

Polycyclic Aromatic Hydrocarbons (PAHs) in the Surface Sediments of Shatt Al-Arab River, Basrah City, Southern Iraq

Wisam A. Farid¹ Assel N. Al-Salman² Wasen A. Ali¹ Hamid T. Al-Saad^{3*}
Sliah Mahdi³ Abdelzahra A. Al-Hello³

1. Department of Community Health Technology, College of Health and Medical Technology in Basrah, Southern Technical University, Iraq

2. Department of Pathology and Poultry, Veterinary College, University of Basrah, Iraq

3. Department of Marine Environmental Chemistry, Marine Science Center, University of Basrah, Iraq

Abstracts

Sediment samples collected from nine sampling sites along the Shatt Al-Arab River, Basrah City, Iraq were analyzed by gas chromatography-flame ionization detector in order to determine the degree and sources of PAHs contamination. The total organic carbon (TOC) content and grain size of sediments were also analyzed. The Shatt Al-Arab River sediments content of PAHs were relatively moderate compared to other world-wide locations contaminated by oil. The total concentrations of PAHs ranged from 30.86 ng/g dry weight in the IX site to 87.79 ng/g dry weight in the VI site with highest content of PAHs were found in the Shatt Al-Arab River sediments near potential oil pollution sources, close to sites II, IV, VI, and VIII. The % TOC was varied from 0.32 to 1.64 %. The concentrations of PAHs in the Shatt Al-Arab River sediments appeared to be related to % TOC or grain size. The selected marked PAHs, the PAHs compounds ratios and the principal component analysis (PCA) suggest that the PAHs have originated from at least three different sources: (1) Pyrolytic-from different combustion processes, (2) petrogenic-from inputs petroleum and petroleum products, and (3) biogenic-from situ organisms. The potential ecosystem risk assessment indicated that PAHs will not cause immediate adverse biological effects in the Shatt Al-Arab River.

Keywords: PAH compounds, Sediments, Shatt Al-Arab River, TOC, Basrah.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a major class of hazardous organic chemical that in the recent years have received much attention because they are widely distributed in the environment, and many of them have mutagenic and genotoxic potential and carcinogenic effects on natural ecosystems (Wang *et al.*, 2011). This is especially true for highly stressed areas such as harbours, estuaries and other shallow coastal zones exposed to anthropogenic influence and various contamination sources.

There are several pathways of PAHs in aquatic environments, including petroleum contamination, direct aerial fallout, and terrestrial runoff. Some PAHs can also be derived from biogenic precursors such as pigments and steroids (Yang 2000; El Nemr *et al.*, 2007; Wang *et al.*, 2011). Perra *et al.*, (2009) stated that PAHs in the environment originate mainly from the accidental spills, partial combustion of fuels, forest and grass fires, biosynthesis by marine or terrigenous organisms, and early diagenetic transformation of non-hydrocarbon natural products to hydrocarbons.

A variety of processes including volatilization, sedimentation, adsorption, chemical oxidation, bioaccumulation, photodecomposition, leaching, and biodegradation are important mechanisms for environmental loss of PAHs (Wang and Fingas, 2003; Venkatachalapathy *et al.*, 2011; Zrafi *et al.*, 2013). The simple aromatics are rapidly lost, but higher molecules weight PAHs are little affected and can be particularly useful in source investigations.

Due to their hydrophobic nature and limited water solubility, most PAHs in aquatic ecosystems rapidly become associated with particles and are deposited in sediments (El Nemr *et al.*, 2007). Therefore, the sediments represent the most important reservoir of PAHs in the marine environment (Perra *et al.*, 2009). Resuspension or bioturbation of sediment into the water column are believed to play a significant role in bioaccumulation of these compounds in the food web (Lee *et al.*, 2005). Since marine sediments are repositories for many of pollutants, many researchers had been studied the relative content of the PAHs in sediments (NRC, 2003). For that reason, sediments are economically attractive in environmental assessment of aquatic ecosystems and can represent an useful tool for monitoring inputs of pollutants in marine environment.

