Chemistry Research Journal, 2020, 5(5):60-77

Available online www.chemrj.org

Research Article

ISSN: 2455-8990
CODEN(USA): CRJHA5

Distribution and Origin of Polycyclic Aromatic Hydrocarbons (PAHs) in the Marine Sediments of Banias City-Tartous - Syria

Dr. Hazem Krawi[1], Dr. Samer Ghadeer[2], Wlaa Ibrahem[1]

[1]Department of Marine Chemistry, High Institute of Marine Research, Tishreen University, Lattakia, Syria
[2]Department of Marine Geology, High Institute of Marine Research, Tishreen University, Lattakia, Syria

Abstract This research studied thedistribution of polycyclic aromatic hydrocarbons (PAHs) in marine sediment. Samples were collected seasonally from several sites of Banias coast between April 2015 and January 2016. The total concentration of PAHs in the studied sediments ranged from 763 to 5884 ng/gdw. The highest concentrations were recorded in summer and the lowest in winter. The source of these compounds was determined according to a set of ratios, which confirmed that the sediments were affected by both petrogenic and pyrogenic sources, with most domination for the PAHs compounds with 5 and 6 rings in all the study seasons.

The sediment samples showed four sediment-sorting types and these are: Sand, Slightly gravelly sand, Gravelly sand, and Gravel. The statistical parameters studies clearly showed that the sediments in general are of medium grain size, poorly to medium sorted, negatively skewed and very negatively skewed and platykurtic to mesokurtic and leptokurtic. These parameters confirm that the sediments were deposited under moderate to high-energy conditions, which affected by both the deposition area nature in addition to the currents and waves movement in the area.

Keywords Marine pollution, polycyclic aromatic hydrocarbons, Petrogenic and pyrogenic source of PAHs, Surface Sediments, Grain size analysis, Organic matter

Introduction

Hydrocarbons are major pollutants in the marine environment, which disrupt the marine ecosystem through their complex behavior in the marine environment [1]. Polycyclic aromatic hydrocarbons (PAHs) are categorized as persistent organic pollutants (POPs) that were classified as dangerous pollutants in the marine environment according to the 2001 Stockholm Convention [2].

PAHs reach the marine environment from natural sources such as natural oil seepage, forest fires, volcanic activities, in addition to the degradation and biosynthetic processes occurring in the marine environment [3-4], but the human sources is considered the most dangerous. Presence of these PAHs in general is related to human activities that contribute to supplying the marine ecosystem in large quantities, especially in industrial cities [5], through emissions from vehicles, engines and industrial factories waste such as metals melting operations, and shipping activities, such as incidents of oil spills from oil tankers, or during loading and unloading operations, especially in coastal ports [6-7].

The pyrogenic PAHs (Pyr) are distinguished by their large molecular weights; they contain more than 3 aromatic rings in their structure, such as Pyrene and Benzo[a]anthracene [8]. They are formed through a set of rapid and incomplete combustion reactions of organic matter at high temperatures [4-5]. While the petrogenic PAHs (Pet) are formed by reorganizing the organic matter at low temperatures and high pressure [7] and they are characterized by containing aromatic compounds with low molecular weights containing two or three rings in their structures, like Phenanthrene and Fluorine [9]. The processes of biosynthesis and biodegradation done by microorganisms such as algae, bacteria and fungi in marine sediments also contribute to release biogenic PAHs into the environment, and releasing the most is Benzo[ghi]perylene, but at very low concentrations [2-6-10].

PAHs widely distribute in all environmental compartments, including atmosphere, water, sediment and living organisms. Where they are found in both molecular and soluble states [11]. PAHs after entering into the marine environment are affected by several physical and chemical processes such as evaporation, photo-oxidation and biodegradation [12]. These compounds tend to absorbat suspended materials in the water column due to their low solubility and high lipophilic [13-14]. Then they are absorbed easily into suspended organic materials in the column water until they finally settles in sediments [6-10], which can be considered as temporary reservoir of pollutants. When the environmental conditions change, these compounds can be resuspended in the water column by the movement of benthic biota and human activities, or by the currents and waves, which make these compounds bioavailable [6-12]. After that they are transferred from water to phytoplankton according to phenomenon of molecular diffusion [15]. The plankton contribute to delivery these compounds to higher levels of food chain, reaching humans [2-16].

PAHs cause environmental and global concern due to their carcinogenic and toxic properties [17]. Experiments prove their disturbing effect on the lymphatic system and blood cell activity [12]. Chronic exposure to these compounds leads to genetic mutations, genetic abnormalities and hormonal imbalances because they tend to integrate into a DNA structure [16]. In addition, they cause skin allergies and neurodevelopmental disorders, which can disrupt work of endocrine glands in the [18-19].

Marine sediments are the main reservoir for PAHs in the marine environment [20]. Thus, the study of marine sediments reflects many of factors that control their deposition, such as the sediment sources and ratios, medium energy, wave strength and its direction, the size of sediment particles and their content of organic carbon [21]. Most studies have confirmed that seawater specifications in most cases don't represent a valid indicator of the state of the marine environment. So the analysis of sediment is an effective way to assess the reality of pollution by hydrocarbons and to give more accurate information about the history of pollution in the area [20].

This research is complementary to other researches that study the reality of the marine ecosystem pollution on the Syrian beach. Moreover, its importance came from the lack of studies in the eastern basin of Mediterranean particularly at Syrian coast [22]. According to the list issued by the United Nations Environment Program in 1997, the Banias beach is one of the hotspots at eastern shore of Mediterranean, Where Banias city includes many industrial factories such as an oil refinery, a thermal station, and an oil transportation company, that contribute in the increase of pollution in this area.

The aim of this study is to determine the concentration of PAHs in marine sediments of several sites of Banias coast, and find their origin and the factors affecting the accumulation of these pollutants in the studied sediments. The research was conducted in the laboratories of the High Institute of Marine Research - Tishreen University- Syria.

Study Area and Methodology

This study included five different sites along Banias coast, taking into account the different human and industrial activities affecting the study sites (Fig. 1).

- ST_1: Banias Refinery and Syrian oil Transport Company.
- ST_2: Sewage drainage of Banias Hospital.
- ST_3: Banias River estuary.
- ST_4: Al-sen River estuary.
- ST_5: Hrisoun River estuary.

Fifty seasonal samples were collected during the period that ranged between spring 2015 and winter 2016. The upper 5 cm layer of sediments was scooped using a tube of polyvinyl (PVC), homogenized on sites, and then stored in already with organic solvent cleaned aluminum foils and kept at4˚C during transportation to the laboratory. When returned to the laboratory, the samples were stored at -20˚C.

Figure 1: Location and sampling sites

Chemical Analysis

The chemicals that in contact with the samples were prepared to be pure before use. The following solvents were used: n-hexane, dichloromethane and acetone with a high degree of purity (SPC, England). Anhydrous sodium sulphate (Qualikems, India), alumina (80-200 mesh) and silica gel (230-400 mesh) (Merck, German) were used. Anhydrous sodium sulphate was purified by heating at 450 °C for six hours [23]. While the materials used to preparation of the chromatographic columns (alumina and silica gel) were purified by with dichloromethane in Soxhlet apparatus for six hours and .dried in an oven at low temperature (≤50 °C) to remove the solvent then kept in sealed glass containers until use [23]. The precleaned adsorbents (alumina and silica gel) were activated by heating in an oven at 200 °C for 4 hours and partially deactivated by adding 5% (wt/wt) distillated water to the silica gel and 2%to the alumina [23]. With anhydrous sodium sulphate dried sediment samples were extracted in the Soxhlet apparatus using dichloromethane after adding the internal standard solution (Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, Perylene-d12). Sulfur was removed from the extracts by adding a few drops of mercury for several times. Extracts were concentrated at a rotary evaporator then with a gentle stream of pure nitrogen gas up to 1 ml [23].

Cleanup are done by using chromatographic columns, where glass burettes are used (1 cm internal diameter) with capacity of 50 ml. A piece of glass wool was placed at the bottom of the column; the column is partially filled with hexane. 8 g of silica gel mixed with hexane are added to the column and then 8g of alumina added in the same way. Finally, 1 g of Na_2SO_4 is put on the upper layer of the adsorbent bed [23]. One mL of the organic extract is pipetted into the column and is drained into the adsorbent bed. The saturated hydrocarbons are eluted with 20 mL of hexane (F_l). Aromatic hydrocarbons are eluted with20 mL of 20% $MeC1_2$ in hexane (vlv) followed by20 mL of 50% $MeC1_2$ in hexane (vlv). These last two fractions ($F_2 + F_3$) are combined and analyzed together [23].

The samples were analyzed using gas chromatography device (Hewlett- Packard 5890) equipped to MS detector, capillary column (DB-5) length 30 m. The carrier gas is helium with a purity of 99.999% at a flow of 2 ml/min, injector temperature 250 °C, temperature of the contact unit between the column and the detector is 200 °C. The separation process has been done according to the following thermal program: **70 °C (4 °C/min) ⟶ 280 °C (20 min).**

The quantitative study was done using a external stander containing a mixture of aromatic compounds of 3 to 6 aromatic rings with known concentration.

The organic matter content in the samples was determined by heating the sample in muffle oven for 6 hours at 550 °C. Then the sample was weighed. The organic matter content was calculated, which represents the difference between the remaining weight of the sample and its original weight [24].

