents (TEQ_{BaP}) and mutagenic equivalents (MEQ_{BaP}) and according to the mean concentrations of PAHs reported; benzo (a) pyrene concentrations for the three study areas were low to the EU guidelines of 6.0 µg kg^{-1} (EC, 2011). On the other hand, the sum of the concentrations Σ BaP + BbF + BaA + Chr for zones I, II and III (13.97, 10.23, 13.23 ng g^{-1} dw) did not exceed the EU limit of 35.0 µg kg^{-1} (EC 2011) and based on the criterion by Barakat et al. (2011), the ΣPAHs concentration in sediment within the study area was considered moderately contaminated, observing the highest concentration in zone I (874.8 ng g^{-1} dw) and lower concentrations for zone II and III (380.25 and 409.19 ng g^{-1} dw, respectively) (**Table 2**), suggesting that the level of contamination in the ecosystem requires attention to improve the quality of the ecosystem, mainly in zone I where the greatest contribution of urban wastewater is made.

For the study of PAHs in muscle tissue in fish (*Megalops atlanticus*), the analysis of length, weight and lipid content in fish caught for last res zones showed no significant differences (ANOVA; $p \geq 0.05$). The fish had an average total length of 36.1 cm and an average weight of 286.1 g; due to their length and weight, it can be inferred that the study area is used by juvenile, as was expected since these organisms in juvenile stages usually inhabit brackish waters (rivers, estuaries and coastal lagoons). On the other hand, Statistical analysis indicates significant no correlation between total PAHs concentration in fish tissues and total lipid content ($p > 0.1$); suggesting the bioavailability of PAHs accumulated in fish lipids frequently occurs via passive diffusion along the surface of the water body from the DP and from the ingestion of SPM (Rojo-Nieto, 2014). However, other factors can be considered, such as the spatial distribution of compounds, trophic level, and behavior of each species in the environment. Previous studies have reported in fish tissue *Megalops atlanticus* a higher PAHs concentration of LHW (190.3 ng g^{-1} dwt) with respect to HMW hydrocarbons (39.21 ng g^{-1} dwt) (Canedo-Lopez et al. 2020), suggesting that these organisms have a greater impact by compounds PAHs of petrogenic origin. This seems to indicate that high molecular weight compounds are strongly absorbed by sediment and decrease their mobility, as reported by Liu et al. (2012), suggesting that LHW compounds in zone II would be in greater presence in the water column where fish may have greater availability (Canedo-Lopez. 2020). Therefore, the bioaccumulation can occur even at small concentration in water (Froehner et al. 2018) during the transit of the species along the lagoon.

The bioaccumulation factor (BAF) estimated for the Caleta lagoon showed for Zones II and III a BAF> 1 with ranges from

2.64 to 3.13, while for zone I a low BAF of 0.227 was observed (**Table 4**). These values suggest a high bioavailability of PAHs in the Caleta lagoon from the exchange zones between the ocean and wastewater. The urban wastewater discharged from zone I flows towards the lagoon outlet mixing with the marine waters, while the tides contribute to the distribution of these PAHs throughout the lagoon, being available by the consuming organisms from DP; which contributes to the high levels of PAHs in sediment observed for zone II and III (75.42 and 118.39 ng g^{-1} wt) and high BAF in fish tissue (**Table 4**). The granulometry study indicates that the low concentration of sand (56.98%) present in zone III showed a high BAF value (0.288), while zones I and II which have high sand contents (70-72%) show a lower bioavailability (BAF) of 0.0121 and 0.198, respectively (**Table 4**). This variation of BAF shows a close relationship between the content of TOC and OM in sediments and the granulometric composition. The hydrophobicity of PAHs suggests greater retention in organic matter; however, the results obtained in the present work (**Table 4**) show those sediments with higher TOC and MO content present lower BAF values, probably suggesting greater retention of PAHs compounds in sediment, which are probably less bioavailable to aquatic organisms, therefore, a greater accumulation of PAHs -HMW could occur in the study area.

Table 4. Bioaccumulation factors (BAFs) and biota-sediment accumulation factors (BSAFs) for the samples of Caleta Lagoon.

Station	ΣPAH_{sed}	ΣPAH_{fish}	%Lip	%TOC	%MO	BAF	BSAF	C_{biota}
Zone I	874.8	10.55	0.681	12.83	22.12	0.0121	0.227	10.55
Zone II	380.25	75.42	0.718	11.33	19.54	0.198	3.13	75.42
Zone III	409.82	118.39	0.605	5.53	9.53	0.288	2.64	118.39

It is a fact that the TOC level in sediments is an important parameter to define the fate and transport of pollutants. In the present study, a positive correlation was observed for PAHs with TOC (r = 0.61) from zone I, II and III, suggesting that the currents and tides are responsible for the accumulation of organic matter and PAHs (Froehner et al. 2018). In the present study, this proposes that high molecular weight PAHs are strongly absorbed by the sediment, as a consequence, the mobility of these PAHs are low, as reported by Liu et al. (2012). This can be observed for zones I and III with high PAHs content of HMW, suggesting a greater retention of PAHs (HMW) in the zone of wastewater discharge (Zone I) and in the marine water inlet zone (Zone III), which corresponds with high values of BSAF and C_{biota} for both zone (**Table 4**). In general, urban wastewater, boat transportation, and poor waste management contribute to the increase in PAHs, therefore the extent of bioaccumulation is greater at the mouth of the Caleta lagoon, due to the exchange of water masses.

Conclusions

The highest concentration of PAHs was mainly observed in the wastewater discharge zone (Zone I) and zone III near the seaport. The wastewater and tidal inputs control the distribution of PAHs throughout the lagoon, presenting a pyrogenic and petrogenic sources. The sediment quality analysis and toxicity criteria show that the lagoon, although it does not require immediate restoration or bioremediation attention; Zone I requires greater control of

wastewater discharges to minimize the impacts that threaten the ecosystem and avoid an increase in toxicity in sediments to protect the species that live there. The carcinogenic (TEQ) and mutagenic (MEQ) risks were low which suggests that such negative effects are unlikely to occur. The LHW compounds would be in greater presence in the water column where fish may have greater availability. The values of BAF, BSAF showed that the bioaccumulation of PAHs occurs in the Caleta Lagoon mainly in the water exchange zones (zone II and III)

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