Shatt Al-Arab River is the most important river in Iraq, because of its economical, social and ecological values. It is the main source of surface water in Basrah City, southern of Iraq. It's water has been used for various purposes including potable water supply, irrigation, fisheries, navigation, and industrial uses. Moreover, Shatt Al-Arab River is the prime fresh water source and pours about 5×10^9 m³ nutrient rich water into the Arabian Gulf each year (Ali *et al.*, 2013). It is also has a particular ecological relevance due to the peculiar multiplicity of aquatic habitats and the presence of species that typically breed in the Arabian Gulf area, nevertheless it is characterized by considerable inputs of different contaminants originated from the urbanized

areas and industrial sites (Moyel and Hussain, 2015). These pollutants may have severe impact on the water quality of the river and eventually upon living aquatic organisms. It is reported that the oil contamination in Shatt Al-Arab River was possibly originated from diverse sources including oil refineries, industrial waste, rural runoff, electricity generating stations, sewage discharges and river transportation activities (Farid *et al.*, 2014). Therefore, this ecosystem during the years, due to its closeness to the Basrah City and richness of human activities (i.e. industrial, aquaculture, and urban activities), has accumulated in sediments the high PAHs levels. The aim of the present work was, thus, to determine the presence, the distribution, and the origin of these compounds in the superficial sediments of Shatt Al-Arab River.

2. Materials and Methods

2.1 Description of study area and sampling: Shatt Al-Arab River originates from the confluence of the two major rivers of Iraq (Tigris and Euphrates) in Qurna at Basrah City. Karun River, the only tributary of the Shatt Al-Arab River, joins its eastern bank south of Basrah City (Figure 1). The length of the Shatt Al-Arab River from Qurna i.e. its place of origin, to its mouth in Arabian Gulf, extends about 175 km. Its width varies at different points, ranging from 0.4 km at Basrah City to 1.5 km at its mouth. The water depth increases in general towards the Gulf with a maximum of 12.2 m. The water level is, however, affected by the high and low tides of the Arabian Gulf where the average tidal range is about 1.7 m. Shatt Al-Arab water characterized as being well mixed with limited vertical stratification of temperature and chlorinities. The water of Shatt Al-Arab mouth may be traced as far as 5 km into the Arabian Gulf. The discharge of this river reaches the waters of Kuwait Bay during the flood season.

Forty surface sediment samples throughout Shatt Al-Arab River were collected during 2015. The sampling sites of the study area were shown in Figure (1) and were geo-located with global positioning system (GPS) to ensure consistency as given in Table (1). The samples were collected from the top 10–20 cm using Van-Veen grab sampler. As soon as the samples had been acquired, they were transported to the laboratory in an ice box and stored frozen at -20°C . Following freeze-dried the samples were sieved through stainless steel sieve with mesh size $62\ \mu\text{m}$ and ground finely with mortar and pestle (to remove large particles and debris) and kept at -20°C until analysis.

