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Original Research

Polycyclic Aromatic Hydrocarbons (PAHs) in Surface Sediments of Two Polluted Lagoons in Saudi Arabia

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Abstract

Al-Arbaeen and Al-Shabab are two highly polluted lagoons lying along the Jeddah Coast. Surface sediments were collected from both lagoons to assess the levels and spatial distribution of polycyclic aromatic hydrocarbons (PAHs), as well as study the effect of environmental conditions on PAH concentrations. The concentration ranges for ∑38-PAHs in Al-Arbaeen and Al-Shabab lagoons were 5.4-5,372 ng/g (mean 1,637 ng/g) and 60-7,927 ng/g (mean 1,323 ng/g), respectively. Pollution levels in both lagoons were in the low-very high range with dominance by three- and four-ring congeners. Pyrene was the dominant congener, while benzo (a) pyrene represented the dominant carcinogenic congener in the study area. The disappearance of most of the low molecular weight congeners may be attributed to temperature and microbial activity. Carcinogenic PAHs contributed 59.9 and 23.6% for Al-Arbaeen and Al-Shabab lagoons, respectively. The diagnostic ratios revealed that the source of PAHs are of mixed origin and site specific. The probable toxic effects on organisms were examined for total and individual PAHs with sediment quality guidelines (ERL-ERM). The detected PAHs levels in the present study were compared with reported levels for coastal worldwide lagoons.

Keywords: polycyclic aromatic hydrocarbons (PAHs), coastal lagoon pollution, sediment quality guidelines, Red Sea

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are an important class of anthropogenic organic contaminants. PAHs are semi-volatile compounds where both urban and industrial activity contributes to increasing its concentrations in various environmental compartments, particularly in highly stressed areas like harbors and shallow coastal lagoons [1]. The high hydrophobicity and strong affinity toward organic matter leads PAHs to accumulate in sediments and suspended organic matter rather than in the dissolved phase [2]. Therefore, sediment could be a reservoir and source for these pollutants [3]. Sources of PAHs in the environment can naturally occur (biogenic) or anthropogenic due to human activities. Anthropogenic sources could be either petrogenic (directly associated with petroleum hydrocarbons) and/or pyrogenic as a result of incomplete combustion of

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recent and fossil organic matter [1]. Due to its toxicity, 16 PAH congeners have been classified as priority pollutants by the United States Environmental Protection Agency (USEPA), and seven of them are considered as probably carcinogenic [4].

Jeddah is the second largest city in Saudi Arabia after the capital Riyadh, and has extended residential areas in the north and industrial areas to the south, including a development extended to the sea along reef flats that utilizes the coastal area for residential and corniche purposes. Domestic and industrial water supply, treatment and disposal of sewage, water draining from both natural and manmade sources and management of the marine environment for commercial and recreational uses are among the most prominent sources for organic and inorganic pollutants in the coastal area of Jeddah. Further sources of organic pollutants in the coastal area are loading/unloading operations in Islamic Harbor, fishing vessels, the desalination plant and atmospheric deposits from the exhaust of around two million cars in the city – which all enrich the coastal area with a wide scope of organic pollutants. Due to pollution stress on the Jeddah coast, many monitoring studies have been done in coastal areas with specific interest in heavily polluted areas like Al-Arbaeen and Al-Shabab lagoons. The studies include heavy metals [5-7], nutrients [8-9], aliphatic and total hydrocarbons, fecal sterols [10-11], and polychlorinated biphenyls [12]; where most of these pollutants were found at high levels. In contrast, the northern coastal part of the city showed very low concentrations for all mentioned pollutants as observed in Obhur creek [8, 10-11].

During the last decade, few scattered studies have been done on PAHs in the Red Sea, where major studies focused along the Egyptian coast on sediments [13], mussels [14], and shrimp [15]. Recently, bioaccumulation of PAHs in brown algae through the Jeddah coast (eastern side of the Red Sea) has been determined [16]. To our knowledge, individual PAHs are not investigated in Jeddah sediments. The objectives of this article aimed to 1- assess the levels of PAHs in surface sediments for an important part of the coastal area of Jeddah covering both Al-Arbaeen and Al-Shabab lagoons as a model for heavily stressed areas by different anthropogenic pollutants over a long period of time. 2- predict the probable sources of PAHs and the study of the effect of environmental parameters on the concentrations of total and individual congeners of PAHs. 3- examining the eco-toxicological risk for PAHs in the sediments with sediment quality guidelines (SQG). 4- finally comparing the detected PAH levels of the studied lagoons with the coastal lagoons all over the world.