Grain size analysis

The dry analysis method of samples (sieving) was used in order to determine the structural characteristics of marine sediments. Therefore, 150 g of each sample was weighed and dried for at least 24 hours in the oven (BM) at 105 °C to remove the moisture before analysis [24]. From the dried samples, 100 mg was taken by the coning and quartering method. The 100 mg of sample is then subjected to sieve analysis in ASTM sieves at one-phi intervals for about 20 minutes in EFL – 2000/1-sieve shaker, according to sieve diameters ranging from (6 mm- 4mm-2mm-1mm-500µm-250µm-125m-63µm). These data were then combined to produce complete grainsize distributions. This basic data i.e. weight percentage frequency data is converted into cumulative weight percentage data, served as basic tool for the generation of other statistical parameters such as mean grain size, sorting coefficient and skewness using USGS GSSTAT [25] and described herein generates statistics to characterize sediment grain-size distributions and calculates the net sediment transport trend vectors. The statistical coefficients were calculated after performing the mechanical analysis of sediments by calculating the statistical coefficients of the granular size by adopting the Folk &Ward scale (1957) [26], in order to find out the size of the grains using the phi function where: Ø = -log2 x (x is the value given in mm). These statistical parameters include both From: These statistical parameters include**:** **(**M_Z Graphic Mean Size) (σ Graphic Standard Deviation**)** **(**S_K Graphic Skewness) (K_G Graphic Kurtosis**()**M_d Graphic Median).

After that, the statistical parameter of the grain size were calculated, then the studied sedimentary samples studied were classified according to Folk & Ward 1957 [26] (Table 1).

Table 1: Folk & Ward's (1957) classification of sedimentary statistical coefficients and their corresponding indices and indicators

Inclusive graphic mean size (MzØ)	Inclusive graphic standard deviation (бiØ)
-2 — -1 Ø gravel	
-1 — 0 Ø very coarse sand	< 0.35 Ø very well sorted
0 — 1 Ø coarse sand	0.35 — 0.50 Ø well sorted
1 — 2 Ø medium sand	0.50 — 0.71 Ø moderately well sorted
2 — 3 Ø fine sand	0.71 — 1.00 Ø moderately sorted
3 — 4 Ø very fine sand	1.00 — 2.00 Ø poorly sorted
4 — 5 Ø coarse silt	2.00 — 4.00 Ø very poorly sorted
5 — 6 Ø medium silt	> 4.00 extremely poorly sorted
6 — 7 Ø fine silt	
Inclusive graphic skewness (Sk_j)	Inclusive graphic Kurtosis (K_G)
+1.0 — +0.3 very positively skewed	< 0.67 very platykurtic
+0.3 — +0.1 positively skewed	0.67 — 0.90 Ø platykurtic
+0.1 — -0.1 nearly symmetrical	0.90 — 1.11 Ø mesokurtic
0.00 perfect symmetrical	1.11 — 1.50 Ø leptokurtic
-0.1 — -0.3 negatively skewed	1.50 — 3.00 Ø very leptokurtic
-0.3 — -1.0 very negatively skewed	> 3.00 extremely leptokurtic

Results and Discussion

The results of the current study, the granular analyzes, all the values of the granular sorting parameters in addition to the percentages of the granular fractions of gravel, sands and silt for all the sediment samples taken from the study areas are included in Table (2). The results of analyzing sedimentary samples in the studied stations according to the classification Folk (1974) [27] showed the identified four sediment-sorting: and these are: Sand, Slightly Gravelly Sand, Gravelly sand, and Gravel (Table 1)**.**

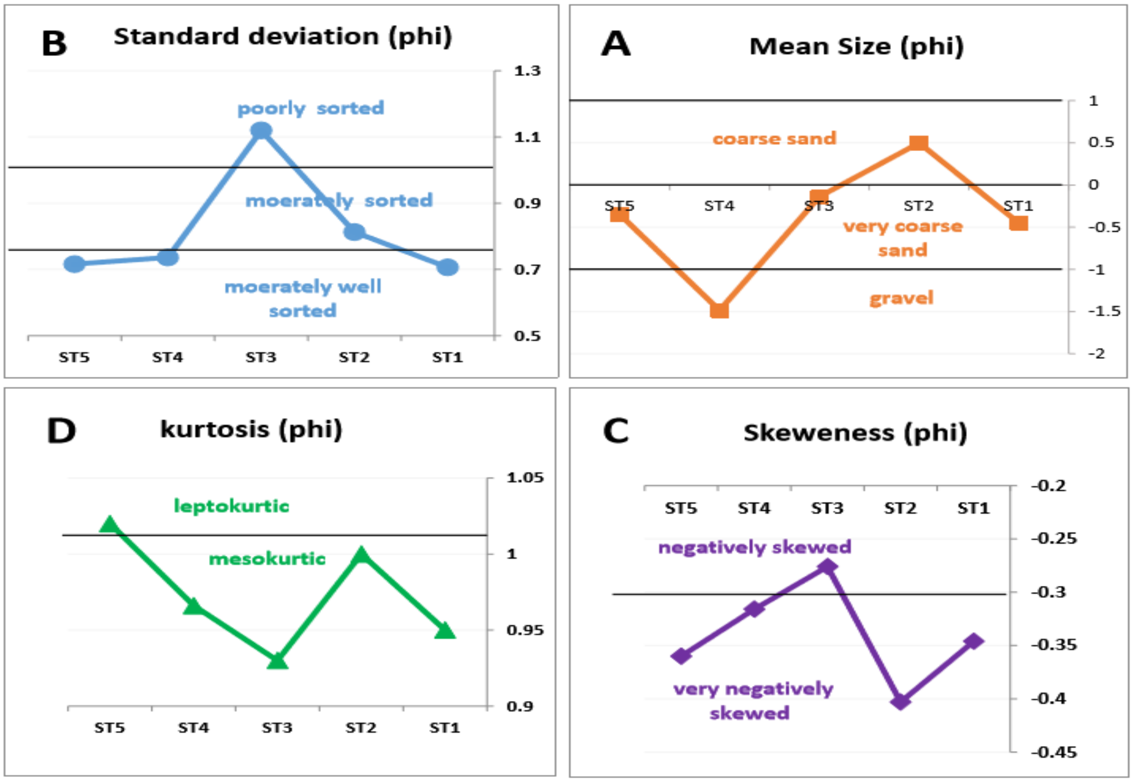

Figure 2: Cumulative histograms of all samples showing the average of: A: Mean, B: Standard deviation, C: Skewness and D: Kurtosis in all studied stations

Statistical Parameter

Mean size (MZ): Mean size is a measure of central tendency. It denotes the size of sedimentary particles, and it mainly refers to the energy conditions of the medium and the role of sea currents and waves in changing the sedimentation environment. The mean grain size of the study area sediments varies from -1.98 ф (gravel) at ST_4 in the winter to 1.85 ф (medium sand) at ST_2 in the summer (Table 2) with an average of -0.38 ф (very coarse sand) (Fig. 2A). According to the mean size results in the studied stations (Table 2), it appears that the sedimentary grains ranged from coarse to medium sand.

Standard deviation (бi): Inclusive graphic standard deviation measures the uniformity of particles size distribution. and mainly indicates the difference in kinetic energy associated with these modes of deposition. It is an important parameter in sediment analysis because it reflects the energy conditions of depositional environment [28]. The moderate sorted indicates the similarity of the granular size, while the poorly sorted is the increase of the ratio from coarse to fine particles.The standard deviation of the study area sediments varies from 0.43 Φ (well sorted) at ST_5 in the winter to 1.37 Φ (poorly sorted) in the summer at ST_3 (Table 2) with an average of 0.818 Φ (moderately sorted) (Fig. 2B).

Skewness (Sk): The graphic skewness measures the systematic of the distribution or predominance of coarse or fine-sediments. Negative skewed valuse indicates the domination of coarse sedimentes that emerges because of high energy conditions [29].Whereas fine skewness of sediments indicates the deposition of the sediments in sheltered low energy environments [30]. Skewness value ranges in between -052 Φ (very negatively skewed) in the summer at ST$_2$ to -0.19 (negatively skewed) Φ at ST$_3$ in the seem season (Table 2) with an average of-0.34 (very negatively skewed) (Fig. 2C). According to the skewness results in (Table 2), it appears that most of the studied samples with negative skewed values are coarse to very coarse samples deposited in high energy environments due to the presence of erosion processes.

Kurtosis (KG): The graphic kurtosis is a quantitative measure to describe the departure from normality of distribution. It is a ratio between the sorting sides and central portion of the detour. The kurtosis values of the study area sediments range from 0.84 Φ in the winter at ST$_2$ (platykurtic) to 1.15 Φ (leptokurtic) at ST$_5$ in the winter, also (Table 2) with an average of 0.97 Φ (mesokurtic) (Fig. 2D). Most samples were platykurtic to mesokurtic and leptokurtic. This variation in the kurtosis values is due to the flow characteristics and the energy change of the of the depositing medium [31].

Table 2: Grain size parameters of sedimentary samples in the studied sites during the period between spring 2015 and winter 2016.