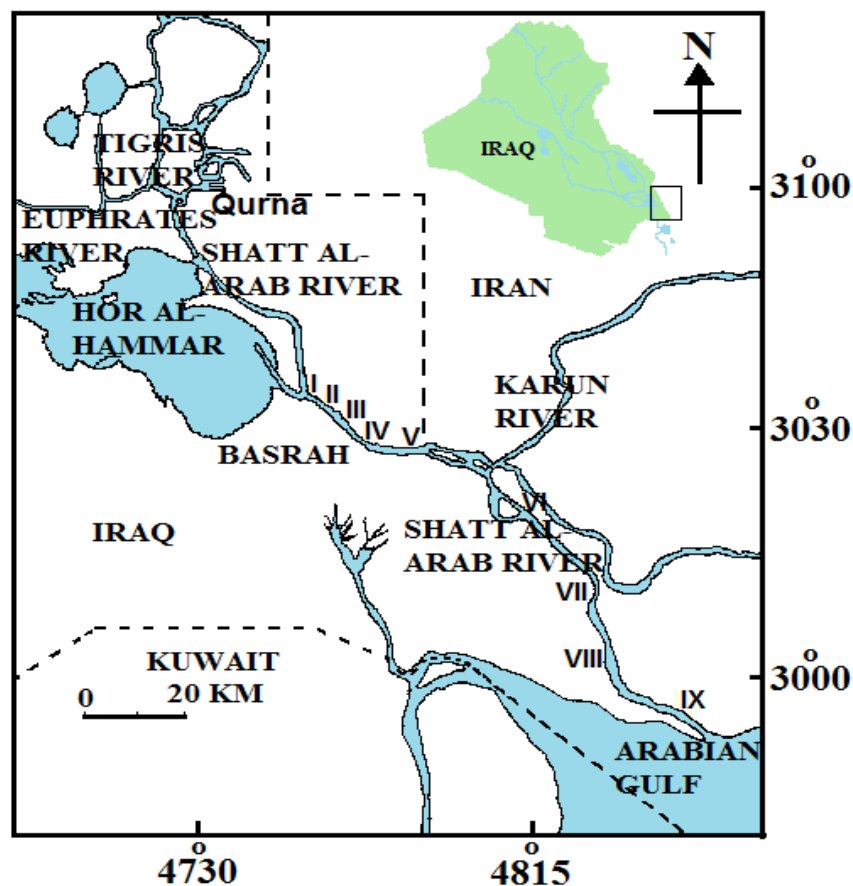


Figure 1. Shatt Al-Arab River and sampling sites.

Table 1. Location of sampling sites.

Sampling sites	Location
I (Garmat Ali)	30°48'10.6" N - 47°45'03.8"E
II (Nahrn-Omer)	30°45'05.0" N - 47°39'53.0"E
III (Al-Hartha)	30°39'48.0"N - 47°44'41.0"E
IV (Basrah)	30°33'00.0"N - 47°47'10.0"E
V (Abu-Al-Khasib)	30°27'44.5" N - 48°00'06.0"E
VI (Abadan)	30°03'42.0" N - 48°27'03.0"E
VII (Al-Seeba)	30°20'16.5" N - 48°15'34.5"E
VIII (Al-Fao)	29°58'28.6" N - 48°29'09.5"E
IX (Ras-Al-Bisha)	29°56'33.8" N - 48°34'37.4"E

2.2 Extraction, fractionation, and analysis of hydrocarbons: Hydrocarbons were extracted from sediments followed the procedure described by Grimalt and Olive (1993) and Wang *et al.* (2011). Fifty g of sediments were soxhlet extracted for 24 hours with 250 ml hexane: methylene chloride (1:1). Elemental sulfur was removed from the extracts using activated elemental copper in order to avoid sulfur interferences when using gas chromatography. The extracts were then fractionated into aliphatic and aromatic hydrocarbons by chromatography column. The column was prepared by slurry packing 10 g of silica (100-200 mesh), followed by 10 g of alumina (100-200 mesh) (silica-gel and alumina were activated at 200 °C for 4 hours and then partially deactivated with 5 % water) and finally 1 g of anhydrous sodium sulphate was added to the surface to avoid disturbance of the top layer when pouring the solvent. The extract was then applied to the head of the column and eluted with 20 ml n-hexane to obtain on the aliphatic fraction and 20 ml of benzene to yield the aromatic hydrocarbons. The aliphatic fraction saved for further analysis and the aromatic fraction were only concentrated on a rotary evaporator, transferred to a vial, and the volume was adjusted to 1 ml exactly using a stream of N₂. An aliquot of 1 µl of extract of aromatic hydrocarbons was subjected to analysis by a Allegiant capillary gas chromatography with flam ionization detector (FID). The fused silica capillary column (100 m x 250 µm x 0.5 µm) used was a wall coated open tubular (methyl silicone) (Agilent US2463233H DB-petrp), with helium as gas carrier at flow rate of 1.5 ml/minute. The operating temperatures for detector and injector were 300 °C and 320 °C, respectively. The temperature of column was held at 50 °C for 8 minute then 8 °C /minute to 350°C. The individual PAHs were identified based on the retention time of an authentic PAHs mixed standard procured from Supelco, USA. The concentrations of PAHs compounds were calculated based on the standard calibration curve of corresponding standard compounds. Recovery assays for standards aromatic compounds ranged from 80 % to 92 %. Standard deviation for the method was less than 10 % based on replicate analysis. Great care was taken to avoid contamination of the samples throughout the analytical procedure. All solvents were distilled twice before use; glassware was rinsed with distilled water and heated in an oven at 450 °C for 24 hours. However, procedural blanks consisting of all reagents and glassware used during the analysis were periodically determined which had shown no detectable interference.

2.3 Grain size analysis: Grain size analysis was carried out using the conventional method of Folk (1974).

2.4 Determination of total organic carbon: The total organic carbon (TOC) in sediment samples were analysed using Walkey's and Black titration method, in which the organic carbon is oxidized by dichromate ions, and the quantity of excess dichromate ions is then back titrated with ferrous ion (Walkey and Black, 1934).

