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Contaminant levels of PAHS, bioaccumulation factor and biota-sediment accumulation factor in a lagoon adjacent to a flora and fauna protection area in Mexico with oil industrial activity

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) in sediment and edible fish (*Megalops atlanticus*) from Caleta lagoon (Terminos Lagoon, Campeche, Mexico) were quantified to evaluate the toxicity and bioaccumulation factor (BAF) and biota-sediment accumulation factor (BSAF). 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 of PAHs of low molecular weight (LMW) (223.96 ng g^{-1} dw), while zones I and III showed higher concentrations of PAHs of high molecular weight (HMW) (629.6 ng g^{-1} dw and 319.12 ng g^{-1} dw, respectively), suggesting petrogenic and pyrolytic sources. The high concentration of LHW PAHs (190.3 ng g^{-1} dwt) in fish tissue indicated a greater availability from the water column. The toxic (TEQ) and mutagenic (MEQ) equivalent quotients and the effects of range-median (ERM) values showed a sediment with low probability of toxicity, while the BAF and BSAF values suggest a high bioavailability of PAHs from the exchange zones between the ocean and urban wastewater.

KEYWORDS: Terminos lagoon, polycyclic aromatic hydrocarbons, sediment quality, toxic equivalent quotient, bioaccumulation factor, biota-sediment accumulation factor.

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are considered as the organic pollutants commonly found in ecosystems and considered as mutagenic and carcinogenic; therefore, a prolonged exposure of PAHs causes effects such as skin cancer, lung, and bladder cancer in humans [1]. The high hydrophobicity that PAHs have allows them to be adsorbed onto organic matter and increase their concentration in the sediment. Therefore many of these PAH compounds can be transferred to benthic organisms, fish and other organisms causing a risk to ecosystems and human health. This leads to effects of bioaccumulation and biomagnification when entering the food chain [2].

Numerous studies have evaluated the concentration and distribution of PAHs in aquatic environments, in addition to the probable ecological and human health risk [3], as well as identified the origin of PAHs in aquatic sediments [4, 5, 6] and evaluated the adverse biological effects of PAHs according to the criteria established by the National Oceanic and Atmospheric Administration [7, 8, 9]. A complement to these studies is the evaluation of the carcinogenic potential (TEQ) based on the toxic equivalency factor (TEF) relative to the most toxic component benzo (a) pyrene and on

the use of the sediment quality guidelines (SQGs) used for historical data interpretation, sediment quality assessments, monitoring programs design and remediation programs [2]. Generally, the evaluation methods available and commonly used in monitoring programs have as main objective the estimation of the concentration of PAHs in water and sediment, as well as the evaluation of the level of transfer or bioaccumulation of these compounds to biota and in fish muscle tissue [10].

In order to predict bioaccumulation, mathematical models based on lipid content in the organisms and compound properties are used. These models are useful when there is a small number of data and it is required to evaluate the extension of damage in a short time [11]. Therefore, two prediction models have been used in lakes or estuaries, namely the bioaccumulation factor (BAF) and the biota-sediment bioaccumulation factor (BSAF) models [12, 13]. Previous studies carried out in a lagoon adjacent to the Terminos Lagoon, a natural protected area in Campeche, Mexico, found out that the levels of PAHs in sediment and fish muscle tissue indicate moderate pollution of petrogenic origin [14]. However, there is little information about the bioaccumulation processes in fishes of this area. In the present study, the content and distribution of PAHs in sediment and fish tissue (muscle) from a lagoon adjacent to the Terminos Lagoon Natural Protected Area were examined to understand the extent of bioaccumulation using BAF and BSAF 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 has an average depth of 1.5 m. The system presents an area of 140 000 m^2 and a volume of 210 000 m^3, and communicates at the west with Terminos Lagoon and the Gulf of Mexico (Figure 1). Oil companies, fisheries and urban developments surrounding this area discharge 613 260 m^3 of wastewater every year, which negatively affect the ecosystem (Figure 1). A common practice is the fishing of Atlantic tarpon (*Megalops atlanticus*) from Caleta lagoon, which is marketed for local consumption. Therefore, it is important to evaluate the concentrations of PAHs in sediment and fish (muscle) to evaluate the extent of bioaccumulation.

