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Source Identification, Toxicity, and Persistence of PAHs in Sediment Core from a Natural Protected Area in Mexico

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Abstract: Sediment cores maintain a historical record of the various sources of polycyclic aromatic hydrocarbons (PAHs). In 2020, one sediment core was collected within the oyster farming area of the Pom–Atasta lagoon system and the Terminos lagoon. A total of 16 PAH compounds were analyzed to identify the historical patterns of PAH inputs and the relationship with sediment materials. The core was classified into three strata at depths of 0.0–0.2 m, 0.2–0.6 m, and 0.6–1.1 m, in which the high content of silt–sand, organic matter, and carbonates indicates a system of high energy and productivity. The hydrology and characteristics of the sediment suggest a free access of adsorbed PAHs to the study area, mainly of pyrolytic origin. The concentration of ∑PAHs decreases from the surface (527.0 ng g^{-1} dw) to a greater depth (75.7 ng g^{-1} dw), which corresponds to 60% of the HMW (high molecular weight) of the total PAHs as combustion products at low temperatures, while LWM-PAH (low molecular weight) inputs are from discharges of petroleum products. The core sediments showed a low probability of toxicity quotient of 9%. The analysis of the carcinogenic toxic equivalent (TEQ^{carc}) in each section of the core was variable, decreasing with the depth from 107.91 ng TEQ g^{-1} dw to 57.65 ng TEQ g^{-1} dw, with the compounds benzo(a)pyrene (53.55 ng TEQ g^{-1} dw) and dibenzo(a,h) anthracene (29.2 ng TEQ^{carc} g^{-1} dw) having the highest TEQ^{carc}. The 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}) indicate a low probability of sediment toxicity. The ecosystem could be under constant threat from increasing anthropogenic activity; therefore, monitoring programs for the conservation of these ecosystems and oyster farms should be considered.

Keywords: sediment cores; Terminos lagoon; polycyclic aromatic hydrocarbons; source and sediment quality; toxic equivalent quotient

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1. Introduction

Sediments are considered reservoirs of organic matter and hydrophobic organic compounds. Some organic contaminants can become adsorbed on fine particles and settle, accumulate in sediments, and be transferred to the food chain or transported to other ecosystems, affecting organisms within the sediments. Among these organic contaminants are polycyclic aromatic hydrocarbons (PAHs), which are hydrophobic and highly persistent in aquatic environments, which constitutes a threat to marine environments due to their high toxicity and their carcinogenic and mutagenic properties. Studies suggest that some PAHs in sediments tend to be more persistent and migrate through the sediment profile [1]. However, migration is affected by various factors, such as the solubility of PAHs in water, dissolved organic carbon (DOC) content, surfactants, colloids, pH, soil porosity, advection and diffusion processes, soil functional groups, and microorganisms and invertebrates [2–4].

Thus, compounds with high water solubility migrate relatively easily within the solid solution, while substances with a high affinity for solid components are transported together with solid particles and subsequently deposited, becoming less bioavailable [5].

Many of the PAHs found in ecosystems are produced by the incomplete combustion of organic material, especially of fossil origin (pyrolytic origin), others by the discharge of petroleum and by-products (petrogenic origin), and others by biogenic transformation (diagenic origin) [6]. Therefore, methodologies can be used to evaluate the source of PAHs using the relationship of low molecular weight (LMW)/high molecular weight (HMW) and the molecular index [7–13]. Similarly, it is possible to evaluate the ecotoxicity of PAH concentrations (ERM quotient), mutagenic equivalent (MEQ), and carcinogenic potential (TEQ) based on the toxic equivalency factor (TEF) relative to the most toxic component, benzo (a) pyrene. All these techniques allow the evaluation of the quality of the sediment and the possible effects on organisms, creating a knowledge base for bioremediation and restoration proposals.

PAH compounds can enter ecosystems through various pathways and accumulate at different depth levels over time; therefore, the persistence of PAHs can be evaluated, as well as the various anthropogenic sources that have exerted pressure on ecosystems. It is recognized that the transport and accumulation of PAHs in coastal lagoons depends largely on the hydrodynamics of these bodies of water [14]. These ecosystems are considered as environments of high productivity and biodiversity. However, they have come to be considered as fragile ecosystems due to anthropogenic effects [15]; therefore, the hydrodynamics of coastal ecosystems allows the creation of necessary bases to know the relationship between seawater flow and the deposition of pollutants.

The Terminos lagoon, declared in 1994 as a Flora and Fauna Protection Area, is one of the most important coastal lagoons in Mexico due to its diversity of species (flora and fauna), and it supports one of the most important economic activities: the exploration and production of hydrocarbons in the Campeche Sound, Mexico. Several studies in Terminos lagoon have evaluated the circulation of water and the influence of river discharges, as well as the displacement and dispersion of polluting substances within the marine environment in correlation with currents, concluding that the circulation pattern determines the nature, texture, and distribution of the sediments [16,17]. The objective of the present study was to evaluate the concentration, sources, toxicity, and persistence of PAHs accumulated in the sediment core within the connection margin between the Pom–Atasta lagoon system and Terminos lagoon, adjacent to an area of high production and exploitation of oysters (*Crassostrea virginica*).