2.5 Statistical analysis: The data of PAHs concentrations were statistically analyzed. Standard errors (SE) were calculated between three repetitions analysis and expressed as mean standard error. Comparisons among multiple sets of samples were achieved by one - way ANOVA. Statistical significance was defined as $P < 0.05$.

Principal component analysis (PCA) was used to distinguish between the samples to assess different sources of PAHs as has been demonstrated by other researches (Dickhut *et al.*, 2000; Nemr *et al.*, 2007; Wang *et al.*, 2011). Data analysis including (PCA) was done on the correlation matrix using SPSS software.

3.Results and Discussion

PAHs are entered in the environmental compartments of both natural and anthropogenic processes (Liu *et al.*, 2009). The analysis of these compounds in the Shatt Al-Arab river sediments revealed their existence for assets pyrolytic or petrogenic. The total concentrations of PAHs in the sediments vary from 30.86 ng/g dry weight in the IX site to 87.79 ng/g dry weight in the VI site (Table 2), with highest contents of PAHs were found in the Shatt Al-Arab River sediments near potential oil pollution sources, close to sites II, IV, VI, and VIII (Figure 2). The Shatt Al-Arab River area is home to many industries and river activities, which may explain the difference

can be observed between the PAHs concentrations in the sediments. Shatt Al-Arab river is subject to hydrocarbons pollution by sewage, industrial wastes and the activities of refining in addition to natural seeps, and other human activities.

The concentrations of PAHs measured in the Shatt Al-Arab River indicate that the contamination is important, and comparable to those found in other places around the world. The comparison revealed, elevated PAHs concentrations in Shatt AL-Arab River sediments compared to those reported by Wang *et al.* (2011) and Zrafi *et al.* (2013). It also indicated that Shatt Al-Arab River showed lower sedimentary concentrations of PAHs compared to those found by De luca *et al.* (2004), Trabelsi *et al.* (2005), Bin *et al.*, (2007), Zrafi - Nouira *et al.* (2008), Qiu *et al.* (2009), and Mahmoodi *et al.* (2012).

The identification of the PAHs pollution origin is based on identifying compounds with specific sources. In fact, the presence of fluoranthene and pyrene indicates the importance of pyrolytic inputs since these compounds are considered as products formed from the condensation of aromatic compounds of low molecular weight at high temperature (Zrafi *et al.*, 2013). Chrysene is a preserved biomarker PAH and was chosen to be a good marker of petroleum compounds because of its resistance to abiotic factors and the degradation of the microorganisms (Yang, 2000). Chrysene showed relatively high concentration in the sediments of II, IV, VI and VII sites, reflecting petrogenic pollution. Perylene was found in a variety of marine sediments. The origin of this compound is still a controversial subject. Aizenshtat (1973) suggested that perylene entirely into marine sediments from land organisms with detrital minerals. However, Wakeham *et al.* (1979) suggested an aquatic rather than a terrestrial precursor for perylene. Venkatesan (1988) showed that perylene can be originated from marine organic detritus. In addition, low levels of perylene can also be derived from anthropogenic input (Pereira *et al.*, 1999). In this study, perylene has been found in all sediments investigated. Its concentrations ranged from 3.45 ng/g at VII site to 8.68 ng/g at I site. The highest concentration of perylene was observed in I, III, V, VIII and IX sites. It is believed that a large amount of perylene found in the sediments of these sites to originate mainly from terrestrial input. The same conclusion was arrived by Pereira *et al.* (1999) and Yang (2000).

Table 2. Total concentrations of PAHs (ng/g) and standard error (ES) in the surface sediments of Shatt Al Arab River.