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 sediment

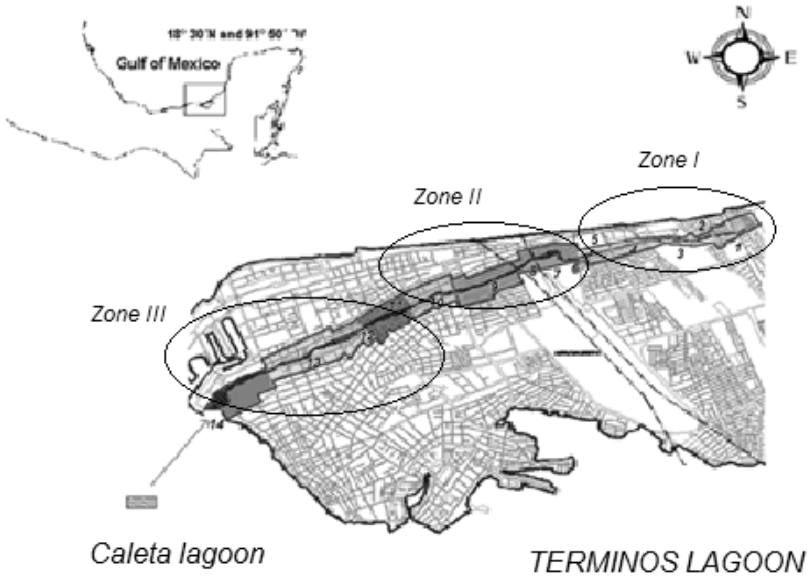

Figure 1. Location of the study area and strata (zone I, II, III) within Caleta lagoon.

samples were dried in a drying oven at 40±5 °C for 48 h and subsequently homogenized [15]. Dry sediment was homogenized and sieved by a sieve of mesh size 250 μm and stored until extraction. The procedure for sediment sample processing has been described by Canedo-Lopez *et al*. [14]. Internal standards (3,6-dimethylphenanthrene and 2,2'-binaphthylene) were added to samples prior to instrumental analysis. Fishes were caught with cast net. The individuals collected were separated into groups according to length, weight and lipid percent. The tissue extraction method for the identification of PAH compounds was carried out as described by El-Deeb *et al.* [16].

The PAH 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 consisted of 50 °C for 4 min, followed by 10 °C min^{-1} increments until 300 °C for 15 min. Analyses were run for sixteen PAH 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. PAH 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 were 91 ± 5% in all sediment samples and 87 ± 6% in fish tissue samples. Limits of detection (LOD) was determined by spiking blank samples with a standard solution (5 ng μL^{-1}) of the determined PAHs and calculated considering the signal-to-noise ratio S/N >2. LOD in the case of PAHs was between 0.5 and 1.0 ng g^{-1}. In addition to PAH quantification, the organic matter content (OM) and organic carbon (OC) in dry sediment were measured using the method explained by Briggs [17]. Dry sediment (2 g) from each sampling station was placed in a clean pre-weighed porcelain dish and heated in a furnace at 550 °C for 4 h. 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, comparing the levels of the present study with the quality guidelines described by Tu *et al*. [2]. The reference values of low-range effects (ERL) and median-range effects (ERM) developed for aquatic environments [7, 8] were used to evaluate the ecotoxicity of PAH 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 number 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 [18]. On the other hand, the toxic carcinogenic equivalent quotient (TEQ) and mutagenic equivalent quotient (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 PAH components in the sediment and, TEF_i and MEF_i represent the toxic and mutagenic equivalent factor, respectively, for PAHs relative to benzo (a) pyrene (BaP) [19, 20, 21].