2. Materials and Methods

2.1. Study Area

The Pom–Atasta system is located in the western portion of the Terminos lagoon between 18°30′ and 18°35′ N and 91°50′ and 92°20′ W. Its geographical location is included within the plain coastal area of the southern Gulf of Mexico, formed by the Grijalva and Usumacinta rivers. It is limited to the east by the Boca de Atasta, which connects it with the Terminos lagoon, and to the west by the Colorada lagoon near the San Pedro and San Pablo riverbeds (Figure 1A), from which part of the seasonal drainage comes. This system is made up of more than 10 interior lagoons of variable dimensions, with a total area of approximately 300 km^2 and an average depth of 2.7 m. These lagoons are: Lodazal, Loros, Puerto Rico, Palmas, San Carlos, Del Corte, Palancares, Atasta, Pom, and Colorada.

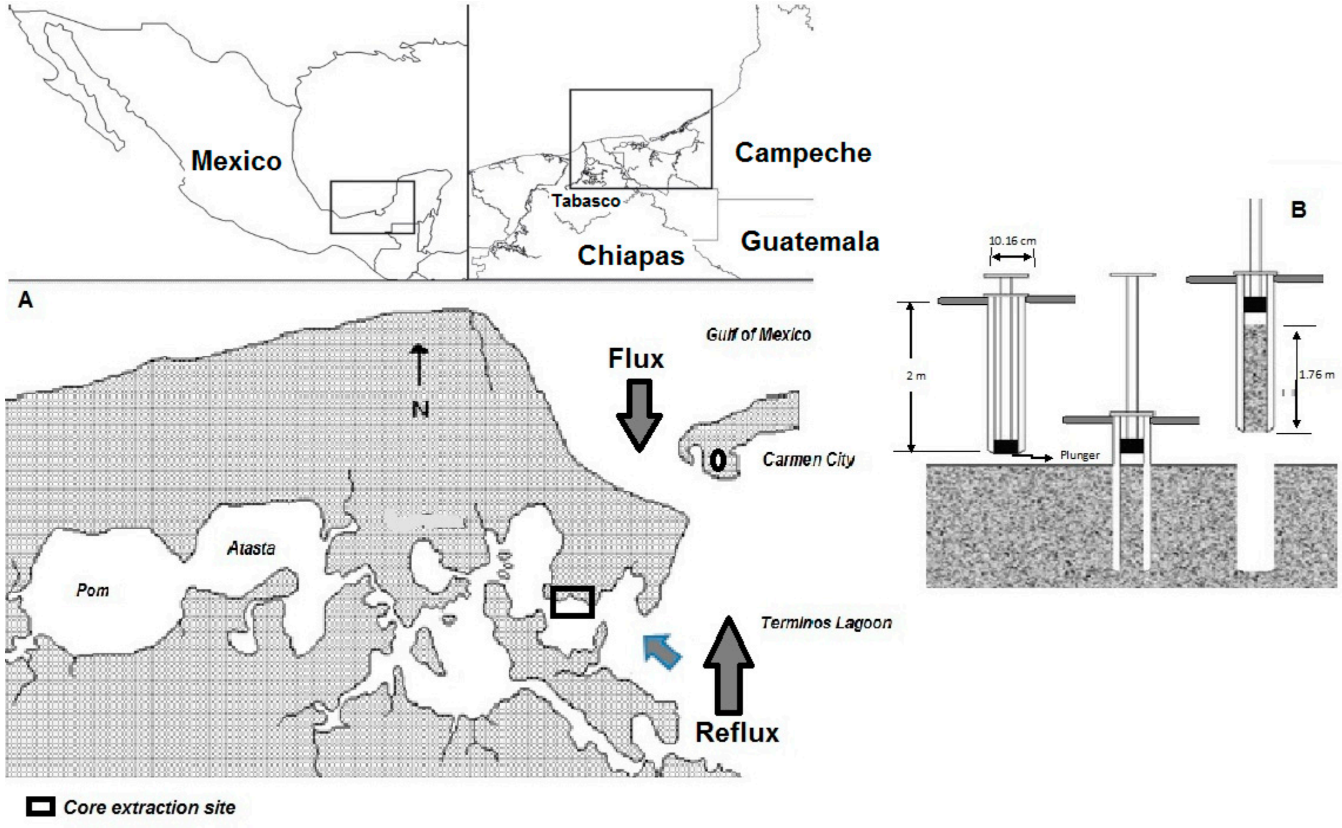

Figure 1. Study area and core extraction site (**A**) and core design (**B**).

2.2. Sediment Core Extraction

The sediment core was extracted between the connection zone of the Pom–Atasta lagoon system and the Terminos lagoon, located at coordinates 18°33′36.99″ N and 91°55′33.65″ W (Figure 1A) within the oyster zone, an area of economic importance for the commercial exploitation of *Crassostrea virginica*. The extraction of the nucleus was carried out with a manual core made of polyvinyl chloride (PVC) of approximately 2 m long and with an external diameter of 10.16 cm (9.56 cm internal diameter). A seal was installed in the lower part to prevent the loss of sediment, and the upper part was sealed to extract the sediment by generating a vacuum and to safely transport the core to the laboratory (Figure 1B). The 1.76 m surface sediment core was cut longitudinally in the laboratory and subsequently a 1 cm-thick subsampling was carried out in both longitudinal portions, and the sedimentary material was placed in different plastic bags. A first batch of samples was frozen (−5 °C) prior to lyophilization. The dry sediment was homogenized and sieved by 250 µm mesh size and stored until extraction of PAHs in accordance with Canedo-Lopez et al. [18], and the second batch of samples was dehydrated at 35 °C for granulometry (textural) analysis.