PAHs	Sites																		Total
	I	SE	II	SE	III	SE	IV	SE	V	SE	VI	SE	VII	SE	VIII	SE	IX	SE	
Naphthalene	2.92	0.45	1.85	0.23	1.19	0.53	1.14	0.31	2.73	0.14	3.32	0.41	2.63	0.35	1.78	0.60	0.79	0.62	18.35
Acenaphthylene	1.83	0.87	3.62	0.46	1.27	0.83	1.25	0.63	1.76	0.92	2.83	0.56	3.29	0.73	1.43	0.48	0.81	0.44	18.09
Acenaphthene	1.56	0.31	1.34	0.27	1.36	0.23	2.83	0.68	2.43	0.97	3.96	0.65	2.43	0.56	1.38	0.34	1.33	0.61	18.62
Fluorene	2.09	0.74	2.24	0.29	1.44	0.85	3.18	0.39	2.37	0.72	3.71	0.44	2.65	0.77	0.83	0.68	1.47	0.62	19.98
Phenanthrene	2.83	0.27	4.75	0.49	2.71	0.51	5.49	0.47	3.26	0.79	5.43	0.56	5.07	0.28	2.28	0.19	1.34	0.11	33.16
Anthracene	3.7	0.98	0.48	0.80	3.68	0.75	0.65	0.17	2.75	0.12	0.60	0.23	0.53	0.33	3.64	0.18	3.57	0.16	19.6
Fluoranthene	4.56	0.10	4.04	0.72	5.79	0.77	5.41	0.45	5.44	0.75	4.71	0.78	4.93	0.77	3.35	0.78	3.86	0.78	42.09
Pyrene	1.60	0.58	9.82	0.66	3.03	0.88	8.93	0.59	2.30	0.78	11.21	0.47	12.59	0.34	1.37	0.65	1.87	0.43	52.72
Benzo[a]anthracene	3.48	0.72	5.89	0.89	4.52	0.74	3.27	0.47	5.53	0.92	6.17	0.75	6.20	0.74	3.84	0.33	2.89	0.18	41.79
Chrysene	5.34	0.87	10.81	0.23	2.26	0.45	7.76	0.93	8.94	0.62	9.42	0.46	8.17	0.34	2.21	0.51	0.92	0.55	55.83
Benzo[b]fluoranthene	3.60	0.68	6.82	0.73	2.03	0.92	5.93	0.28	3.30	0.78	7.21	0.17	5.59	0.13	1.37	0.91	1.37	0.23	37.22
Benzo[k]fluoranthene	1.34	0.39	5.38	0.89	2.07	0.74	6.23	0.64	2.23	0.92	6.64	0.93	7.47	0.84	0.62	0.57	1.28	0.85	33.26
Perylene	8.68	0.63	3.53	0.51	7.75	0.58	6.65	0.18	8.13	0.18	4.22	0.21	3.45	0.16	7.57	0.73	6.48	0.36	56.46
Benzo[a] Pyrene	1.56	0.69	6.92	0.92	2.19	0.82	6.41	0.35	4.44	0.82	5.71	0.14	5.93	0.67	1.35	0.73	0.86	0.73	35.37
Indeno [1,2,3-cd] Pyrene	2.67	0.54	5.22	0.57	1.25	0.61	5.56	0.37	3.54	0.89	7.43	0.25	6.69	0.22	1.44	0.10	1.34	0.56	35.14
Benzo[ghi]perylene	2.68	0.43	5.53	0.34	1.25	0.23	6.65	0.19	3.12	0.11	5.22	0.83	5.45	0.93	0.57	0.58	0.68	0.87	31.15
Total	50.44		78.24		43.79		77.34		62.27		87.79		83.07		35.03		30.86		835.43

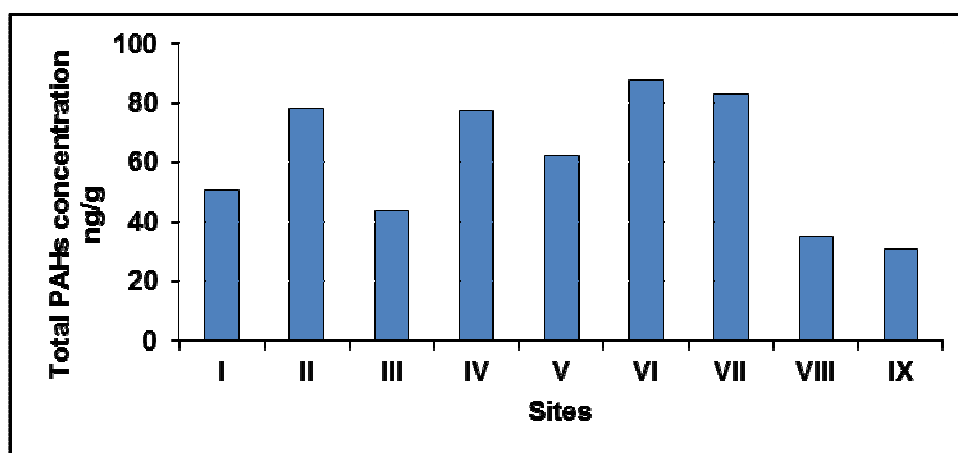


Figure 2. The spatial profiles of the total concentrations of PAHs in surface sediments of Shatt Al-Arab River.