On the other hand, according to the sediment quality criteria (SQC), when sediments have PAHs concentrations lower than the SQC-Low, the

Table 1. Toxic equivalency factor (TEF) and mutagenic equivalency factor (MEF) for PAHs 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	-	-

sediment has no adverse effects on the ecosystem. When the concentration of PAHs in sediment has concentrations higher than the SQC-Up, 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 [2].

Bioaccumulation models

Understanding the accumulation of pollutants in ecosystems and the way it is transferred to the food chain can be analyzed through models determining the bioaccumulation factor. The bioaccumulation factor (BAF) and biota-sediment bioaccumulation factor (BSAF) were applied [10] 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 is 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 of organic carbon in sediment (%).

The predominant pathway through which PAHs reach humans is from sediment to organisms. Therefore, the concentration of PAHs accumulated *via* the food chain can be represented by the following equation [21].

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

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, $OC_{sediment}$ is the fraction of organic carbon in sediment of the study area, and $BSAF_i$ is the individual PAH biota-sediment accumulation factor [21, 22].

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 PAH individual and principal components analysis.

RESULTS AND DISCUSSIONS

According to Balgobin and Ramroop [21], the PAHs can enter marine environments by atmospheric deposition, river discharges or discharges from anthropogenic activities. Since PAHs are hydrophobic, they can combine with dissolved phase (DP), suspending particulate matter (SPM), and sediment, allowing the accumulation of PAH and transfer to the food chain. In the present study, in 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 (LMW) PAHs of 223.96 ng g^{-1} dw, unlike zone I and zone III, which present a higher concentration of high molecular weight (HMW) PAHs (629.6 ng g^{-1} dw and 319.12 ng g^{-1} dw, respectively). Pearson's correlation coefficient analysis 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 is 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 the ocean by one mouth (west mouth), zone III has a greater tidal influence. Probably the exchange or mixing flows cause a higher concentration of suspended solids, distributing pollutants from the marine environment throughout the Caleta lagoon. The transport of suspended particulate matter (SPM) and dissolved particles (DP) allow the distribution of PAHs along the Caleta lagoon; 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 [21, 23]. The classification analysis of PAHs from sediments showed that the PAHs from zone II and III have similar origin (Figure 2), while in zone I, the wastewater discharge and fossil fuel burning (from vehicles and motorboats traffic) tend to change the original environmental conditions. It is a fact that the occurrence of PAHs 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 [4, 15].

In the present study, the calculated LMW/HMW ratio for zone II was greater than 1, indicating a petrogenic source; in contrast, zones I and III showed ratios less than 1, indicating a pyrolytic source (Table 2) [24, 25]. In general, the ΣPAHs concentration in sediment from the Caleta lagoon indicates a mixture of both sources. Accidental spills from small boats, wastewater discharge and fuel burning by vehicles are activities that directly influence the lagoon and are routes for transporting PAHs within the ecosystem; similar results were reported by Canedo-Lopez *et al*. [14]. Based on the Pearson's 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 ($r = 0.9$), and 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 a similar origin, which agrees with the persistence of compounds of high molecular weight from sediment of the Caleta lagoon. The ERM quotient presented a value of 0.11 in zone I, which receives wastewater and waste input, indicating a 21% probability that the sediments could become toxic to organisms; on the other hand, for zones II and III the ERM quotient values were lower than 0.11 with a 9% probability of being toxic (Table 2).

This suggests that although the Caleta lagoon does not require immediate restoration or bioremediation