Location	Season	Sediment type	Gravel %	Sand %	Silt %	Median	Mean (Mz)	Sorting (σ1)	Skewness (S$_K$)	Kurtosis (K$_G$)
ST$_1$	Spring	*Gravelly Sand*	7.051	92.487	0.46	-0.43	-0.58 VCS	0.86 MS	-0.30 NSK	0.88 PK$_G$
	Summer	*Slightly Gravelly Sand*	1.513	98.393	0.09	0.17	0.06 CS	0.53 MWS	-0.39 VNS$_K$	1.02 MK$_G$
	Winter	*Gravelly Sand*	8.484	91.262	0.25	-0.70	-0.84 VCS	0.73 MS	-0.35 VNS$_K$	0.95 MK$_G$
ST$_2$	Spring	*Sand*	0	99.947	0.05	0.43	0.33 CS	0.55 MWS	-0.34 VNS$_K$	1.02 MK$_G$
	Summer	*Slightly Gravelly Sand*	0.8	96.535	2.661	2.05	1.85 MS	0.76 MS	-0.52 VNS$_K$	1.15 LK$_G$
	Winter	*Gravelly Sand*	11.635	88.266	0.09	-0.45	-0.68 VCS	1.13 PS	-0.35 VNS$_K$	0.84 PK$_G$
ST$_3$	Spring	*Gravelly Sand*	12.854	86.041	1.10	-0.75	-0.87 VCS	1.09 PS	-0.21 NS$_K$	0.88 PK$_G$
	Summer	*Gravelly Sand*	10.862	87.252	1.882	-0.42	-0.54 VCS	1.37 PS	-0.19 NS$_K$	0.86 PK$_G$
	Winter	*Slightly Gravelly Sand*	0.43	97.947	1.620	1.18	0.98 CS	0.90 MS	-0.43 VNS$_K$	1.05 MK$_G$
ST$_4$	Spring	*Gravelly Sand*	10.581	89.115	0.30	-0.93	-1.04 G	0.77 MS	-0.29 NS$_K$	0.95 MK$_G$
	Summer	*Gravelly Sand*	15.156	84.80	0.04	-1.32	-1.44 G	0.70 MWS	-0.36 VNS$_K$	1.04 MK$_G$

	Winter	*Sandy Gravel*	32.215	67.671	0.11	-1.87	-1.98 G	0.74 MS	-0.30 NS_K	0.91 MK_G
ST_5	Spring	*Slightly Gravelly Sand*	2.68	97.296	0.02	0.10	-0.11 VCS	0.76 MS	-0.47 VNS_K	1.02 MK_G
	Summer	*Gravelly Sand*	18.674	81.314	0.01	-1.29	-1.42 G	0.96 MS	-0.26 NS_K	0.90 MK_G
	Winter	*Slightly Gravelly Sand*	0.62	99.368	0.01	0.54	0.48 CS	0.43 WS	-0.35 VNS_K	1.15 LK_G

G: Gravel, **VCS**: Very Coarse Sand, **CS**: Coarse Sand, **MS**: Medium Sand **WS**: Well Sorted, **MWS**: Moderately Well Sorted, **MS**: Medium Sorted, **PS**: Poorly Sorted **PK$_G$**: Platykurtic, **MK$_G$**: Mesokurtic, **LK$_G$**: Leptokurtic
NSY: Nearly Symmetrical, **NS$_K$**: Negatively Skewed, **VNS$_K$**: Very Negatively Skewed.

PAHs in sediments

The 16 PAHs are: naphthalene (Na), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorine (Fl), Phenanthrene (Phen), Anthracene (Ant), Fluoranthene (Flou), pyrene (Pyr), benzo[a]anthracene (BaAnt), Chrysene (Chr), Benzo[b]fluoranthene (BbFlou), Benzo[k]fluoranthene (BkFlou), Benzo[a]pyrene (BaPyr), Di-benz[a,h]anthracene (DaAnt), Benzo[ghi]perylene (BPer) and Indeno[1,2,3-cd]pyrene (Ind).

The total concentration of PAHs in studied sediments ranged between 763 and 5884 ng/gdw (figure 3). The highest concentrations were observed in ST_1in summer and the lowest concentrations was recorded at ST_5 in the winter. These concentrations varied according to seasonal and spatial changes. The concentration of individual compounds ranged between (2031-0.396 ng/g dw), the highest was for Di-benz[a,h]anthracene in the ST_1 in summer and the lowest was for Acenaphthene in the ST_3 in spring.

Temporal changes showed high concentrations of PAHs containing 5 and 6 aromatic rings during all study seasons. These high concentrations can be explained by the low hydrolysis of these compounds, their high affinity for organic matter [12] and their resistance to biodegradation[32]; hence, these compounds tend to be adsorbed on the suspended material in the water column and at organic matter present in sediment [33],unlike the concentrations of compounds with low molecular weights containing 3 and 4 aromatic rings were low in most seasons, due to their high solubility in water compared to the compounds of higher molecular weights [34], in addition to, their susceptibility to biodegradation in sediments [35].

It was observed in this research that the concentrations of PAHs decreased in the spring and winter than those observed in summer. However, it could be due to the change in river flow and its dynamics in the estuaries during both spring and winter [36]. High energy resulting from the increased flow of River in rainy seasons (especially observed in spring) make it easy to transport large sediment particles with small specific surface, which have less ability to accumulate PAHs. The reason also can be due to increasing the biodegradation occurring during spring [37]. The dynamic stability during summer contributes to increase the ability of suspended particles in the water column to absorb organic carbon and PAHs [3].

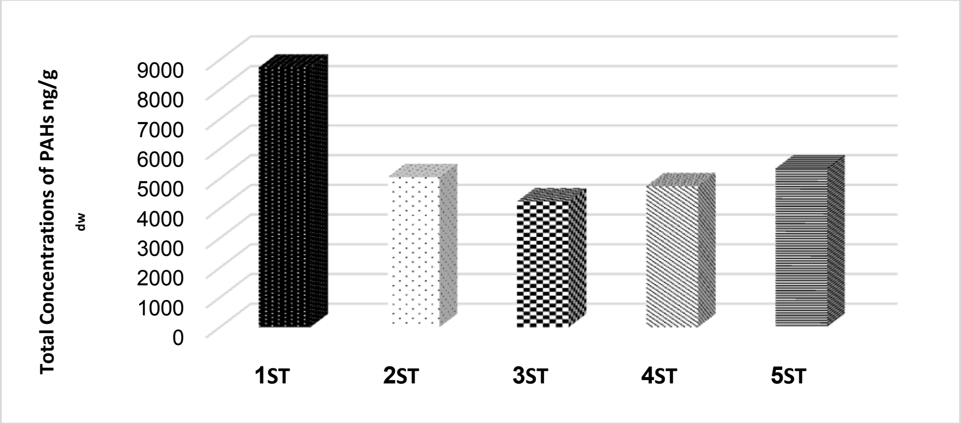

Figure 3: Total concentrations of PAHs in sediment samples.

The highest total concentration of PAHs was recorded in ST_1 (Fig. 3 & 4), this can be attributed to its nearness to the sewage and industrial wastewater outlet of Baniasrefinery. The pollution in areas near the oil installations occurs through oil outflow during loading, unloading of oil or through oil refining operations in refineries that require large quantities of water discharged loaded with hydrocarbons and other pollutants [38]. The total concentrations in ST_2 were lower than those in first station (Fig. 3 & 5).

The stations ST_3, ST_4 and ST_5, represent the estuaries in this research. Estuaries are generally areas with complex dynamics, in which mixing processes occur between fresh and marine water in variable rates depending on several factors such as river flow and the tidal processes [39]. The concentrations of PAHs decreased in the studied estuaries as follows: $ST_5 > ST_4 > ST_3$ (Fig. 3).

The concentration of PAHs was high in the sediments of station ST_5 (Hrisoun River) (Fig. 8), compared with the two other estuaries ST_3 (Fig. 6) and ST_4 (Fig. 7) due to the geography of the area. ST_5 is directly open-area to the sea (Fig. 1), and the high salinity in the estuary area can play an important role to increasing the organic carbon in its sediments, cause to its richness in algae and bacteria [40]. This leads to an increase in the absorption of hydrophobic pollutants, including PAHs, into the organic matter because of its hydrophobic properties and high affinity [12]. Whereas ST_4 (Arab al-Milk area) (Fig. 1) forms a semi-closed area, in which mixing processes between fresh water from river and marine water is low, making the estuary area affected by the pollutants carried by the Sin River water from the lands. In addition, this area is affected by fishing boats movement. The ST_3 station (estuary of Banias River) (Fig.1), is a semi-open area with little exposure to the currents and wave movement, besides, it is near to the port of Banias, and its direct impact by ship unloading and shipping operations, as well as ship and boat engine emissions. Many of studies have shown that the high concentrations of PAHs is related to the extent of the closeness of the stations to the ports and sewage outlets of city [7].