2.3. Determination of PAHs

The extraction of the PAH compounds was performed every 10 cm. Samples of twenty grams of sediment were Soxhlet-extracted in fiberglass thimbles using 200 mL of methylene chloride for 8 h. Each sample was spiked with 2-fluorobiphenyl as a surrogate standard. The second fraction containing PAHs was collected and concentrated to 0.5 mL with nitrogen flow. Prior to instrumental analysis, 3,6-dimethylphenanthrene and 2,2-binaphthylene were added to the samples as internal standards. The PAH content was analyzed by gas chromatography with flame ionization detection (Agilent Technology, model 7890). A capillary column of silica phenyl methyl silicone of 30 m × 0.32 mm with a 0.25 µm-thick layer was used. Nitrogen was the carrier gas at a rate of 1.5 mL min^{-1}. Temperatures of the injector and detector were 350 °C and 360 °C, respectively. The temperature oven program was 50 °C for 4 min, followed by 10 °C min^{-1} and increasing until 300 °C for 15 min. Analyses were run for sixteen PAHs: 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 [18].

Quality assurance and quality control protocols (QA/QC) were implemented in the PAH analytical procedures. To monitor potential contamination resulting from laboratory procedures, one procedural blank was prepared for each set of samples. For the recovery and analytical response variability measurement, internal standard reference compounds were also included. Recoveries of the surrogate standard were 91 ± 5% in all sediment 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. The LOD in the case of PAHs were between 0.5 and 1.0 ng g^{-1}.

2.4. Granulometric Analysis

For the granulometric analysis, 50 intercalated samples of the superficial 100 cm were used. It was carried out using fifteen particle size classes, from fine sand (1000 microns) to clay (2 microns). The measurement was made by LA-960 Horiba laser diffraction at the Environment and Development Laboratory of the Oceanological Research Institute of the Autonomous University of Baja California. The organic matter content (OM) and organic carbon (OC) in dry sediment was measured using the method explained by Briggs [19]. Dry sediment (2 g) from each station was placed in a clean preweighed 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.

Inorganic carbon (C_{inorg}), total carbon (CT), and $CaCO_3$ in the sediment were determined with a carbon dioxide analyzer (UIC, Inc., Joliet, IL, USA, Model CM150) equipped with acidification and combustion modules, model CM5120, with a precision of the $CaCO_3$ standard of ±0.093%. For C_{inorg}, approximately 25 mg of the sample was treated in the acidification module, adding 5 mL of $HClO_4$ (2 N) to obtain CO_2(g). To determine the CT, approximately 20 mg of the sample was introduced into the combustion module at a temperature of 930 °C and in an oxygen-rich environment. The CO_2 generated in both modules was transported to the electrochemical cell for quantification of $CaCO_3$. Total organic carbon (TOC) was determined by subtracting C_{inorg} from CT. A $CaCO_3$ powder standard (Mallinckrod 4072) was used for the calibration of the equipment with a recovery percentage of 101.51 ± 0.32% (n = 22) and a relative standard deviation of 0.34%.

2.5. Sediment Quality Evaluation

The ERM and ERL reference values developed for aquatic environments [20–22] were used to evaluate the ecotoxicity of PAH concentrations (*ERM quotient*) in sediments (Equation (1)).

$$ERM\ quotient = \sum \frac{Ci/ERMx}{n} \tag{1}$$

where *Ci* is the measured concentration of the examined component (*x*) in the 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 at *ERM quotient* ranges of 0.11–0.5, 0.51–1.5, and greater than 1.5, respectively [23].

Table 1. Toxic equivalency factor (TEF), mutagenic equivalency factor (MEF), and ERL and ERM reference values for PAHs and half-life time $T_{1/2}$ (days) of PAH degradation in soils.

PAH	Abbreviation	Rings	TEF_i	MEF_i	NOAA-ERL	NOAA-ERM	Literature Data * $T_{1/2}$
Naphthalene	Nap	2	0.001		260	2100	-
Acenaphthylene	Acy	3	0.001		44	640	-
Acenaphthene	Ace	3	0.001		16	500	-
Fluorene	Fl	3			19	540	340
Anthracene	Ant	3	0.01		85	1100	160
Phenanthrene	Phen	3	0.001		240	1500	310
Fluoranthene	Flu	4	0.001		290	600	110–4745
Pyrene	Pyr		0.001		670	2600	250
Chrysene	Chr		0.01	0.017	-	-	390
Benzo(a)anthracene	BaA		0.1	0.082	261	1600	240–730
Benzo(b)fluoranthrene	BbF	5	0.1	0.25	-	-	87–5183
Benzo(k)fluoranthrene	BkF		0.1	0.11	-	-	139–4015
Benzo(a)pyrene	BaP		1	1	430	1600	151–5329
Dibenzo(a,h)anthracene	DhA		1	0.29	63	260	240–730
Benzo(ghi)perylene	BgP	6	0.01	0.19	-	-	173–657
Indeno(1,2,3-cd)pyrene	InP		0.1	0.31	-	-	58–730

* Kusmierz et al. [4].