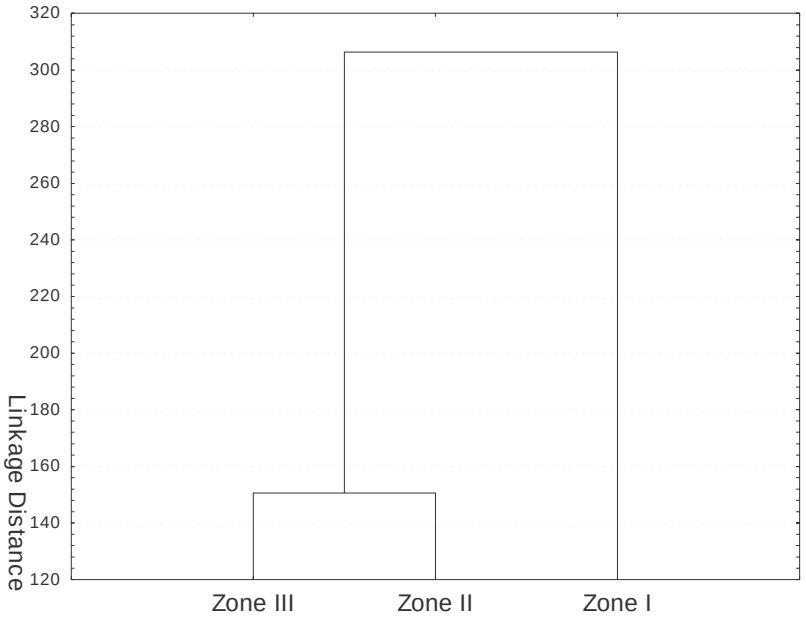

Figure 2. Dendrogram of classification analysis showing the association of the three study areas with regard to the PHA content in sediment.

Table 2. Concentration of PAHs components (ng g^{-1} wt ± Standard Deviation) 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	n.d	n.d
Fluorene	Fl	5.14±3.1	41.1	3±2.1	30.0	2.69±1.1	26.9
Phenanthrene	Phen	n.d	n.d	2.98±1.3	30.0	n.d	n.d
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 rings)			245.2		223.9		90.1
ΣHMW (5-6 rings)			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 $P \leq 0.05$); n.d. (not detected)

Table 3. Pearson's 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

attention, an adequate environmental program could minimize impacts, especially in zone I, and thus control a possible increase in sediment toxicity and consequently help protect the ecosystem's species. Sediment quality criteria (Table 1) are consistent with the results of the ERM quotient. In all zones, PAH concentrations are below the SQC-Low indicating that the sediment has no adverse effects on the ecosystem.

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 PAH components contribute to the increase in carcinogenic and mutagenic chemicals in humans according to the MEF and TEF factors. Zone I showed the highest TEQ_{BaP} value (12.13 ng g^{-1}) for dibenzo (a, h) anthracene and 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. In zones II and III the estimated TEQ_{BaP} ranges from 4.70 to 5.75 ng g^{-1}, while MEQ_{BaP} values varied from 1.36 to 1.67 ng g^{-1}; some of the 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. Balgobin and Ramroop [26] reported higher TEQ_{BaP} values with ranges from 3.01 ng g^{-1} to 22.37 ng g^{-1} and MEQ_{BaP} with values from 3.98 ng g^{-1} to 38.61 ng g^{-1}. The authors mention that the sites with the highest incidence of PAHs from 4 to 6 rings are those that represent a higher risk of carcinogenesis and mutagenesis for human health; however, for the study area they suggested a low carcinogenic and mutagenic factor.

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 toxic carcinogenic equivalents (TEQ_{BaP}) and mutagenic equivalents (MEQ_{BaP}) according to the mean concentrations of PAHs reported, indicate a low probability of sediment toxicity. Benzo (a) pyrene concentrations for the three study areas were low according to the EU guidelines of 6.0 ng g^{-1} [27]. 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 ng g^{-1} [27]. Although in terms of ERM quotient the probability of toxicity was low for the Caleta lagoon area, some concentrations of PAHs in sediment have been associated in the literature to a contaminated ecosystem. Concentrations of ΣPAHs in sediment with ranges from 0 to 100 ng g^{-1} dw are considered as minimal contamination; sediments with concentration ranges from 100 to 1000 ng g^{-1} dw are classified as moderately contaminated; while values greater than 5000 ng g^{-1} dw represent extremely contaminated areas [28].

Based on this criteria, 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 contribution of urban wastewater is the greatest.