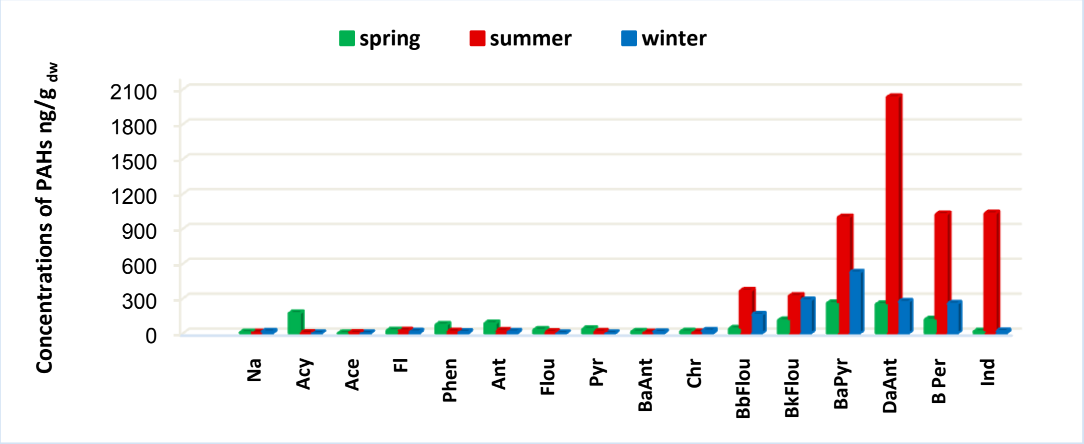

Figure 4: Concentrations of PAHs in sediment of ST_1 station

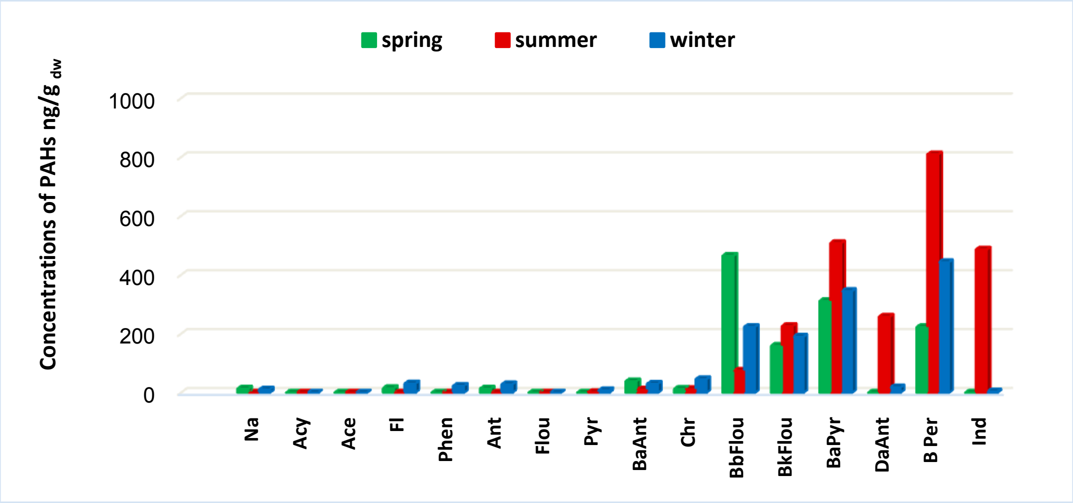

Figure 5: Concentrations of PAHs in sediment of ST_2 station

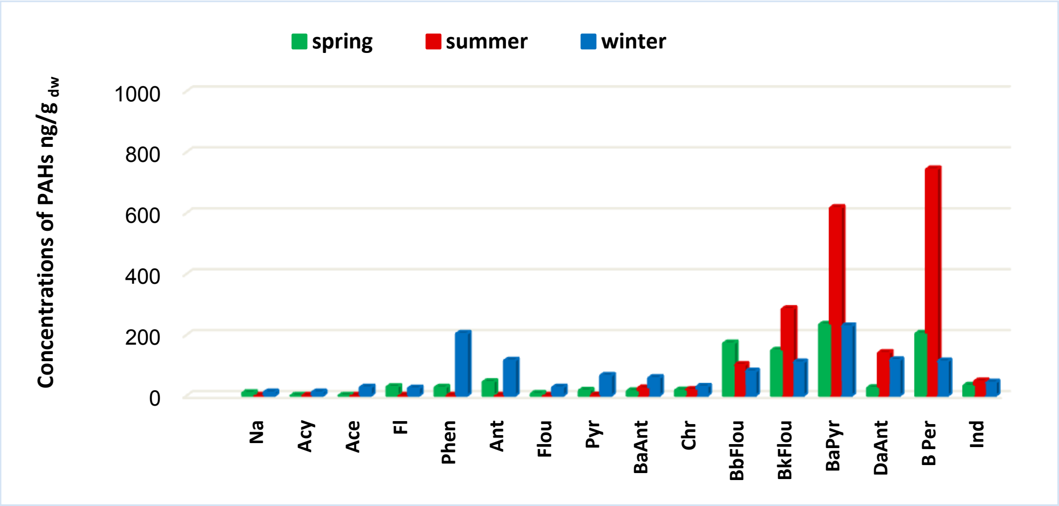

Figure 6: Concentrations of PAHs in sediment of ST_3 station

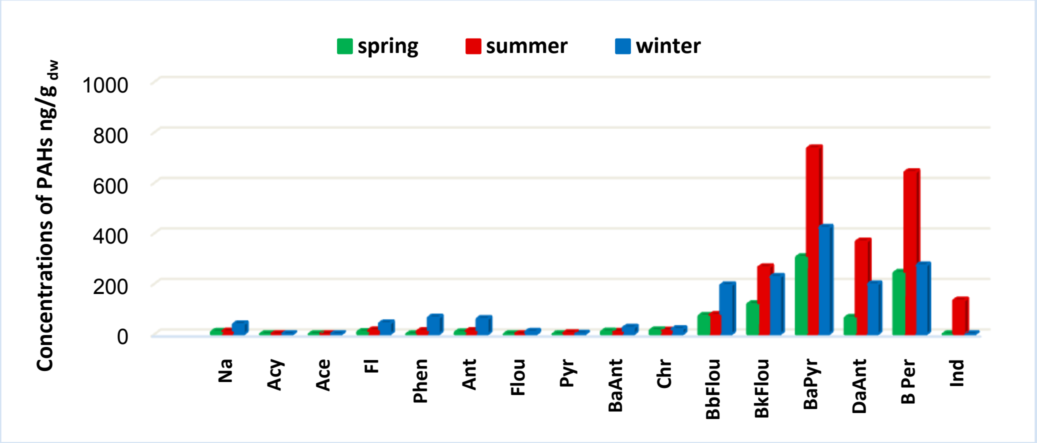

Figure 7: Concentrations of PAHs in sediment of ST_4 station

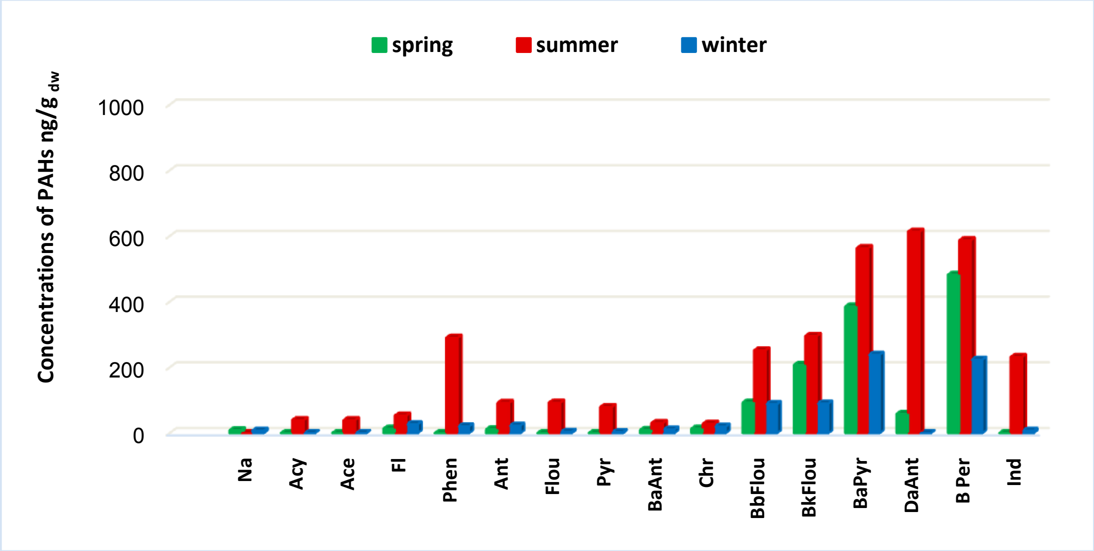

Figure 8: Concentrations of PAHs in sediment of ST_5 station

The distribution of PAHs was studied according to the number of their rings. The compounds with 5 and 6 rings dominated in all the studied stations as a result of high concentrations of both Benzo[a]pyrene and Di-benz[a,h]anthracene, while a slight increase in the percentages of compounds with 6 rings was observed because of high concentration of Benzo[ghi] perylene in spring (Fig. 9). However, in the summer, a slight convergence was observed in the percentages of PAHs with 5 and 6 rings in most stations due to high concentrations of Benzo[a]pyrene and Di-benz[a,h]anthracene with 5 rings, also Indeno[1,2,3-c,d]pyrene and Benzo[ghi]perylene with 6 rings (Fig. 10). Most studies indicated that the presence of high concentrations of Benzo [ghi] perylene in marine sediments is due to fuel and diesel engines [16].