Materials and Methods

Study Area

Al-Arbaeen and Al-Shabab lagoons are about 1 km apart and merge to connect with the Red Sea via a 500 m-wide opening. The Al-Arbaeen and Al-Shabab lagoon inlets are having length of 1.5 and 1 km with mean widths of 300 and 170 m and mean depths of 6 and 5 m, respectively. These two inlets have been used for the wastewater dumping site for Jeddah since the 1970s. Al-Arbaeen lagoon daily receiving about 100,000 m^3 of partially treated sewage water [17]. Al-Shabab inlet has an elongated shape that favors communication and exchange with the open sea, while Al-Arbaeen inlet has a more complex T-shape composed of two loops extending in an almost NE-SW direction (Fig. 1). This configuration

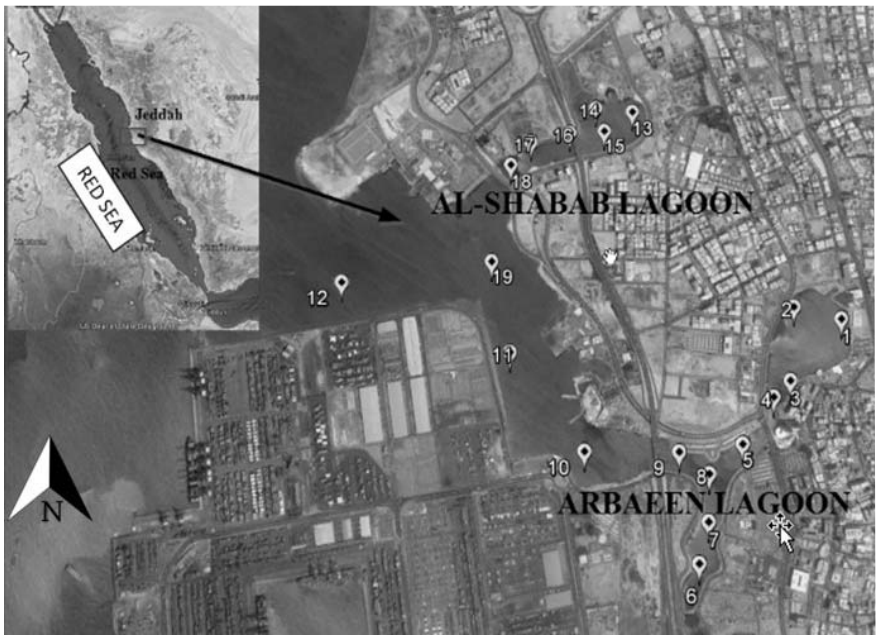

Fig. 1. Study area showing sampling sites from both lagoons: Al-Arbaeen (1-12) and Al-Shabab (13-19).

renders the exchange with the open water difficult and may extend the flushing time of the inlet.

During 2001 Jeddah municipality made a rehabilitation program for both lagoons, where around 3 m thick sludge was dredged to maintain the water column saturated with dissolved oxygen, which might bring the system back to oxic respiration; moreover, twenty air pumps were fixed in each lagoon for the same purpose. Recently, environmental conditions of the lagoons were back to near the situation before the rehabilitation process due to continuous partial treated sewage dumping [18]. These conditions enhance revisiting lagoons to monitor environmental parameters and ecological risk assessment. The sampling sites presented in Fig. 1 **(**sites from 1 to 12 represent Al-Arbaeen lagoon, while sites 13 to 19 represent Al'Shabab lagoon) and Obhur creek (site 20-21, not included in the map).

Sample Collection and Preparation

Twenty-one surface sediment samples were collected from the study area using a Van Veen grab (top 5 cm) during November 2015. The samples were preserved at -20ºC until analysis. Sediment samples were freeze-dried, homogenized, and sieved through a stainless steel sieve (125 µm).

Organic Carbon, Carbonate, and Grain Size Analysis

Organic carbon in the sediments was analyzed using the wet dichromate-sulphuric acid oxidation method [19]. Diluted hydrochloric acid (HCl 37%, BDH) was used for treating the dry powdered samples to determine the carbonate content. The standard dry sieving technique was used for sediment grain size fractions, which were classified as fine (mud<0.063 mm), sand (0.063-2 mm) and gravel (>2 mm) [20].

Extraction and Cleanup

Approximately 40 g of freeze-dried sediment sample were extracted using soxhlet with 100% dichloromethane (DCM) for 24 hours. Sulfur was removed by the addition of metallic copper. All samples were spiked with deuterated recovery surrogate mixture PAHs (naphthalene-d8, phenanthrene-d10 and chrysene-d12) (250 µl, 5 ppm) prior to extraction. The extracts were concentrated to approximately 1 ml and transferred to a silica-alumina column for cleanup and fractionation. The column was packed from top and bottom with pre-combusted anhydrous Na_2SO_4 at 450ºC for six hours. Silica gel (230-400 mesh) and alumina (neutral, 70-230 mesh) were activated at 230°C for 12 hours and then partially deactivated with 5% deionized water. The elution was done using n-hexane (F1) for aliphatic fraction followed by n-hexane/ DCM (70:30 v/v) (F2) for PAH fraction [21]. The F2 fraction was concentrated using a gentle stream of pure N_2 to nearly 1 ml DCM. Deuterated internal standard mixture (acenaphthene-d10, flourene-d10 and perylene-d12; 100 µl, 5 ppm) was added just before injection into GC-MS.