The analysis of the low and high molecular weight PAHs was useful in the characterization of petroleum pollution and feature interpreted in fingerprinting sources of oil spilled and provide additional

diagnostic information. The sediments of Shatt Al-Arab river showed the high molecular weight PAHs predominance (4-6 ring) over low molecular weight (Figure 3). Petrogenic source contains relatively higher concentrations of low molecular weight PAHs individual (2 - 3 ring) compounds, while a high molecular weight parent PAHs dominance is a typical characteristic of a pyrolytic source combustion origin (Perra *et al.*, 2009; Lee *et al.*, 2005). High molecular weight PAHs have been recognized as directly carcinogenic and evidence suggests that the environmental persistence and genotoxicity of PAHs increase as the molecular size of the PAHs increases up to four or five fused benzene rings (Cerniglia *et al.*, 1992). On the other hand dominance of the high molecular weight PAHs could be because of their strongly adsorbed by sediments while low molecular weight PAHs are subject to several degradation (Wang and Fingas, 2003).

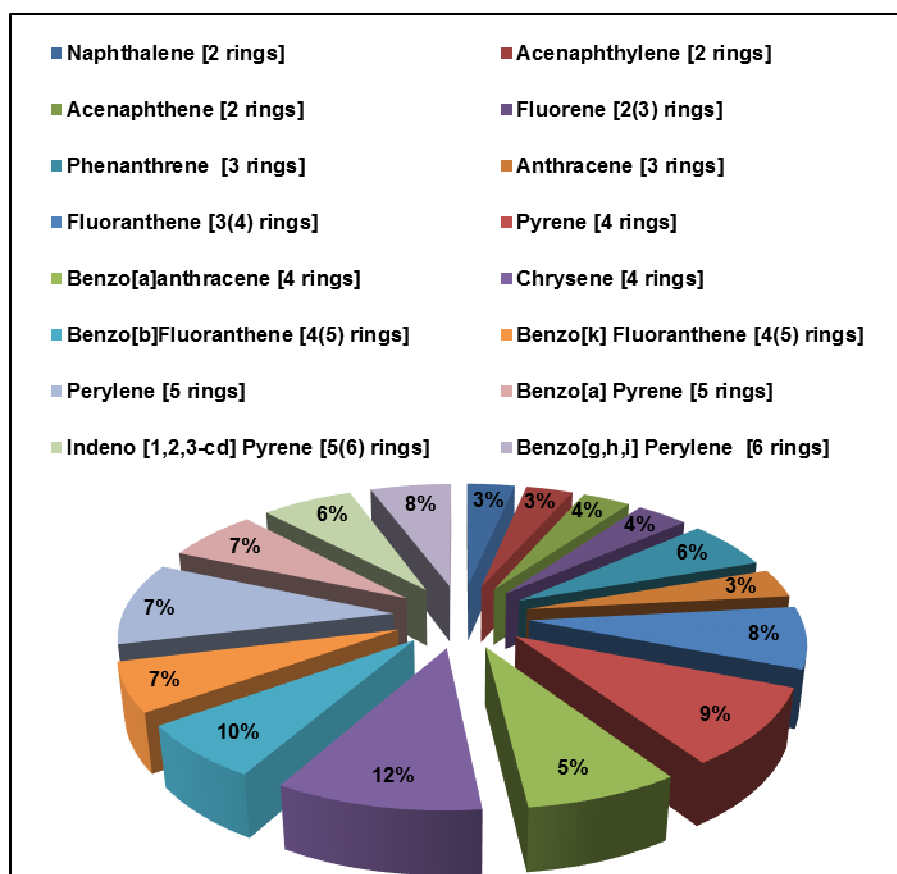


Figure 3. The distribution of PAHs (ng/g) in surface sediments of Shatt Al-Arab River.