The concentration of benzo[a] pyrene commonly increased, which led to domination of PAHs with 5 aromatic rings in sediments of most stations. It was also observed increasing the concentrations of low molecular weight LMWPAHs (compounds with three rings) in the ST_1 station during the spring (Fig. 9). This increasing refers to high concentration of Acenaphthene, because the area is directly affected by wastewater of oil refining operations in the Banias Refinery, which is taken out in the near-estuary area. Moreover, the concentration of these PAHs were high in ST_5during summer because of high concentration of Phenanthrene (Fig. 10). And also in ST_3 in winter (Fig.11), because of high concentration of both Phenanthrene and Anthracene in the sediments of this station. Hence, this area are affected by petroleum pollution, because petroleum PAHs are characterized by their high concentrations of Phenanthrene [41]. The four-ring compounds were associated with high concentrations of the aromatic three-ring compounds, where the highest concentrations were recorded in the ST_3 in winter, as a result to the increase the concentrations of Benzo[a]anthracene and Pyrene, due to their proximity to the sewage water associated with the flow of Banias River**.**

In this study, high concentrations of Benzo[a]perylene were monitored in estuaries (ST_3, ST_4, ST_5), where the highest value was recorded at station ST_3 (743.44 ng/g $_{dw}$) (Fig. 6). However the estuaries receive large inputs of carbon and nutrients from land, and the presence of microorganisms like algae, bacteria, and fungi in enhancing the processes of synthesis and biodegradation [42], which produce particularlylow concentrations of Benzo[a]perylene [4]. This corresponds with many studies that confirmed that increase in the level of human activities and the accompanying in emissions from vehicle exhaust and fishing boats, may contribute to an increase in the concentration of Benzo[a]perylene in the environment surrounding estuaries [43].

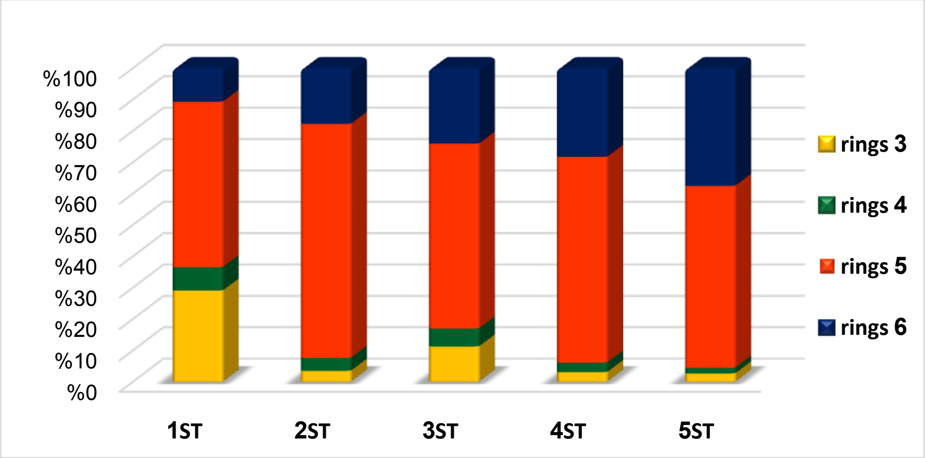

Figure 9: The percentage of PAHs concentration in the spring according to the number of rings in the studied samples

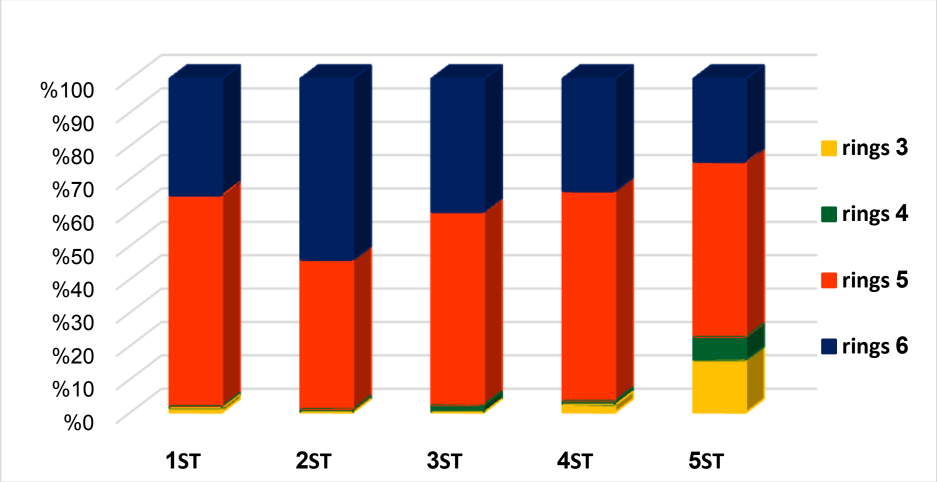

Figure10: The percentage of PAHs concentration in the summer according to the number of rings in the studied samples

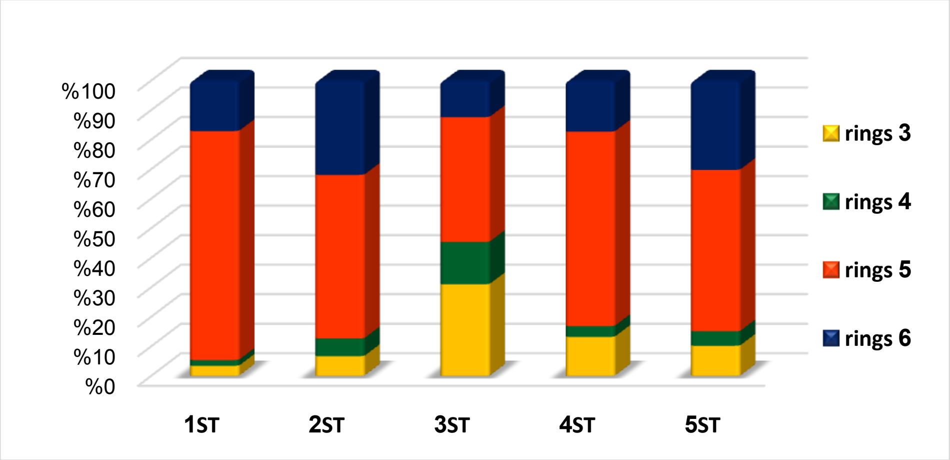

Figure 11: The percentage of PAHs concentration in the winter according to the number of rings in the studied samples

The main sources of PAHs in the marine environment are due to petrogenic (Pet) and pyrogenic(Pyr) sources [10]. A group of ratios and applications used globally were used to determine the most likely source of PAHs arriving to the marine environment. Three ratios were used in this research that were distinguished from others by giving results more accurate to determine the source of pollution in the studied sediments. The most important of them are: the ratio of fluoranthene to pyrene ((Flou / Pyr). The values of this ratio ranged in this study between (3.88-0.36), where the source of petroleum pollution (Pet) when the ratio is (Flou / Pyr <1) [10], as such in ST_1 stations in spring and summer, and in ST_3 station in spring and winter (Table 3). When the ratio values are increased to (Flou / Pyr> 1), the source is (pyrogenic source) (Pyr) [44] as in ST_4 in winter, and station ST_5 in summer and winter (Table 3).

The ratio (Flou / Flou + Pyr) distinguishes the pyrogenic source from petroleum was also used, in addition to the mixed source resulting from combustion of oil and fossil fuels. The values of this ratio ranged between (0.79-0.26) (Table 3). So when the ratio was (Flou / Flou + Pyr <0.4), the source was petroleum (Pet) [8], as such in station ST_3 in spring and winter (Table 3). But when the ratio becomes (Flou / Flou + Pyr> 0.5) it characterizes the burning of coal, wood and grass and indicates heat sources (Pyr) [9], which were monitored at station ST_4 in winter and station ST_5 in summer and winter (Table 3). While when this ratio is between (0.5-0.4) it often characterizes the mixed source of PAHs [45], which were recorded at station ST_1 in spring and summer(Table 3**).**

The ratio (Ind / Ind + BPer) suggest to petrogenic source (Pet) when it is (<0.2) [14] which is observed in most stations during seasons (Table 3), but when its value increases to become (> 0.5) it refers to pyrogenic sources (Pyr) resulting from the combustion of wood and coal [45]. Nevertheless, when the value was between (0.2-0.5) it results from the Petroleum Combustion (PC) [8-9] as such stations ST_1, ST_2 and ST_5 during the summer and station ST_3 in the winter (Table 3).