Quantification and Qualification of PAHs

PAH analysis was done using GC-MS (Schimatzu 2010) with a DB-5MS column (30 m* 0.25 µm, RTX). The temperature was programmed initially at 100ºC with a one-minute hold, and then ramped to 6ºC/minute to 300ºC and held for three minutes. The electron energy of the mass spectrometer was 70 eV. Individual PAHs were identified based on both retention time and mass spectrum of selected ions with the external calibrated standards. Priority 16 PAH parent targets were: naphthalene (NAP) (m/z 128), acenaphthylene (ACY) (m/z 152), acenaphthene (ACP) (m/z 154), flourene (FLR) (m/z 166), phenanthrene (PHE) (m/z 178), anthracene (ANT) (m/z 178), flouranthene (FLT) (m/z 202), pyrene (PYR) (m/z 202), benzo (a) anthracene (BaA) (m/z 228), chrysene (CHR) (m/z 228), benzo (b) flouranthene (BbF) (m/z 252), indeno [1,2,3-cd] pyrene (IcP) (m/z 276), dibenzo [a,h] anthracene (DahA)(m/z 278), and benzo [ghi] perylene (BgP) (m/z 276). Alkylated PAH homologs were quantified using the response factor of the corresponding non-alkylated parent PAH [22]. Numbers were added to the parent congeners to indicate the abbreviations for respective alkylated parent PAHs (ex. PHE2: dimethylphenanthrene).

Quality Control and Quality Assurance

Procedural blanks (one blank for each five samples) and duplicate samples (10% of the analyzed samples) were performed at the same time with analysis. Calibration standards were run at the beginning of each working day before each sample batch to establish the calibration curves for PAHs. All samples were spiked with surrogate deuterated mixture before extraction. Deuterated internal standard mixture was added just before GC-MS injection. The recoveries of sediment samples ranged between 71-112% with RSD <19%. The concentrations in the procedural blanks were no more than three times the method detection limit. Detection limits (DL) were calculated through five-point calibration curve and extrapolated for determining the y axis intercept [23], which ranged from 0.42 to 3.21 ng/g. All results were expressed as dry weight basis, and those samples with concentrations less than DL were reported as not detected (ND).

Results and Discussion

Levels of Polycyclic Aromatic Hydrocarbons (PAHs)

Total PAH (∑38 PAHs) concentrations for Al-Arbaeen Lagoon ranged from 5.4 to 5,371.8 ng/g (∑16 PAHs: 5.4-2,543.3 ng/g) with an average 1,682.3 ng/g (∑16 PAHs average 561.6 ng/g), while Al'Shabab

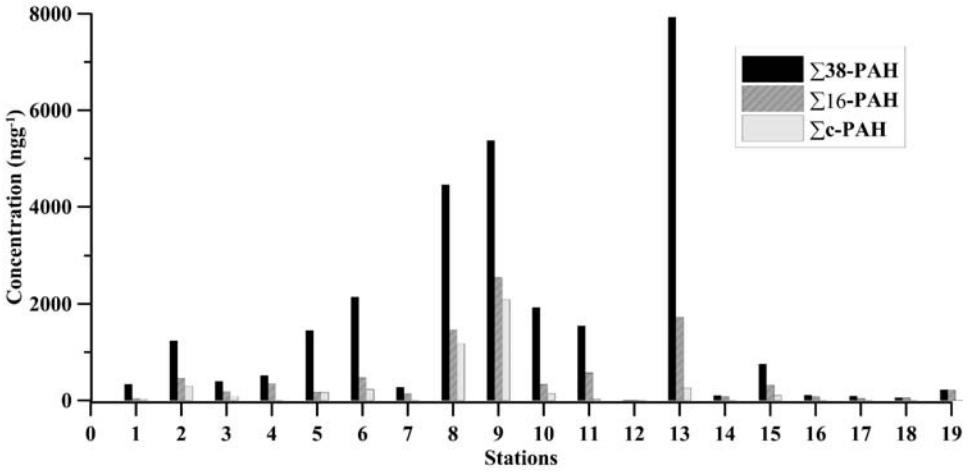

Fig. 2. Distribution of ∑38 PAHs, ∑16 PAHs, and ∑c PAHs (ng/g) for both lagoons.

Lagoon showed comparable values for ∑38 PAH ranging from 60 to 7,927.2 ng/g (∑16 PAHs: 39.3-1,729.1 ng/g), with an average of 1,323.5 ng/g (∑16 PAHs average 359.6 ng/g). As expected, Obhur creek showed a very low concentration and recorded only 15 ng/g. The range of PAH concentrations found in the present study (except for Obhur creek) was around five orders of magnitude higher than those reported in the Egyptian Red Sea coast (ranging between 0.74 to 456 ng/g (average 33 ng/g)) [13], where most samples were collected from remote areas.

The highest concentrations for ∑38 PAHs in Al-Arbaeen Lagoon were observed at Station 9 (5,371.8 ng/g) followed by Station 8 (4,454.7 ng/g) (Fig. 2), where both stations were located near to sewage disposal point (Fig. 1). Moreover, Station 9 presents an assemblage point for the T structure of the lagoon. On the other hand, the highest concentration (7927.2ng/g) in Al-Shabab lagoon was recorded at the innermost part (Station 13) of the lagoon (Fig. 1), where the shallow depth and restricted water circulation allow such accumulation of organic matter. The textural classification for stations 8, 9, and 13 are sandy-mud; moreover, significant positive correlation was observed between TOC and total PAHs (r = 0.98).