On the other hand, the toxic carcinogenic equivalents (*TEQ*) and mutagenic equivalent (*MEQ*) can be calculated using the toxic equivalent factor (*TEF*) and mutagenic equivalent factor (*MEF*) for PAHs (Table 1) through the following Equations (2) and (3).

$$TEQ = \sum Ci \times TEF_i \tag{2}$$

$$MEQ = \sum Ci \times MEF_i \tag{3}$$

where Ci is the concentration of PAH components in the sediment, and TEF_i and MEF_i represent the toxic and mutagenic equivalence factors, respectively, for PAHs relative to benzo(a) pyrene (BaP) [24–26].

3. Results and Discussion

3.1. Sediment Characteristics

According to the sediment grain size in each subsample obtained from the core profile, three strata were identified that did not show statistically significant differences (ANOVA) and therefore were grouped into depth ranges (Table 2). Sand, clay, and silt materials are distributed in these zones; therefore, the first stratum (A) corresponds to a depth range of 0.0–0.2 m ($p \geq 0.89$), and stratum B ($p \geq 0.92$) and C ($p \geq 0.94$) were determined at depth intervals of 0.2–0.6 m and 0.6–1.1 m, respectively (Table 2).

Table 2. Content (%) of clay, sand, and silt in the sediment core.

Depth (m)	Zone	Clay	Sand	Silt
0–0.2	A	0.9 ± 0.04^{a}	31.36 ± 26.5^{a}	67.73 ± 25.6^{a}
0.2–0.4	B	3.71 ± 1.69^{b}	10.61 ± 49.6^{b}	85.66 ± 36.1^{b}
0.4–0.6		3.32 ± 0.75^{b}	13.20 ± 33.6^{b}	83.47 ± 25.5^{b}
0.6–0.9	C	2.58 ± 0.15^{c}	21.01 ± 8.1^{c}	76.41 ± 7.4^{ab}
0.9–1.1		2.86 ± 0.44^{c}	22.48 ± 20.9^{c}	75.31 ± 17.5^{ab}

In-line, different letters indicate significant differences (Tukey; $p \geq 0.05$).

The content of materials found in the core profile indicates that the sediments are composed mostly of silt–sand and less clay content. The percentages of these materials vary with respect to depth, with higher sand content (31.36%) in the first meters of 0.0–0.2 m, decreasing at depths of 0.2–0.6 m in the range of 10.61–13.20%, and a slight increase in 21.01–22.48% at a depth of 1.1 m, while the content of clay and silt (%) were lower mainly in the upper layer. However, an increase is observed after 0.2 m (Figure 2), suggesting a high dynamic of the ecosystem with the influence of marine and fluvial currents that contribute to the transport and deposition of sand and silt. According to Flemming [27], sandy sediments indicate high-energy conditions, as observed in the mouths of communication with the sea, as well as in areas close to these or with greater marine influence. The granulometric analysis allows us to understand those changes in the dynamics of the sediments. In the present study, the low clay content indicates hydrodynamic conditions of high energy, which is consistent with the high sand content typical of lotic environments.

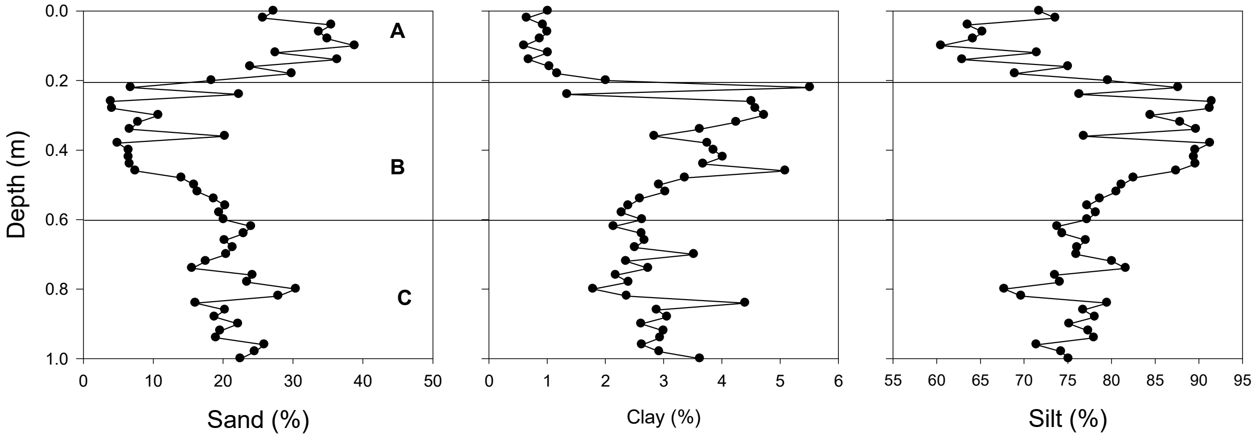

Figure 2. Content (%) of sand, clay, and silt in the sediment core with respect to depth (A, B, C: sediment stratus).