The ratio (BaPyr / Bper) was adopted to show the contribution of PAHs resulting from combustion processes, especially fuel combustion in vehicle exhausts, which some of them reach the marine environment, via moist and dry precipitation [46]. When this ratio is (> 0.6) it indicates a significant contribution of PAHs produced from vehicle exhausts (Traffic Emissions) (TE) [8-47] which was observed in all study stations and in all seasons, this ratio ranged between (0.62) in the ST_2 station in the summer and (2.18) in the ST_1 station in the spring (Table 3) **.**

Table 3: The source of PAHs in the sediments of the studied stations

		ST_1		**ST_2**		**ST_3**		**ST_4**		**ST_5**	
Season	**The ratios**	**Value**	**Source**	**Value**	**Source**	**Value**	**Source**	**Value**	**Source**	**Value**	**Source**
Spring	Flou/Pyr	0.82	***Pet***	-	-	0.36	***Pet***	-	-	-	-
	Flou/Flou + Pyr	0.45	***FFC***	-	-	0.26	***Pet***	-	-	-	-
	Ind/Ind + Bper	0.11	***Pet***	-		0.13	***Pet***	-		-	
	BaPyr/Bper	2.18	***TE***	1.39	***TE***	1.14	***TE***	1.25	***TE***	0.79	*TE*
Summer	Flou/Pyr	0.83	***Pet***	-	-	-	-	-	-	1.16	*Pyr*
	Flou/Flou + Pyr	0.45	***FFC***	-	-	-	-	-	-	0.53	*Pyr*
	Ind/Ind + Bper	0.5	***PC***	0.37	***PC***	0.05	***Pet***	0.17	***Pet***	0.28	*PC*
	BaPyr/Bper	0.97	***TE***	0.62	***TE***	0.82	***TE***	1.14	***TE***	0.95	*TE*
Winter	Flou/Pyr	-	-	-	-	0.41	***Pet***	3.88	***Pyr***	1.39	*Pyr*
	Flou/Flou + Pyr	-	-	-	-	0.29	***Pet***	0.79	***Pyr***	0.58	*Pyr*
	Ind/Ind + Bper	0.06	***Pet***	0.009	***Pet***	0.27	***PC***	-	-	0.03	*Pet*
	BaPyr/Bper	2.05	***TE***	0.77	***TE***	2.02	***TE***	1.54	***TE***	1.06	*TE*

The results mentioned in (Table 4) showed a decrease in the concentrations of PAHs in sediments in the studied stations in this research, compared to two studies that curried out at Tartous coast. The first was in 2002-2001 [22] and the second one was conducted in 2013 in the same area [48]. However, they are lower than those of Tunisian city [7] and the coast of the China Sea [49]. But they are greater than the concentrations recorded in the study [50] in Iranian coast, where pollution was classified as moderate. Baumard et al. (1998) [51] categorized the PAHs levels in the aquatic, environment from 0-100 ng /g (low), 100-1000 ng /g (moderate), 1000-5000 ng /g (high) and >5000 ng /g (very high). According to this categorization, the PAHs levels can be classified from low to high in Banias coast**.**

Table 4: Comparison of PAH concentrations in surface sediments of different worldwide locations and this study

Country	**Site**	**Pollution Level**	**Rang (ng.g^{-1} sed. dw)**	**Reference**
Syria	Coastal of Banias city	Low to high	0.396-2031.4	This study
Syria	Coastal of Tartous city 2001-2002	Low to Moderate	nd-264.9	[22]
Syria	Coastal of Tartous city 2010	Low	1.76-55.28	[48]
Syria	Coastal of Lattakia city 2000-2001	Low to Moderate	11.6-562.67	[52]
Tunisia	Gulf of Gabès, Sfax-Kerkennah channel	Moderate to very high	175-10769	[7]
Iran	Gorgan Bay, Caspian Sea	Moderate	107.9-516	[50]
France	Bay of Banuyls-sur-mer	Low	21-23	[53]
Italy	Gulf of Trieste	Moderate to high	214-4416	[54]
China	Yangtze River Delta region	moderate	471.30	[37]
China	Zhucheng, Coal-fired power plant	high	1031.8-3744.8	[49]

There are several factors that mainly control the presence and distribution of aromatic hydrocarbons in marine sediments,one of the most important of them is the size of sediment particles, where the size of the grains plays an important role to determination the transport mechanism, as the larger particles will be difficult to transport compared to the small molecules that transport easily [55]. It was observed that the organic matter content in sediments were related to the sediments nature.They werehigh in fine sandy sediments, and low in coarse sand and gravel. The deposition process subject to a set of interfering factors that affect the correlation and the values of its coefficients, and accordingly the correlation relationship between sediment size and its content of organic matter was studied.The results showed direct positive relationship ($R^2 = 0.8$) between the Mean size and organic matter contented in sediments (Fig. 12)**.**

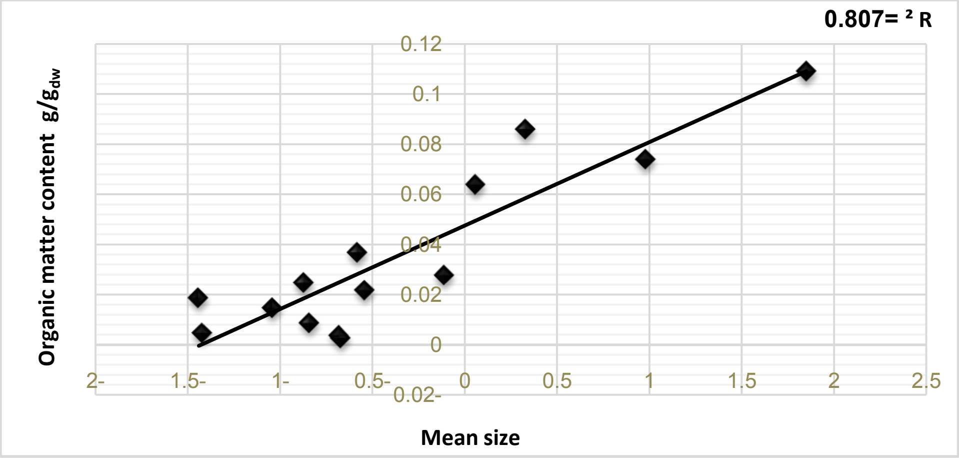

Figure 12: The relationship between mean size of sediments and their content of organic matter.

Most studies confirmed that the main controller for the accumulation of organic pollutants in sediments is their organic matter content. Where they confirmed existence a positive correlation between the concentration of organic pollutants and organic matter in sediment, the most important of these are PAHs [13-56]. In the current study, the correlation coefficient between total concentration of PAHs and the sediment content of organic matter showed a direct correlation between the concentrations of PAHs and the organic matter in marine sediments (R^2 = 0.66) (Fig. 13); Hence, the organic matter plays is main role in transporting these compounds to sediments [57].

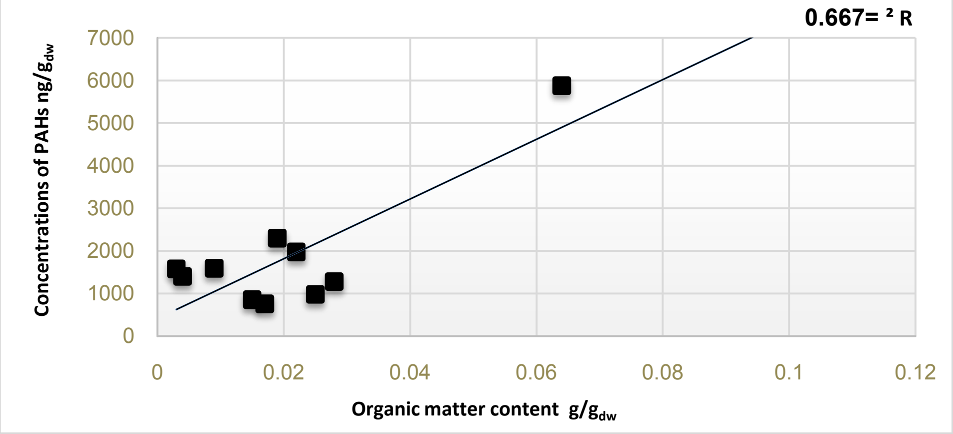

Figure 13: The relationship between concentration of PAHs and the organic matter content in the sediment of the studies stations.

The type of organic matter can have a clear effect on PAHs concentrations and their accumulation in sediments [56]. Yang *et al.*, (2015) [18] found that PAHs were not affected by grain size, but were associated with the least density fraction derived from plants and the coal. While Simpson *et al.*, (2014) [58] suggested that PAHs are associated with the total organic carbon present in sediments only in highly polluted sites when the total concentration exceeds (PAHs> 2,000 ng.g^{-1}). Whereas Mostafa *et al.*, (2009) [59] indicated that the distribution and concentrations of aromatic hydrocarbons in sediments are closely related to the source of pollution more than the type of sediments. Bouloubassi and Saliot (1993) [60] also found that the distribution of PAHs varies according to their source. He indicated that the PAHs from the natural source were bound to the coarse particles, while the compounds of the human source were bound to the smaller molecules.

The correlation relationship between the concentrations of PAHs and the organic matter in the studied sediments was studied depending on the source of pollution in stations. A positive and direct correlation was observed between the concentrations of PAHs and the content of organic matter in the sediments of sewage stations (ST_1), (ST_2) (R^2 = 0.73) (Fig. 14). In contrary, there is no correlation between the concentrations of PAHs in the sediments of estuaries and the organic matter in sediments (R^2 = - 0.09).

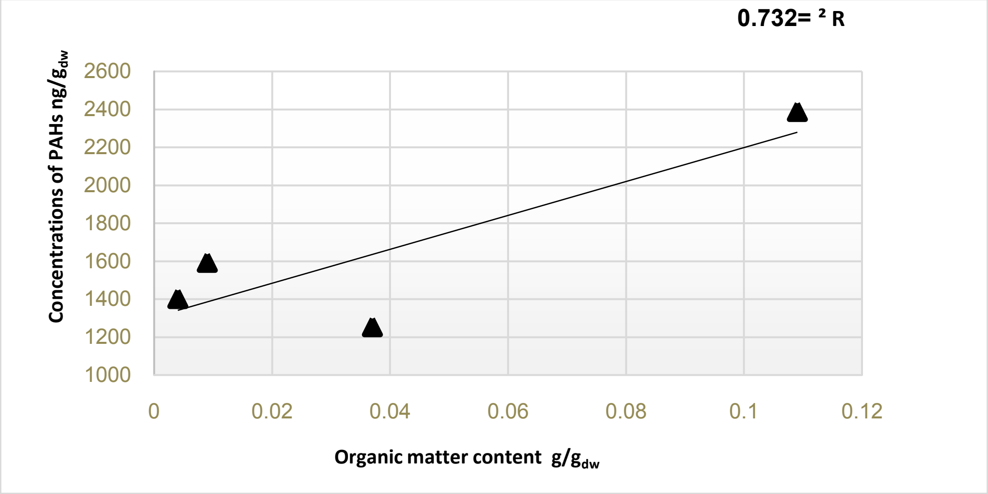

Figure 14: The relationship between concentration of PAHs and content of organic matter in sewage stations (ST_1, ST_2).