PAH pollution levels in the sediments are classified as: low (0-100 ng/g), moderate (100-1,000 ng/g), high (1,000-5,000 ng/g), and very high (>5,000 ng/g) [24-25]. Accordingly, only stations 9 (Al-Arbeean lagoon) and 13 (Al-Shabab lagoon) represent the very highly polluted areas, while station 12 that located outside the lagoons and away from discharge point, showed a very low concentration for ∑38 PAHs (5.4 ng/g), with 1,000 order of magnitude lower than most inner lagoon stations, which may confirm the stagnant state of pollutants. Consequently, both lagoons are classified as being low-to-very highly polluted by PAHs [24-25].

Characteristics of sediments in the study area (grain size, carbonate percentage, and TOC contents) are summarized in Table 1. The mean sand value for Obhur creek showed the highest value of 91.2%, while the values for Al-Arbaeen and Al-Shabab lagoons were 38.3% and 44.9%, respectively. On the other hand, mud fractions in Al-Arbaeen and Al-Shabab lagoons represent the major fraction, with mean values of 60.8% and 55.1%, respectively. These data are consistent with previous studies [6, 12], where the sewage disposal into both lagoons is considered the main reason for such increase in the mud fraction. Strong positive correlation was found between mud percentage and mean concentration of total PAHs (r = 0.9714), while a negative correlation was found between sand percentage and PAHs (r = - 0.9614). As expected, sediments contain higher finer fractions contain higher concentrations of PAHs, where greater surface area of the smaller particles provide a larger area for the adsorption of organic matter [26].

Table 1. Summary of ranges, means, and standard deviations for TOC, carbonate, and grain size analysis of the sediments in the studied lagoons.

Site name	TOC %	$CaCO_3$ %	Mud %	Sand %	Gravel %	Textural classification
Obhur Creek	0.2-0.34 (0.28±0.1)	69-89.9 (80.3±9.2)	0.04-4.86 (1.4±2.1)	92.2-97-1 (91.2±4.3)	1-14.3 (7.4±5.2)	Sand
Al-Arbaeen Lagoon	2.8-8.5 (4.9±4.3)	11.3-62.2 (50.1±10.5)	6.9-92.9 (60.8±32.2)	6.9-88.1 (38.3±37.2)	0-4.9 (0.9±0.04)	Sandy-mud
Al-Shabab Lagoon	2.5-11.8 (4.6±2.3)	38.7-66.4 (39.1±14.1)	21.4-88.5 (55.1±27.3)	11.5-78.6 (44.9±27.2)	0-0.07 (0.01±1.5)	Sandy-mud

Individual Congeners and Ring Size

PAHs are distinguished between low molecular weight (LMW≤3 fused rings) and high molecular weight (HMW≥4 fused rings) congeners [24]. Although PAHs are hydrophobic, two-ring PAHs (and to a lesser extent three-ring PAHs) dissolve in water [1]. As expected, due to the low solubility, four-ring compounds were dominant in the sediments for most stations in both lagoons with high contributions of two- and three-ring compounds at stations 9 and 11, while station 16 showed fully four-ring compounds. Station 9 showed chrysene as the highest concentration for the individual parent congener at Al-Arbeean lagoon (2,088.7 ng/g), while pyrene was the most dominant congener in Al-Shabab lagoon with the highest value of 1,471 ng/g at Station 13, these data are consistent with very low concentrations of chrysene (6.04 ng/l) and pyrene (4.67 ng/l) in water columns in the same area [16]. Among 21 analyzed stations, most of the parent low molecular weight (2-3 rings) compounds were absent; however, their corresponding alkylated derivatives are present in abundance. Only phenanthrene, as the most persistent three-ring congener due to its extra stability structure [27], was detected in oxic (stations 10-12 and 16-21), hypoxic (stations 13-15), suboxic (stations 6-9), and anoxic (stations: 1-5) stations in both lagoons. Moreover, phenanthrene was detected in Obhur creek as the sole parent PAH congener in this clean area located 40 km north of the polluted lagoons. The absence of the low molecular weight PAH congeners can attribute to the relative high temperature all year in the study area (min. 23ºC during January, max. 32ºC during July), leading to escape of light PAH congeners through volatilization in such shallow water depth as well as high degradation in hot climatic conditions [28]. The effect of temperature on PAH concentrations clearly appeared in the seasonal variations in PAH concentrations for both water and algae in Jeddah Coast [16]. Such behavior frequently occurs in hot areas like Al-Kifil, Iraq [29], and western Saudi Arabia [30]. This phenomenon was also recognized with light polychlorinated biphenyl (PCBs) congeners in Jeddah coast [12].