On the other hand, the calcium carbonate concentration was variable in the first 0.2 m of depth with a range of 17.82–47.86%, while at depths greater than 0.4 m the calcium carbonate content gradually decreased with respect to depth from 33.32% to 23.3% (Figure 3d). Studies suggest that calcium carbonate enrichment was directly associated with coarse-sized particles (<63 µm) of biogenic origin, particularly in sediments collected at greater depths [28].

However, the present study showed a higher content of fine sediments and calcium carbonate than that reported by Corredeira et al. [29] in the range of 10–12.8%. Calcium carbonate enrichment was only observed in the first 0.2 m, becoming homogeneous at greater depths, with a low correlation between calcium carbonate content (r^2 = 0.051) and porosity along the core profile (Figure 3a), which suggests the presence of sediments with homogeneous sedimentological characteristics and which is an indication of high biological productivity in the system lagoon of Pom–Atasta. Similarly, the total organic carbon (TOC) profile, as shown in Figure 3c, fluctuates uniformly between 3.8 and 6.7%, which is probably related to a constant flow of particulate material homogeneous in its size and composition of TOC, showing a low correlation of the TOC (r^2 = 0.61) that suggests a relative degradation of the organic material after its deposition, as can be observed in the profile of organic matter (OM) and total organic carbon (TOC) (Figure 3b and Figure 3c, respectively).

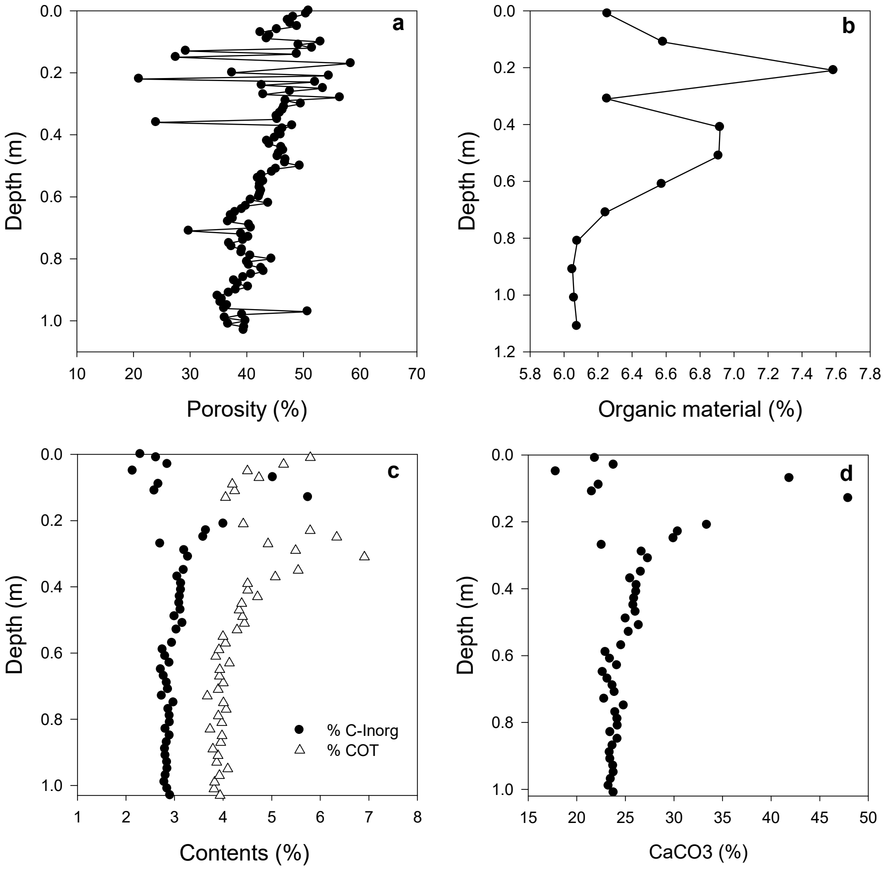

Figure 3. Content (%) of porosity (**a**), organic matter (**b**), total organic carbon (**c**), and carbonate (**d**) in the sediment core.

Similar results were reported by Partida-Gutiérrez et al. [30] in sediment cores in the southern region of the California basin, concluding that the low correlation between the surface area and the TOC percentage may be related to the degradation of organic matter of marine and terrestrial origin. This is consistent with the report by Rasheed et al. [31]; the degradation rate of organic matter and organic carbon is higher in sandy sediments than in sediments with clay and silt; therefore, the content of organic matter can become high in silt–clay sediments due to its high surface area and great affinity with organic matter, becoming adsorbed or absorbed and deposited in the sediment where it is partially mineralized. This agrees with the results obtained in the sediment core, with an increase in OM and TOC from the surface to 0.4 m, corresponding to a higher content of clay and silt with respect to other deeper sections of the core (Figures 2 and 3). This means that the mineralization processes occur mainly in the first 0.4 m. Similar results were reported by de la Lanza-Espino et al. [32] for sediments from a tropical coastal lagoon system in northeastern Mexico, observing a higher OC content (from 2253 to 4080 μmol d^{-1}) in silt/clay sediment samples compared to sandy sediments (from 662 to 2440 μmol d^{-1}).