With the development of environmental geochemistry, some criteria, such as phenanthrene/anthracene, fluoranthene/pyrene, anthracene/anthracene+phenanthrene, fluoranthene/fluoranthene+pyrene, and benzo(a)anthracene/benzo(a)anthracene+chrysene, ratios values, have been developed in order to discrimination between PAHs from different origins (Tolosa *et al.*, 2004; Bin *et al.*, 2007; Yang *et al.*, 2009). These criteria are based on the properties in the composition and distribution pattern of PAHs as a function of the emission source. Phenanthrene/anthracene ratio less than 3 refers to the origin of pyrolytic and it shows the origin of petrogenic when more than 3 (Tolosa *et al.*, 2004); fluoranthene/pyrene ratio < 1 is characteristic of the source of petrogenic and > 1 characterize the source of pyrolytic (Zrafi *et al.*, 2013); anthracene/anthracene+phenanthrene ratio < 0.1 are observed in the petroleum inputs or diagenesis sources, while the values > 0.1 are characteristic of combustion processes (Yang, 2000); fluoranthene/fluoranthene+pyrene ratio < 0.4 means the source of petrogenic as a property of fuel combustion (gasoline, diesel and oil crude), 0.4 to 0.5 means the combustion of petroleum, and > 0.5 means the combustion of coal, wood, kerosene, terrestrial plants and biomass (pyrolytic) (Yunker, *et al.*, 2002); and benzo (a) anthracene/benzo (a) anthracene+ chrysene ratio < 0.20 indicates petroleum input, 0.20 to 0.35 petroleum and oil combustion, and > 0.35 combustion (Wang *et al.*, 2011). The ratios indicate that the PAHs in sediments of II, IV, VI and VII sites exhibited evidence of petroleum derived pollution, diagenetic and combustion sources while the PAHs in sediments of I, III, V, VIII and IX sites may be originated from a source of pyrolytic (Table 3), while petroleum-derived pollution cannot be ignored. As well as the input of pyrolytic as the main source, petrogenic input may also be a source of PAHs in these sites because many of the oil activities in the Shatt Al-Arab river that could contribute to PAHs.

Table 3. Values of PAHs ratios for the surface sediments of Shatt Al Arab River.

PAHs ratios	Sites								
	I	II	III	IV	V	VI	VII	VIII	IX
Phenanthrene/Anthracene	0.76	9.13	0.73	8.71	1.18	7.38	9.56	0.62	0.37
Fluoranthene/ Pyrene	2.85	0.41	1.91	0.6	2.36	0.61	0.39	2.44	2.06
Anthracene/Anthracene+Phenanthrene	0.56	0.09	0.57	0.09	0.45	0.09	0.09	0.61	0.72
Benzo [a] Anthracene/ Benzo[a] Anthracene+ Chrysene	0.39	0.35	0.66	0.29	0.38	0.26	0.33	0.63	0.75
Fluoranthene/ Fluoranthene+ Pyrene	0.74	0.29	0.65	0.37	0.70	0.38	0.28	0.70	0.67

The principal component analysis (PCA) was used here to determine the sources of PAHs pollution in Shatt Al- Arab Rive sediments. Three main components found in the results of the PCA represent 40.6%, 19.8% and 11.5% of the total variance, respectively (Table 4). The first factor (PC₁) was heavily loaded on low molecular weight PAHs, which was identified as petroleum-related. The second one (PC₂) had high loadings on parent PAHs compounds, which was probably pyrolytic. The third factor (PC₃) was heavily loaded on none of the individual PAHs and represents an anonymous source. The results of the PCA indicated to the mixed sources of PAHs in the sediments of Shatt Al-Arab River.

Table 4. Factor loadings of three principal components (PCs) for PAHs in surface sediments of Shatt Al Arab River.

PAHs	PC ₁	PC ₂	PC ₃
Naphthalene	0.93	0.23	0.26
Acenaphthylene	0.91	0.42	0.18
Acenaphthene	0.86	0.33	0.51
Fluorene	0.94	0.19	0.18
Phenanthrene	0.86	0.28	0.54
Anthracene	0.73	0.27	0.20
Fluoranthene	0.38	0.77	0.28
Pyrene	0.15	0.97	0.30
Benzo [a] Anthracene	0.34	0.84	0.56
Chrysene	0.36	0.93	0.07
Benzo [b] Fluoranthene	0.34	0.85	0.34
Benzo [k] Fluoranthene	0.24	0.79	0.37
Perylene	0.44	0.89	0.14
Benzo [a] Pyrene	0.23	0.82	0.23
Indeno [1,2,3-cd] Pyrene	0.19	0.78	0.15
Benzo [g,h,i] Perylene	0.34	0.85	0.09
Variance %	19.6 %	40.8 %	11.5 %