On the other hand, the fishes caught (*Megalops atlanticus*) showed no significant differences (ANOVA; $p \geq 0.05$) in the length (average: 36.1 cm), weight (average: 286.1 g) and lipid content for the three zones. No significant correlation between the PAH concentration in fish tissue and total lipid content ($p > 0.1$) was observed, suggesting that 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 [29]. However, other factors can be considered, such as the spatial distribution of compounds, trophic level, and behavior of each species in the environment; in addition, the size and nutritional conditions can affect absorption, as well as the metabolic process and excretion. The present study suggests a higher PAH concentration of LHW in the tissue of the fish *Megalops atlanticus* (190.3 ng g^{-1} dwt) with respect to HMW hydrocarbons (39.21 ng g^{-1} dwt), which is similar to that reported by Canedo-Lopez *et al.* [14], suggesting that the PAHs of petrogenic origin have a greater impact on these organisms. This seems to indicate that high molecular weight compounds are strongly absorbed by sediment and decrease their mobility and bioavailability, as reported by Liu *et al.* [30], suggesting a greater presence of LMW compounds of zone II in the water column where the bioavailability is greater. Therefore, the bioaccumulation can occur even at small concentration in water [10] during the transit of the species along the lagoon.

The biota-sediment bioaccumulation factor (BSAF) estimated for the Caleta lagoon showed for Zones II and III a BSAF> 1 with ranges from 2.64 to 3.13, while for zone I a lower BSAF 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 in zone I flows towards the lagoon outlet mixing with the marine waters, while the tides contribute to the dispersion of these PAHs throughout the lagoon; the above is reflected in the high levels of PAHs in muscle tissue in fish observed in zones II and III (75.42 and 118.39 ng g^{-1} wt) and the high BAF in sediment (Table 4). The granulometric analysis indicated that the low proportion of sand (56.98%) in zone III is related to a high BAF value (0.288), while zones I and II with higher sand contents (70-72%) showed a lower BAF of 0.0121 and 0.198, respectively (Table 4). This variation of BAF shows a close relationship between the content of total organic carbon (TOC) and organic material (OM) in sediments and the granulometric composition [31]. The hydrophobicity of PAHs suggests greater retention in organic material; however, the results obtained in the present study (Table 4) show lower BAF values in those sediments with higher TOC and MO content, probably indicating a greater retention of PAHs in sediment and a lower bioavailability for aquatic organisms; therefore, a greater accumulation of HMW PAHs in sediment could occur in the study area.

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 ($r = 0.61$) in zones I, II and III suggesting that the

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

currents and tides are responsible for the accumulation of organic material and PAHs [10]. The present study shows that the high molecular weight PAHs are strongly absorbed by sediment, suggesting the ecosystem is a sink for HMW PAH as reported by Liu *et al*. [30]. The above can be observed in zones I and II which present a relative high content of HMW PAH, suggesting a greater retention of this compounds in the zone of wastewater discharge (Zone I) and in the marine water inlet zone (Zone III). 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) the lowest in the zone II and zone III near the seaport. Water inputs and tide control the distribution of PAHs in the lagoon, with the origin of PAHs being a mixture of pyrogenic and petrogenic sources. The sediment quality analysis and toxicity criteria suggest that the Caleta lagoon does not require immediate restoration or bioremediation attention but Zone I require greater control of wastewater discharges to minimize the impacts that threaten the ecosystem and avoid an increase in toxicity in sediments and protect the species that live there. The carcinogenic (TEQ) and mutagenic (MEQ) quotients were low which suggests that such negative effects are unlikely to occur. The bioavailability of PAHs accumulated in fish tissue frequently occurs *via* passive diffusion along the surface of the water body. This seems to indicate that HMW compounds are strongly adsorbed by sediment and decrease their mobility, while the water column where the availability of fish is greater has a greater presence of LMW compounds. The values of BAF and BSAF showed that the bioaccumulation of PAHs occurs in the Caleta Lagoon with the greatest presence in zone III in the mixing zone between wastewater and seawater.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analysis, or interpretation of data; in the writing of the manuscript, or in the decision to publish.

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