In particular, environmental factors are closely related to the variability of calcium carbonates, organic and inorganic carbon, and organic matter (OM) on the surface of the sediment core (Figure 3), which contributes to a homogeneous sediment at lower depth levels. The sediment core extracted from the water mass exchange zones from the Terminos lagoon and the Pom and Atasta lagoons suggest that the study site presents high biological dynamics and productivity, with the marine currents (hydrodynamics) and the terrestrial and fluvial contributions contributing to the characteristics of the sediments [33]. According to Magni et al. [34], hydrodynamics and geomorphology play an important role in the distribution and transportation of fine sediments and organic matter. In the present study, the thixotropic property of silt and clay allows the OM content to become homogeneous throughout the depth of the core. This suggests that the sediments of the Terminos lagoon have acted as a trap for organic carbon and organic matter, which is frequently associated with the content of silt and clays in mangrove sediments from tropical regions. In this context, organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) are more likely to enter and be retained in this type of ecosystem, which becomes threatened by the anthropogenic activities that occur in the region.

The hydrodynamics in Terminos lagoon indicate that during the three climatic seasons (rainy, northern, and dry), the highest flow velocity (0.497–0.598 m s^{-1}) is observed in the Boca de Carmen area, in contrast to the Boca de Puerto Real (0.35–0.441 m s^{-1}), suggesting that high flows in the Boca de Carmen influence sedimentation within the core extraction site (Figure 1) [35]. Studies suggest that the resulting circulation in Terminos lagoon is induced by tidal and wind forcing simultaneously; thus, the largest inflow (flow) of water mass through the Boca de Carmen comes from marine waters, circulating in the direction of east to the central part of the Terminos lagoon, while the reflux is an opposite pattern from the mouth of the Candelaria and Mamantel rivers. The flow speed decreases rapidly to magnitudes close to 0.10 m s^{-1} in channels and shallow areas, so that the sediments in the study area probably have marine and pluvial characteristics [36].

3.2. PAH Source and Toxicity

PAHs are widely distributed in the environment and can be emitted from various sources to become deposited in sediments within aquatic systems and become part of a record of likely sources of PAHs over time. In the present study, the analysis of the concentration of PAHs in each subsample of the core (10 cm deep) showed a high significant variability (p = 0.0042) from the surface to 1.7 m deep. This has been attributed to the distribution and concentration of materials such as clay, silt, sand, and organic matter along the core profile, which also contributes to the fact that some PAHs become accumulated in said materials or migrate to deeper areas, increasing their persistence. In the present study, it was possible to observe that the concentration of PAHs in the core sediment decreases with increasing depth (Figure 4). The range of ΣPAHs in the 17 core subsamples was 527.0 ng g^{-1} dw at the top, decreasing to 75.7 ng g^{-1} dw at greater depths, with a mean range of 5–35.1 ng g^{-1} dw. A similar trend has been reported by various authors, concluding that this decrease in PAHs in aquatic sediment cores is attributed to the fact that these ecosystems contain a recorded history of anthropogenic PAH input but that fossil fuel combustion has been the primary source in sediment cores [37,38]. According to the criteria to infer the level of contamination, concentrations of ΣPAHs in sediments 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 [39]. Therefore, in the present study, it is possible to conclude that the surface sediment (0–0.2 m) shows moderate contamination, the most prevalent being acenaphthene, flouranthene, benzo (a) anthracene, benzo (a) pyrene, and benzo (k) fluoranthene.

Along the depth of the sediment core, two possible sources (petrogenic and pyrolytic) were identified according to the number of aromatic rings, called polycyclic aromatic hydrocarbons of low molecular weight (LWM, from 2 to 3 rings) and high molecular weight (HWM, from 4 to 6 rings). The results suggest that both LWM hydrocarbons (from 96.2 to 292.8 ng g^{-1} dw) and HWM hydrocarbons (from 80.0 to 261.8 ng g^{-1} dw) prevail throughout the core profile (Figure 4). The proximity of the study area to the oil exploration and production seaport, as well as the transit of small boats and contributions from the rivers, could contribute to the transport and presence of LWM PAHs [20], while PAHs from HWM suggest deposits from combustion processes becoming retained and deposited in the sediment. The ΣLWM/ΣHMW rates for each depth section of the core confirm that there is a greater persistence of PAHs of pyrolytic origin with respect to that of petrogenic origin (Figure 4).

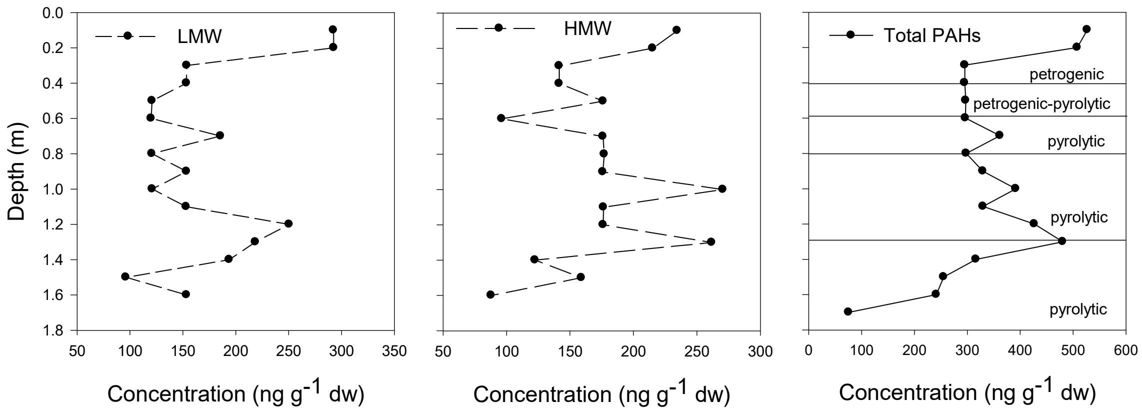

Figure 4. Concentration of ΣPAHs (LWM and HMW) and identification of PAH source in the sediment core.