Microbial degradation may also play an important role in the disappearance of low molecular weight congeners in the study area. The two studied lagoons are heavily stressed with treated and untreated sewage disposal [9, 17-18] for a long time, which led to switching of oxic and suboxic conditions to completely anoxic conditions especially in Al-Arbaeen lagoon, where bottom water dissolved oxygen was zero under 3 m depth in most stations with the appearance of H_2S, while Al-Shabab lagoon showed comparatively well-mixed conditions [31]. Aerobic bacterial degradation of PAHs occurs through oxygenase-mediated metabolism, where oxygen acts as the final electron acceptor and co-substrate for the hydroxylation and oxygenolitic ring cleavage of the aromatic ring, while anaerobic catabolism is primarily based on reductive reactions using nitrate or sulfate ions as electron acceptors [32-33]. In the present study, different metabolic products such as hydroxyl, diol, ketone, nitro, and carboxylic acid derivatives for naphthalene, phenanthrene, anthracene, and acenaphthene congeners were observed alternatively in most stations. However, most of these compounds were observed in the inner part of Al-Arbeean lagoon (Station 2). Some of these compounds can be more toxic, water-soluble, and mobile than their parent PAHs [34]. It is worth to mention that the rates of microbial anaerobic degradation of PAHs are slower than aerobic conditions in most of the bacterial strains [35]. So, besides the low water circulation and different sewage disposal quantities, anaerobic conditions could be another factor for the high concentration of the average total PAHs in Al-Arbeean lagoon compared with Al-Shabab lagoon [36].

Alkylated PAHs of lower molecular weight congeners dominated over the parent compounds that disappear in most stations, except for fluorine at stations 7 and 8 and phenanthrene at suboxic-anoxic stations in Al-Arbaeen Lagoon. High concentrations were recorded for dimethylnaphthalene (2,088.7 ng/g) at station 9, trimethylphenanthrene (1,006.6 ng/g) and dimethyl-pyrene (551.8 ng/g) at Station 8, and tetra-methyl phenanthrene at station 13 (1,053.5 ng/g). These data are consistent with the petrogenic origin for PAHs, which are often marked by the abundance of alkyl-substituted PAHs such as alkyl naphthalenes and alkyl phenanthrenes [24].

The Probable Origin of PAHs in the Study Area

The major sources of PAHs in the environment are petrogenic, pyrogenic and biogenic [1]. Petrogenic PAHs are originally introduced to the environment through different sources of crude oil like exploration, tanker operations, and oil spill accidents. On the other hand, pyrogenic PAHs are produced mainly due to the incomplete combustion of organic matter like fossil fuel, wood, garbage, and coal [37]. In pyrogenic origin, the PAH mixture produced is characterized by unsubstituted and high molecular weight congeners, while petrogenic origin produces alkyl-substituted low molecular weight congeners [38]. It is highly difficult to discriminate between the pyrolytic and petrogenic origins of PAH mixture due to the complexity governing PAH distribution in marine sediments and the coexistence of PAH congeners from different sources [39]. However, several molecular ratios of selected PAH compounds have been used to provide information about PAH origin and sources. In the present study, due to the absence of some PAH congeners that are below detection limits, only four indices were used as fingerprints for PAH origin identification. These indices are HMW/LMW, A-PAH/P-PAH (alkylated/parent PAH), MP/P (methylated phenanthrene/phenanthrene), and the pyrogenic index which is ratio of the sum of the concentrations of EPA priority unsubstituted three- to six-ring PAHs to the

Table 2. Selected indices for pyrolytic and petrogenic origins of PAHs.

Diagnostic ratio [24]	Pyrogenic	Petrogenic	Al-Arbaeen		A-Shabab	
			Min.	Max	Min.	Max
HMW/LMW	>1	<1	0	3.3	1	30.5
A-PAHs/P-PAHs	Low	High	0	7.6	0.1	3.6
MP/P	<1	>2	0	33.5	-	-
Pyrogenic index	>0.8	<0.228	0.13	2.07	0.28	18.61

sum of the concentrations of four targeted alkylated PAH homologues (naphthalenes, phenanthrenes, fluorenes, and chrysenes) (Table 2) [38]. Fig. 3(a-c) present the original source ratios based on the applied evaluation indices. Stations 1, 2, and 8 in Al-Arbaeen Lagoon indicate petrogenic origin, while both stations 4 (Al-Arbeean) and 18 (Al-Shabab), which are located under heavily trafficked bridges, showed pyrogenic origins. However, values from the four indices revealed the mixed origin of PAHs for the remaining stations. These data are consistent with the forensic study of aliphatic hydrocarbon origins for sediments in the same area [10].