Conclusions

- The total concentrations of the studied aromatic hydrocarbons in sediment increased in summer in most stations compared to the other two seasons, while the spring recorded the lowest concentrations over the course of the study seasons. The reason can be attributed to the dynamics of the medium and its high energy resulting from the heavy rainfalls that contributed in creating an environment not suitable for the precipitation of organic matter**.**
- The total concentrations of aromatic hydrocarbons in ST_1 were the highest among all the studied stations, it could be due to their direct effect by the wastewater resulting from the discharging and oil refining operations in the Banias Refinery**.**
- The total concentrations ofaromatic hydrocarbons in the studied estuaries varied according to the geography of the area, where the concentrations decreased according to the following: ST_4> ST_5>ST_3.
- The high concentrations in ST_4 station are due to the nature of the region that forms a semi-closed basin in which the mixing processes between marine water and fresh water of the river decrease. in addition, the river receives large discharges of sewage while in ST_3 station, the reason may be attributed to its proximity to the port of Banias and its direct impact by ships' unloading and shipping operations and emissions of boat engines**.**
- High molecular weight PAHs with 5 and 6 rings dominated in the sedimentof the stations in all seasons, with a clear presence of 3 rings compounds in some stations**.**
- The factors used internationally to distinguish between the petrogenic and pyrogenic sources of PAHs indicated that the source of these compounds in all the studied sites in most seasons oscillated between petrogenic sources (ST_1 and ST_3) stations, and pyrogenic source (ST_4, ST_5) (estuaries).
- Grain size distribution and organic matter content are main factors that control pollutant concentration and ratios in coastal sediments.
- Grain size statistical parameters are good indicators of sediment source and dynamic energy of the medium.

References

[1]. Botello, A; Villanueva, S. & Diaz, G. (1997). Petroleum Pollution in Gulf of Mexico and Caribbean Sea. Institutede Cienciasdel Mary Limnologia, UNAM, Mexi co D.F., Mexico. *Rev Environ Contam Toxicol*, 153, 91-118.

[2]. Liehr, G. A. (2005). Distribution and Ecotoxilogical Effects of Polycyclic Aromatic Hydrocarbons (PAHs) in Sediments from the western Baltic Sea. *Dissertation, Rostock, Germany*, 134.

[3]. Wang, S; Liu, G; Yuan, Z. & Da, C. (2018). N-Alkanes in sediments from the Yellow River Estuary, China: Occurrence, sources and historical sedimentary record. *Ecotoxicology and Environmental Safet*, 150,199-206.

[4]. Nikolaou, A; Kostopoulou, M; Lofrano, G. & Meric, S. (2009). Determination of PAHs in Marine Sediments: Analytical methods and Environmental Conceres. *Global NEST Journal Greece*, 11(4), 391-405.

[5]. Abdel-Shafy, H. A. & Mansour, M. S. M. (2016). A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. *Egypt. J. Pet.,* 25(1), 107-119.

[6]. Neff, J. M. (1979). *Polycyclic aromatic hydrocarbons in the aquatic environment*. Applied Science, London, UK, 262.

[7]. Zaghden, H; Tedetti, M; Sayadi, S; Serbaji, M; Elleuch, M. B, & Saliot. A. (2017). Origin and distribution of hydrocarbons and organic matter in the surficial sediments of the Sfax-Kerkennah channel, Tunisia, Southern Mediterranean Sea. Mar. *Pollut. Bull*, 105, 70-89.

[8]. Yunker, M. B; Macdonald, R. W; Vingarzan, R; Mitchell, R. H; Goyette, D. & Sylvestre, S. (2002). PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry,* 33(4), 489-515.

[9]. Maioli, L. G; Rodrigues, K. C; Knoppers, B. A. & Azevedo, D. A. (2010). Distribution and sources of polycyclic aromatic hydrocarbons in surface sediments from two Brazilian estuarine systems. *J. Braz. Chem. Soc. Brazil*, 21(8), 1543-1551.

[10]. Penko, L. (2010). Polycyclic aromatic hydrocarbons in the seawater and sediments of the gulf of Trieste. Master's thesis, *University of Nova Gorica Slovenia*, 71.

[11]. Culotta, L; De Stefano, C; Gianguzza, A; Mannino, M. R. & Orecchio, S. (2006). The PAH composition of surface sediments from Stagnone coastal lagoon, Marsala (Italy). *Mar. Chem*, 99,117-127.

[12]. ATSDR," Agency for Toxic Substances and Disease Registry", (1995).*Toxicological Profile for Polycyclic Aromatic Hydrocarbons. Department of Health and Human Services.* Public Health services. Atlanta, GA. U.S. Georgia USA.

[13]. Liu, Y. P; Wang, Y. H; Ye, C; Xie, B. & Yang, H. (2017). Sedimentary Record of Polycyclic Aromatic Hydrocarbons from the Shuanglong Catchment, Southwest China. *J. Chem*., 1.

[14]. Klimkowicz-Pawlas, A; Smreczak, B. & Ukalska-Jaruga, A. (2017). The impact of selected soil organic matter fractions on the PAH accumulation in the agricultural soils from areas of different anthropopressure. *Environ Sci Pollut Res*, 24, 10955-10965.

[15]. Hargrave, B. T; Harding, G. C; Vass, W. P; Erickson, P. E; Fowler, B. R. & Scott, V. (1992). Organochlorine pesticides and polychlorinated biphenyls in the Arctic Ocean food web. *Arch. Environ. Contam. Toxico*l, 22(1), 41-54.

[16]. Zhang, Y; Dong, S; Wang, H; Tao, S. & Kiyama, R. (2016). Biological impact of environmental polycyclic aromatic hydrocarbons (ePAHs) as endocrine disruptors. *Environ. Pollut*, 213, 809-824.

[17]. Liang, J; Fang, H. L; Wu, L. H; Zhang, T. L. &Wang, X. X. (2016). Characterization, distribution, and source analysis of metals and polycyclic aromatic hydrocarbons (PAHs) of atmospheric bulk deposition in Shanghai, China. *Water, Air, and Soil Pollution,* 227(7), 234-241.

[18]. Yang, Q; Chen, H. &Li, B. (2015). Polycyclic aromatic hydrocarbons (PAHs) in indoor dusts of Guizhou, southwest of China: status, sources and potential human health risk. *PLoS One10*, 1-17.

[19]. WHO, "World Health Organization". (2003). *Polynclear aromatic hydrocarbons in drinking water background document for development of WHO guidelines for drinking water quality Geneva*, WHO/SDE/WSH/03.04/59.

[20]. Hostettler, F. D; Pereira, W. E; Kvenvolden, K. A; van Geen, A; Luoma, S. N; Fuller, C.C. &Anima, R. (1999). A record of hydrocarbon input to San Francisco Bay as traced by biomarker profiles in surface sediment and sediment cores. *Mar. Chem,* 64,115-127.

[21]. Goswami, P; Ohura, T; Guruge, K. S; Yoshioka, M; Yamanaka, N; Akiba, M. & Munuswamy, N. (2016). Spatio-temporal distribution, source, and genotoxic potential of polycyclic aromatic hydrocarbons in estuarine and riverine sediments from southern India. *Ecotoxicol. Environ. Saf*, 130, 113-123.

[22]. Nasser, M. & Hwejeh, I. (2009). Distribution Study of Polycyclic Aromatic Hydrocarbons (PAHS) in Water and Surface Sediments of Tartous City Coast Using Extraction and GC Technique. Tishreen University Journal for Research and Scientific Studies. *Basic Sciences Series,* 31(1).

[23]. UNEP, "United Nations Environment Program". (1992). *Determination of petroleum hydrocarbons in sediments.* Reference Methods for Marine Pollution Studies, 20, 78.

[24]. Heiri, O; Lotter, A. F. & Lemcke, G. (2001). Loss on ignitions a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. *Journal of paleolimnology Netherlands,* 25: 101-110.

[25]. Poppe, L. J; Eliason, A. H. & Hastings, M. E. (2004). A Visual Basic program to generate grain-size statistics and to extrapolate particle distributions. *Computers and Geosciences*, 30,791-795.

[26]. Folk, R. L. & Ward, W. C. (1957). Brazos River bar: a study in the significance of grain size parameters. *Journal of Sedimentary Petrology*, 27, 3-26.

[27]. Folk, R. L. (1974). *Petrology of Sedimentary Rocks. Hemphill Publishing* Co. Austin, TX, 182.