Pearson's correlation analysis (Table 3) allowed the identification of PAHs from the same source, and the low correlation also suggests that some LWM-PAHs present along the core profile are likely to be degraded by some physicochemical or biological processes. It is a fact that changes in the concentration of PAHs in sediments are the result of various processes, such as volatilization, leaching, degradation, and binding with soil particles. The group of PAHs with 2 to 3 rings are recognized as the most susceptible to degradation, and this probably explains the low concentration of LMW-PAHs deeper in the core, although an increase in LMW-PAHs at a depth of 1.2 m was observed, while a greater persistence of HMW-PAHs (4 to 6 rings) at greater depths may occur, which is consistent with the positive correlations for this group of PAHs (Table 3), suggesting that HMW-PAHs have a lower rate of degradation in sediment. however, it is not ruled out that migration processes may occur, as reported by Kusmierz et al. [4], which can occur due to various factors such as the PAH solubility in water, dissolved organic carbon, colloids, pH, porosity of soil, and functional groups. The low values of correlation coefficients (-0.02 to -0.49) obtained in the present study for PAH groups of 4–6 rings indicate a probable migration from the surface layer to the subsurface layer. The process of migration and the persistence of high molecular weight compounds are related to the half-life time ($T_{1/2}$) of PAH degradation in soils reported in the literature, which is high for Chrysene; Fluoranthene; Benzo(a)anthracene; Benzo(a)pyrene; Benzo(b)fluoranthrene; Benzo(k)fluoranthrene; Dibenzo(a,h)anthracene; Benzo(ghi)perylene; and Indeno(1,2,3-cd)pyrene (Table 3). Therefore, the analysis of HMW-PAHs in the sediment core suggests a null degradation and greater persistence in sediment, allowing a probable migration to deeper layers and thereby becoming confined for long periods of time, as can be observed in Figure 4, where the accumulation of PAH compounds (LMW and HMW) occurs to a depth of 1.2 m. Similar results have been reported in ecosystems impacted by hydrocarbon spills, suggesting that many of these compounds migrate to greater depths, becoming accumulated within the sediment without changes in their concentration for long periods of time [40].

In addition to anthropogenic inputs, it has been recognized that early diagenesis of certain precursor molecules can produce polycyclic aromatic hydrocarbons such as perylene, phenanthrene, and chrysene derivatives [37]. The increase in the concentration of some of these compounds with increasing depth in the core is often interpreted as evidence of in situ diagenesis. However, in the present study, in each deep section of the core a low variation in the concentration of phenanthrene and chrysene was observed, suggesting a lower diagenic contribution compared to anthropogenic contributions (petrogenic and pyrolytic sources).

Table 3. Pearson's correlation coefficient matrix of PAHs in sediment core.

	Nap	*Acy*	*Ace*	*Fl*	*Ant*	*Phen*	*Flu*	*Chr*	*BaA*	*BbF*	*BkF*	*BaP*	*DhA*	*BgP*	*InP*
Nap	1.00														
Acy	0.21	1.00													
Ace	−0.14	−0.18	1.00											LWM	
Fl	0.39	−0.12	0.30	1.00											
Ant	0.25	−0.39	−0.06	−0.04	1.00										
Phen	0.21	−0.06	0.33	0.54	−0.39	1.00									
Flu	0.55	0.11	0.03	0.22	0.72	0.11	1.00								
Chr	0.67	0.14	−0.17	0.27	0.56	0.14	0.84	1.00							
BaA	0.08	0.54	−0.02	0.19	−0.04	−0.12	0.22	0.27	1.00						
BbF	0.30	0.07	0.19	0.12	0.38	0.06	0.54	0.45	0.13	1.00					
BkF	0.38	0.19	0.29	0.02	0.33	0.18	0.63	0.47	0.02	0.34	1.00			HMW	
BaP	0.30	0.06	0.19	0.12	0.39	0.06	0.54	0.45	0.12	1.00	0.34	1.00			
DhA	0.01	0.38	0.32	0.37	−0.44	0.38	−0.04	0.05	0.37	−0.40	0.20	−0.40	1.00		
BgP	−0.28	0.17	0.21	−0.04	−0.14	0.16	0.04	−0.06	−0.04	−0.17	0.07	−0.17	0.14	1.00	
InP	−0.49	−0.10	0.46	−0.19	−0.17	−0.10	−0.31	−0.24	−0.17	0.10	−0.12	0.10	0.18	0.18	1.00

In the present study, combustion products from pyrolytic processes at low temperatures or petrogenic sources could explain the increase in HMW [20], while LWM concentrations suggest contributions from the discharge of petroleum products into rivers and the ocean from different sources (oil leakage, groundwater contamination, dry and wet atmospheric deposition, and by direct discharge from anthropogenic activities into the sea [41] (Figure 4)).The PAH compounds of 4 to 6 rings, although in greater presence at greater depths, show a low probability of ERM toxicity quotient of 9% (Figure 5), which is consistent with the ERL levels and ERM (Table 1).