Carcinogenic PAHs and Ecological Risk Assessment

Among the 16 priority PAHs, carcinogenic congeners are: benzo (a) anthracene, chrysene, benzo (b) flouran-trene, benzo (k) flouranthrene, benzo (a) pyrene, indeno (1,2,3-CD) pyrene, and dibenzo (a,h) anthracene [4]. The sum of potentially carcinogenic PAHs (∑c PAH) for Al-Arbaeen and Al-Shabab lagoons ranged from ND-2,088.7 ng/g (average 471.6 ng/g) and ND-258.4 ng/g (average 181.5 ng/g) with percentage contributions of 59.9% and 23.6%, respectively, from the total Σ16 PAHs. Benzo (a) pyrene was the dominant carcinogenic congener in both lagoons. Chrysene, benzo (a) pyrene,

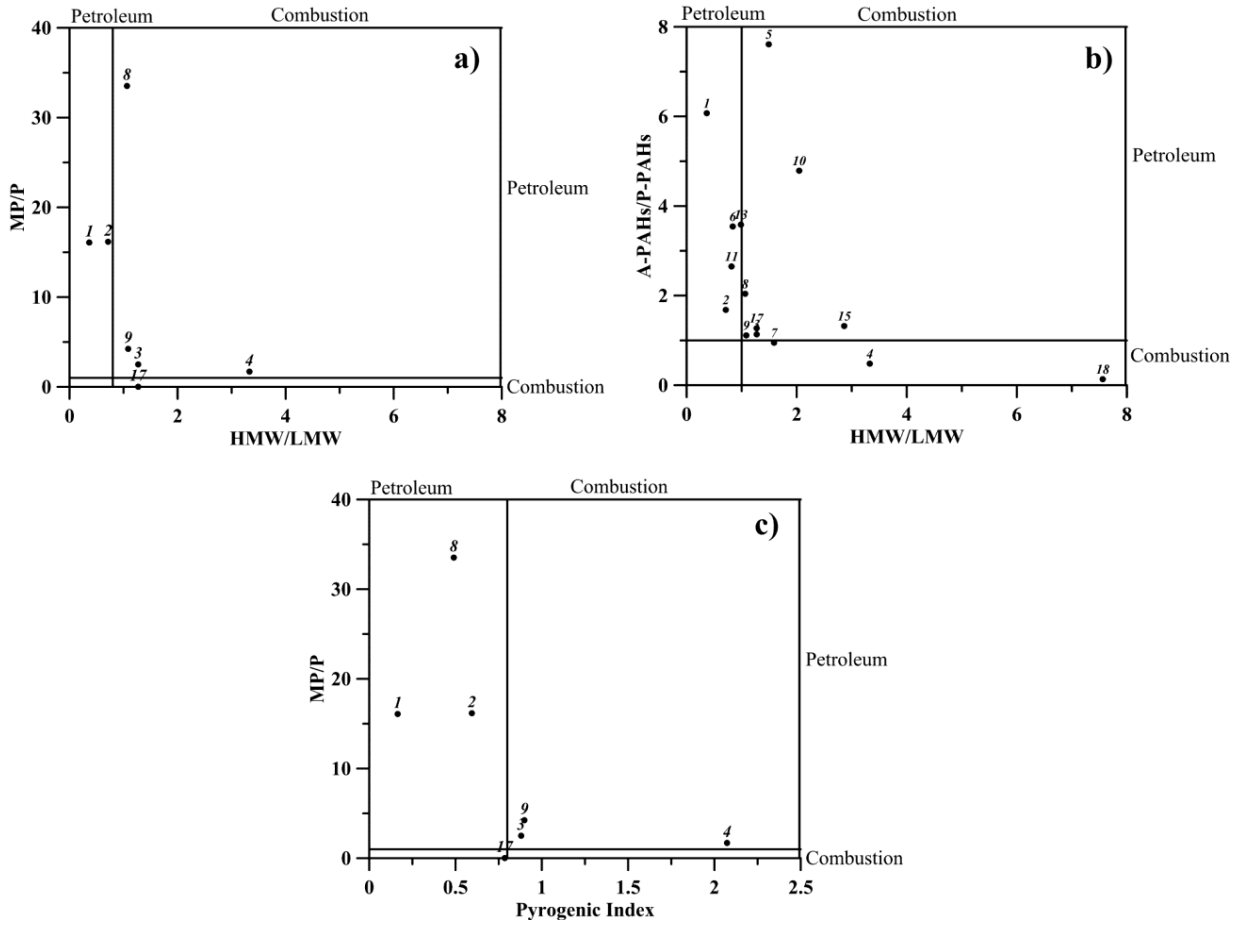

Fig. 3. Origin distribution of both lagoon stations based on diagnostic indices.

Table 3. Sediment quality guideline values (SQG) for PAH compounds and the concentration values in the study area (ng/g).

	SQG [39]		Al-Arbaeen		Al-Shabab		Stations of ERL~ERM	>ERM
Compounds	ERL	ERM	Range	Mean	Range	Mean		
NAP	160	2,100	ND	ND	ND	ND	-	-
ACY	44	640	ND	ND	ND	ND	-	-
ACP	16	500	ND	ND	ND	ND	-	-
FLR	19	540	7.6-9.9	8.7	ND	ND	-	-
PHE	240	1,500	5.4-73.8	35.9	ND-39.3	39.3		-
ANT	85	1,100	ND	ND	ND	ND	-	-
FLT	600	5,100	39.6-162.3	100.9	59.9-104.5	82.1	-	-
PYR	665	2,600	54.4-380.8	164.5	16.3-1,470.7	323.3	St.13	-
BaA	260	1,600	ND-13.0	13.0	ND	ND	-	-
CHR	380	2,800	51.5-2,088.7	684.4	ND	ND	St. 8, 9	-
B(b)F	-	-	15.9-287.8	81.4	ND	ND	-	-
B(k)F	-	-	10.7-30.4	20.5	51.3-97.6	74.4	-	-
BaP	430	1,600	12.7-344.8	113.1	7-207.1	107.1	-	-
IcP	-	-	16.1-120	68.1	ND	ND	-	-
DahA	63	260	ND-35.9	35.9	ND	ND	-	-
BghiP	85	330	18.8-546.2	141.5	ND-10.8	10.8	-	St. 11
∑16-PAH	3,912	25,340	5.4-2,543.3	561.6	39.3-1,729.1	359.6	-	-