[28]. Joseph, S., Thrivikramaji, K.P. & Anirudhan, S. (1997). Textural parameters, discriminant analysis and depositional environments of the Teri sands, southern Tamil Nadu. *Jour. Geol. Soc. India* 50, 323-329.

[29]. Ghadeer. S. GH. (2017). Textural Characteristics and distribution of Coastal Sediments in the northern section of the Syrian continental shelf. *Tishreen University Journal for Research and Scientific Studies - Basic Sciences Series*, 39, 73-87.

[30]. Reddy, D., Karuna Karudu, T., & Deva Varma, D. (2008). Textural characteristics of southwestern part of Mahanadi Delta, east coast of India. *Jour. Ind. Assoc. Sed*. 27, 111-121.

[31]. Sahu, B. K. (1964). Depositional mechanisms from the size analysis of classic sediments. *Journal of Sedimentary Petrology*, 34, 73-83.

[32]. Misaki, K; Takamura-Enya, T; Ogawa, H; Takamori, K.&Yanagida, M. (2016). Tumour-promoting activity of polycyclic aromatic hydrocarbons and their oxygenated or nitrated derivatives. *Mutagenesis*, 31, 205-213.

[33]. Putri W. A. E; Purwiyanto A. I; Fauziyah, S; & Agustrian, F. (2020). Identification polycyclic aromatic hydrocarbons (PAHs) in the Banyuasin river estuary, South Sumatera. *Earth and Environmental Science*, 404, 012-038.

[34]. Sarria-Villa, R; Ocampo-Duque, W; Páez, M. & Schuhmacher, M. (2016). Presence of PAHs in water and sediments of the Colombian Cauca River during heavy rain episodes, and implications for risk assessment. *Sci. Total Environ*, 540, 455-465**.**

[35]. Shi, Z., Tao, S., Pan, B., Fan, W., He, X.C., Zuo, Q., Wu, S.P., Li, B.G., Cao, J., Liu, W.X., Xu, F.L., Wang, X.J., Shen, W.R. & Wong, P.K. (2005). Contamination of rivers in Tianjin, China by polycyclic aromatic hydrocarbons. *Environ. Pollut*, 134, 97–111.

[36]. Edward. A. (2014). Senyawa polisiklik aromatik hidrokarbon (PAH) dalam air laut di Teluk Jakarta Depik, 3: 207-215.

[37]. Wang, J; Zhang, X. F; Ling, W. T; Liu, R; Liu, J; Kang, F. X. & Gao, Y. Z. (2017). Contamination and health risk assessment of PAHs in soils and crops in industrial areas of the Yangtze River Delta region, China. *Chemosphere*, 168, 976-987.

[38]. Hayek, S. H; Ammar, G. H. &Mohammad, D. (2013). Optimal management of Banias spring water resources using WEAP- Syria. *Tishreen University Journal for Research and Scientific Studies*, 35(9), 183-196.

[39]. Norrie, C. R; Dunphy, B. J; Baker, J. A. & Lundquist, C. J. (2016). Local-Scale variation in trace elemental fingerprints of the estuarine bivalve Austrovenus Stutchburyi within and between estuaries. *Marine ecology progress series*, 559, 89-102.

[40]. Renaud, S. M. & Parry, D. L. (2016). Microalgae for use in tropical aquaculture II: effect of salinity on growth, gross chemical composition and fatty acid composition of three species of marine microalga. *Journal of Applied Phycology*, 6, 347-356.

[41]. Crnković, D; Sekulić, Z; Antonović, D; Marinković, A; Popović, S; Nikolić, J. & Drmanić, S. (2020). Origins of Polycyclic Aromatic Hydrocarbons in Sediments from the Danube and Sava Rivers and Their Tributaries in Serbia, *Pol. J. Environ. Stud*, 29 (3), 1-10.

[42]. Ogrinc, N; Fontolan, G. & Fagneli, J. (2005). Carbon and nitrogen isotope compositions of organic matter in coastal marine sediments (Gulf of Trieste, N Adriatic Sea): indicators of sources and preservation. *Journal of Marine Chem*, 95, 163-181.

[43]. Nekhavhambe, Y. J, Ree, T. V. & Fatoki, O. S. (2014). Determination and Distribution of Polycyclic Aromatic Hydrocarbons in Rivers, Surface Runoff, and Sediments in and around Thohoyandou, Limpopo Province, South Africa. *Water SA*, 40(3), 415-424.

[44]. Kim, M; Kennicutt II, M. C. & Qian, Y. (2008). Source characterization using compound composition and stable carbon isotope ratio of PAHs in sediments from lakes, harbour, and shipping waterway. *Science of Total Environment*, 289, 367-377.

[45]. Keshavarzifard, M; Zakaria, M. P; Hwai, T. S; Halimoon, N; Mustafa, S; Vaezzadeh, V. & Weiyun, C. (2014a). Polycyclic aromatic hydrocarbons (PAHs) in sediments from Prai and Malacca Rivers, Peninsular Malaysia. *In from sources to solution*, 415-420. Springer. Doi: 10.1007/978-9814560-70-2.

[46]. Jiang, Y. F; Yves, U. J; Sun, H; Hu, X. F; Zhan, H. Y. &Wu, Y. Q. (2016). Distribution, compositional pattern and sources of polycyclic aromatic hydrocarbons in urban soils of an industrial city, Lanzhou, China. *Ecotoxicol Environ Saf*, 126, 154-162.

[47]. Katsoyiannis, A; Sweetman, A. & Jones, K. (2011). PAH molecular diagnostic ratios applied to atmospheric sources: a critical evaluation using two decades of source inventory and air concentration data from the UK. *Environ Sci Technol*, 45: 8897-8906.

[48]. Krawi, H; Laika, H. E. &Shaaban, A. (2013). Sources of Polycyclic Aromatic Hydrocarbons (PAHs) in Marine water and sediments of Tartous City-Syria. Tishreen University Journal for Research and Scientific Studies. *Basic Sciences Series*, 35(2).

[49]. Cheng, Q; Wei, Ge. W; Chai1, C. h; Wu, J; Ma, D; Zeng, L; Zhu, X; Chen, Q. &Li. J. (2019). Polycyclic Aromatic Hydrocarbons in Soil Around Coal-Fired Power Plants in Shandong, China. *Pol. J. Environ. Stud*, 28(1), 53-64.

[50]. Araghi, P. E; Bastami, K. D. &Rahmanpoor, S. (2013). Distribution and sources of polycyclic aromatic hydrocarbons in the surface sediments of Gorgan Bay, Caspian Sea. *Marine Pollution Bulletin*, 89(1), 494-498. doi:10.1016/j.marpolbul.2013, 12.001.

[51]. Baumard, P; Budzinski, H; Michon, Q; Garrigues, P; Burgeot, T. &Bellocq, J. (1998). Origin and bioavailability of PAHs in the Mediterranean Sea from mussel and sediment records. *Estuarine Coastal Mar. Sci*, 47(1), 77-90.

[52]. Mohamad, I; Hwejeh, I. &Aghiourli. A. A. (2004). Contribution to Study the State of Polycyclic Aromatic Hydrocarbons (PAHS) in Tidal Sediments of Lattakia Coast. Tishreen University Journal for Research and Scientific Studies. *Basic Sciences Series*, 26(3).

[53]. Charles, F; Nozais, C; Pruski, A. M; Bourgeois, S; Méjanelle, L; Vétion, G; Rivière, B; & Coston-Guarini, J.(2012). Ecodynamics of PAHs at a peri-urban site of the French Mediterranean Sea. *Environ. Pollut*, 171,256-264.

[54]. Bajt, O. (2014). Aliphatic and Polycyclic Aromatic Hydrocarbons in Gulf of Trieste Sediments (Northern Adriatic): Potential Impacts of Maritime Traffic. *Bull. Environ. Contam. Toxicol*, 93, 299-305.

[55]. Oyedotun. T. & System. J. (2016). Coast Zone. Sediment Characterization in an Estuary Beach Manag, 19, 33-42.

[56]. Chen, H; Gao, G; Liu, P; Pan, R; Liu, X. &Lu, C. (2017). Determination of 16 Polycyclic Aromatic Hydrocarbons in Tea by Simultaneous Dispersive Solid-Phase Extraction and Liquid–Liquid Extraction Coupled with Gas Chromatography–Tandem Mass Spectrometry. *Food Anal. Methods*, 4, 1-11.

[57]. Lambert, S. M; Porter, P. E. & Schieferstein, H. (1965). Movement and sorption of chemicals applied to the soil. *Weeds*, 13(3), 185-190.

[58]. Simpson, C. D; Mosi, A. A; Cullen, W. R. & Reimer, K. J. (1996). Composition and distribution of polycyclic aromatic hydrocarbon contamination in surficial marine sediments from Kitimat Harbor, Canada. *Sci. Total Environ*, 181, 265-278.

[59]. Mostafa, A. R; Wade, T. L; Sweet, S. T; Al-Alimi, A. K. A. & Barakat, A. O. (2009). Distribution and characteristics of polycyclic aromatic hydrocarbons (PAHs) in sediments of Hadhramout coastal area, Gulf of Aden, Yemen. *J. Mar. Syst*, 78 (1), 1-8**.**

[60]. Bouloubassi, I. & Saliot, A. (1993). Dissolved, particulate and sedimentary naturally derived polycyclic aromatic hydrocarbons in a coastal environment: geochemical significance. *Marine Chemistry*, 42(2), 127-143.