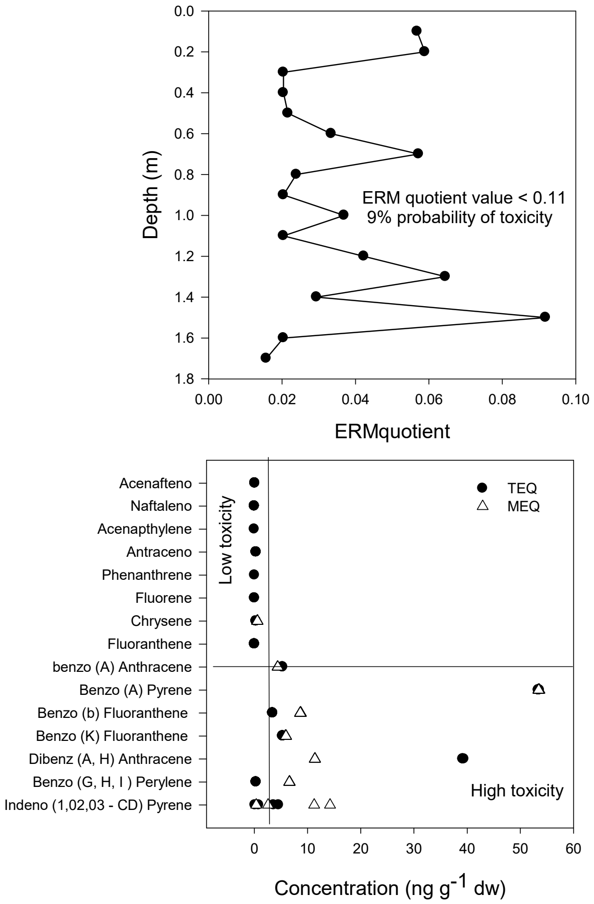

Figure 5. Ecotoxicity (ERM quotient) and toxic carcinogenic equivalent (TEQ) and mutagenic equivalent (MEQ) of PAHs at the depth of the sediment core.

The analysis of the mutagenic toxic equivalent (TEQ^{carc}) in each section of the core was variable, decreasing with greater depth. For the first 0.3 m, a higher TEQ was observed with a range of 102.38–107.91 ng TEQ g^{-1} dw, while from 0.4 m to 1.7 m the range was 57.65–63.46 ng TEQ g^{-1} dw. The TEQ^{carc} values obtained in the present study were lower than those reported by Tu et al. (2018), in river mouth sediments, of 183–262 ng TEQ g^{-1} dw, predominantly Benzo (a) pyrene (131–188 ng TEQ g^{-1} dw).

On average, the sediment core shows that the compounds benzo(a)pyrene 53.55 ng TEQ g^{-1} dw) and dibenzo(a,h) anthracene (29.2 ng TEQ g^{-1} dw) had the highest TEQ^{carc}, suggesting two carcinogenic compounds throughout the nucleus (Figure 5). This should lead to proposed monitoring programs for the sediments and the sources of the generation of PAHs in the study site due to the persistence observed along the core profile of these two compounds. 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 (0.114 ng g^{-1} cm^2) were low according to the EU guidelines of 6.0 ng g^{-1}. Similarly, this agrees with the sum of the concentrations Σ BaP + BbF + BaA + Chr (0.262 ng g^{-1} cm^2), which did not exceed the EU limit of 35.0 ng g^{-1} [42]. In summary, the characteristics of the core sediment extracted from the Pom–Atasta–Terminos lagoon system suggest a high-energy system, which influences the characteristics of the sand–silt-type sediment, allowing the absorption of OM and hydrocarbons (PAHs). The analysis of PAHs in the sediment core showed a greater presence of pyrolytic sources resulting from the combustion of hydrocarbons, while low molecular weight hydrocarbons are related to hydrocarbon spills, wastewater discharges and river discharges; however, the toxicity levels were not high according to the TEQ^{carc} and ERM quotient parameters.

4. Conclusions

The content of PAHs in the core sediment allows an analysis of persistence and sources according to the rates of $\Sigma LWM/\Sigma HMW$ for each deep section of the core, suggesting that the study area has a greater accumulation of PAHs of pyrolytic origin. On the other hand, the analysis of PAHs in each section of the core suggests a low risk of toxicity and carcinogen. However, some of the PAHs found in the core sediment, such as benzo (a) pyrene and dibenzo (a,h) anthracene, have been associated with a higher TEQ^{carc}, which can become a threat to organisms and consumers. Therefore, given the proximity of oyster farms and various natural resources to anthropogenic activities, it is advisable to install monitoring programs for the conservation of these ecosystems and preserve the health of the oyster farms, which is a national economy and food source for the inhabitants of Mexico.

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Data Availability Statement: The concentration of PAHs and granulometry data used to support the findings of this study are included within the article and could be made available from the corresponding author upon request.

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