and benzo (k) flouranthene were more contributed in Al-Arbaeen lagoon, while benzo (a) pyrene and benzo (k) flouranthene appeared in Al-Shabab lagoon with the highest values at inner stations (1-5 and 13-15) and reduced toward the outside of the lagoon. It is worth mention that both chrysene and benzo (a) pyrene showed the highest bioaccumulation factors for shrimp [15] and brown algae [16] in the Red Sea.

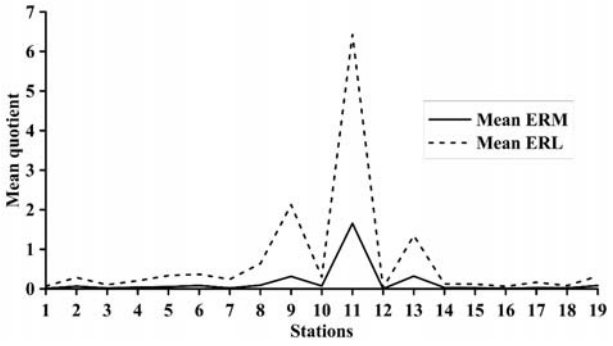

Fig. 4. Distribution of mean values of ERL-ERM quotient in the study area.

The development and application of sediment quality guidelines (SQGs) were greatly widespread and aimed to determine whether the sedimentassociated contaminants impaired the aquatic system. Long and Morgan derived the effect range low (ERL) and effect range median (ERM), which define three ranges associated with adverse effects [39]: rarely (below ERL), occasionally (above the ERL but below ERM), and frequently (above ERM). Whenever contaminant concentrations exceed ERM, the sediment samples were predicted to be toxic. For assessing the potential effects of PAHs, mean ERL/ERM quotient was applied [40]. Mean ERL quotient for total Σ16 PAHs were >1 for stations 9 and 13, while station 11 exceeded ERM (Fig. 4). In Al-Arbeean lagoon, individual congener chrysene exceeds ERL quotient at stations 8 and 9, while benzo (g,h) perylene at station 11 exceeds ERM. On the other hand, at station 13 (Al-Shabab lagoon) ERL quotient was greater than one for pyrene (Table 3). Although few individual congeners at specific stations exceeded ERL value and only one exceeded ERM, adverse biological effects hardly occur since mean ERL quotients were <1 for total PAHs in the majority of stations.

Table 4. Comparison of PAH concentration levels of the present studied lagoons with different lagoons all over the world.

Country	Lagoon	∑PAH ng/g	Pollution level	Sources	Origin*	Ref.
Benin	Cotonou	25.1-1,411	Low-high	Petroleum trade and waste oil	Petro.	[59]
Brazil	Patos	37.7-11,780	Low-very high	Industry and shipping	Mix of petro. and pyro.	[43]
	Rodrigo de la Freita	405-11,734	Low-very high	Traffic of boats and motor vehicles	Mix of petro. and pyro.	[44]
China	Yuandang	203.7-15,90.5	Moderate-High	Vehicle emissions, petroleum spills, and coal combustion	Predominantly pyro.	[58]
Cote d'Ivoire	Ebrie	ND-770,240	Low very high	Industrial activities	NR#	[50]
France	Berre	334-853	Low-Moderate	Industrial and municipal wastewater	Predominantly pyro.	[57]
	Etang de Thau	59-7,679	Low-very high	NR#	NR#	[48]
Iceland	Skongalon and Skogar	6-309	Low-Moderate	Hydrothermal	Pyro.	[54]
Italy	Venice	15.1-388.9	Low-Moderate	Industries, road, and ship traffic	Pyro.	[45]
	Santa Giusta	3.8-250.8	Low-Moderate	Urban wastewater and boat traffic	Pyro.	[51]
	Orbetello	3.8-250	Low- Moderate	Urban wastewater and boat traffic	Mix of petro. and pyro.	[51]
	Lesina	8.51-70.41	Low	Urban wastewater, boat traffic, and agricultural runoff	Pyro.	[51]
	Varano	6.61-55.06	Low	Urban wastewater and agricultural runoff	Petro.	[51]
	Pialassa Baiona	3,030-87,150	High-very high	Industrial activity	Predominantly pyro.	[41]
	Stagnone	72-18,381	Low-very high	Aquagenic and anthopogenic activities	Predominantly pyro.	[42]
	Marano and Grado	ND-1,056	Low-high	Industry, fisheries, and agricultural activities	Predominantly pyro.	[56]
Tunisia	Bizerte	16.9-394.1	Low-Moderate	Industrial and town discharge	Pyro.	[55]
	Ghar El Melh	39.59-655.28	Low-Moderate	Maintenance of boats, painting, and agricultural activities	Pyro.	[47]
Mexico	Coastal lagoons	14.9-61	Low	Agriculture, fisheries, and fish factories	Mix of petro. and pyro.	[46]
Morocco	Coastal lagoons	6.6-82	Low	Traffic of petroleum tankers, aquaculture, discharge of untreated urban waters	Mix of petro. and pyro.	[52]
Saudi Arabia	**Al-Shabab**	**60-7,927.9**	**Low-very high**	**Municipal sewage, traffic**	**Mix of petro. and pyro.**	**This study**
	Al-Arbaeen	**5.4-5,371.8**	**Low-very high**	**Municipal sewage, traffic**	**Mix of petro. and pyro.**	**This study**
Spain	Mar Menor	0.5-242.2	Low-Moderate	Flood events	Predominantly pyro.	[53]
USA	Johnston Atoll	9.2-7,243	Low-very high	Military activities	NR	[49]
Vietnam	Coastal lagoons	112-628	Low-moderate	Fishing and aquaculture activities	Petro.	[60]

*Ptro. = petrogenic, Pyro. = pyrogenic, # NR= not reported

Comparison of ∑ PAHs in Lagoons with Worldwide Data

The pollution levels in both lagoons on Jeddah coast are classified as low-to-very highly polluted areas. Comparing the mean values for total PAH levels for the studied lagoons, Al-Arbaeen is slightly higher than Al-Shabab for both Σ38 PAHs and Σ16 PAHs; the same order was observed for carcinogenic PAHs (ΣcPAHs), which were found two orders of magnitude higher in Al-Arbaeen than Al-Shabab. The comparatively high PAH levels in Al-Arbaeen could be attributed to the difference in the amount of wastewater input and geographical shape for Al-Arbeen lagoon, which restricted the water circulation inside the lagoon.

Table 4 presented the concentration levels of PAHs for some lagoons of different areas in the world. For individual congeners, pyrene and phenanthrene were the dominant compounds in both Al-Arbaeen and Al-Shabab similar to Pialassa Baiona and Stagnone lagoons in Italy [41-42], while the studied lagoons resemble Patos and Rodrigo de la Freita lagoons in Brazil [43-44], Venice [45], coastal lagoons in Mexico [46], and Ghar El Melh in Tunisia [47], where pyrene was the dominant compound. Comparing total PAH levels, the present concentration ranges were comparable with Etang de Thau, France [48], and Johnston Atoll in the USA [49]. Whereas the concentrations are far below the levels reported in Patos and Rodrigo de la Freita lagoons [43-44], Ebrie lagoon in Cote d'Ivoire [50], and Italy's Pialassa Baiona and Stagnone lagoons [41-42]. Moreover, the range of PAH concentrations found in the present study was around 100 orders magnitude higher than Italy's Lesina and Varano lagoons [51], and coastal lagoons in Mexico and Morocco [46, 52]; 30 orders of magnitude higher than Italy's Santa Giusta and Orbatello lagoons [51], and Spain's Mar Menor lagoon [53]; and 25, 20, 18, 9, 7, 5, and 5 magnitudes higher than Skongalon and Skogar lagoons in Iceland [54], Venice [45], Bizerte [55], Italy's Marano and Grado lagoons [56], Berre in France [57], Yuandang in China [58], and Cotonou in Benin [59], respectively.

The present study showed pyrogenic and petrogenic mixed origins for PAHs, which is analogous to Patos and Rodrigo de la Freita lagoons in Brazil [43-44], Orbetello lagoon in Italy [51], and coastal lagoons in Mexico [46]. The main sources of PAHs in Al-Arbeen and Al-Shabab were atmospheric deposition due to vehicle traffic and municipal sewage. As shown in Table 4, industrial activities [41, 43, 45, 50, 55, 57] along with municipal and urban runoff [51-52, 55, 57] contributed the dominant sources to PAH pollution in world lagoons. Moreover, agricultural runoff [46, 51], aquaculture [42, 46, 52, 60], petroleum spill, boat traffic [44, 52, 59] and motor vehicles [44-45, 58] also had considerable input.

Conclusions

The mean values for total Σ38 PAHs and Σ16 PAHs in Al-Arbaeen were slightly higher than Al-Shabab lagoon, and carcinogenic PAHs were consistent with this trend. Forensic study showed that sources of PAHs are of petrogenic and pyrogenic mixed origin where traffic and municipal sewage were found as the main inputs. The pollution levels in both lagoons were in the low-very-high range. The absence of low molecular weight PAH compounds indicates the effect of high temperatures in the study area and aerobic/anaerobic microbial degradation. Adverse biological effects hardly occur because mean ERL values were less than one for total PAHs. However, adverse effects due to individual congeners may likely occur at specific stations. The low water circulation and semi-closed structure of the lagoons leads to incarceration of pollutants to a great extent inside the lagoons, and this conclusion is supported by the great drop of total PAH values outside the lagoons.

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