There are many factors that affect the level of PAHs in the sediments including the compounds chemical characteristics and the sediment composition such as organic carbon content, clay content, and sedimentary depositional patterns (El Nemr *et al.*, 2007). The effect of TOC and grain size on the PAHs concentrations in Shatt Al-Arab Rive sediments was investigated in the present study. The % TOC and grain size of the recent sediments given in Table (5). The % TOC values ranged from 2.54 in the V site to 4.95 % in the VI site. The variation in % TOC between the study sites could be due to different organic matter sources and sedimentary environments. A positive relationship between the total concentrations of PAHs and % TOC in Shatt Al-Arab Rive sediments was found (Figure 4). The importance of sedimentary organic matter on the PAHs partitioning in sediments had been well documented by Chiou *et al.* (1998). They found that the high partitioning of PAHs to sedimentary organic matter was mainly due to the significant aromatic fraction of the organic matter. They considered the sedimentary organic matter as a natural “heterogeneous polymer” where PAHs interact more favorably with the aromatic regions.

The PAHs compounds are of concern because of their acute toxicity, mutagenicity, or carcinogenicity (Wang *et al.*, 2011). Sediment quality guidelines are an important tool to assess the pollution in marine and estuarine sediments (Long *et al.*, 2006; Quiroz *et al.*, 2010). The effects range low, effects range median, threshold effects level and probable effects level values, were used to assess the ecological toxicity of individual PAHs concentrations in sediments of Shatt Al Arab River (Table 6). In the three ranges of chemical concentrations, adverse biological effects are expected rarely (< effects range low/threshold effects level), occasionally (\geq effects range low/threshold effects level and < effects range-median/probable effects level), and frequently (\geq effects range median/probable effects level) (Long *et al.*, 1995; Liu *et al.*, 2009). The evaluations have shown that concentrations of all PAHs were below their respective effects range low and probable effects level values in all studied sites from the comparison of pollutants levels with sediment quality guidelines (Figure

5 and 6). It may be concluded that PAHs will not cause adverse biological effects in the sedimentary environment of Shatt Al-Arab River at the present time.

Table 5. Sedimentological parameters of Shatt Al Arab River.

Sampling sites	Type of sediment	TOC %
I	Muddy sand	0.57
II	Sandy mud	0.60
III	Mud	0.83
IV	Sandy mud	1.64
V	Sandy mud	1.00
VI	Sandy mud	0.95
VII	Sandy mud	0.32
VIII	Sandy clay	0.72
IX	Sandy mud	0.67

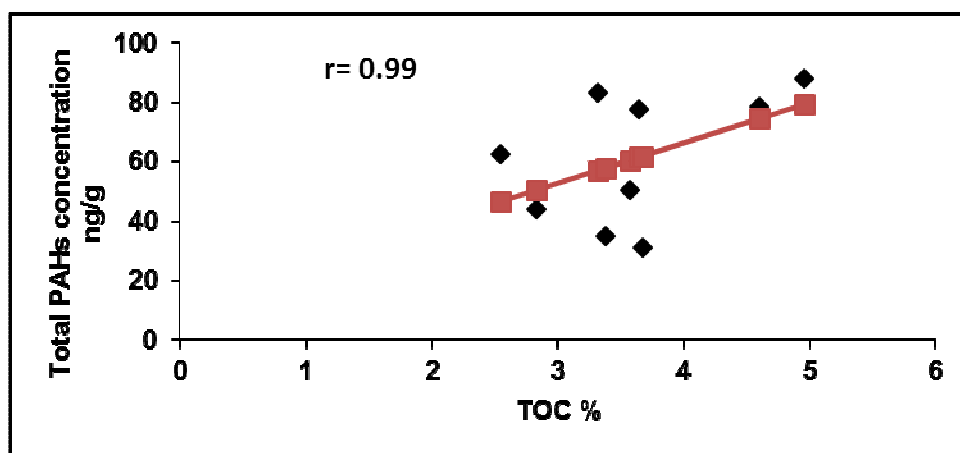


Figure 4. The relationship between total concentration of PAHs and % TOC of Shatt Al- Arab River surface sediments.

Table 6. Toxicity guidelines of PAHs for sediments matrices (ng/g) and average concentrations of PAHs in the surface sediments of Shatt Al-Arab River.

PAHs	Effects range low	Effects range median	Threshold effects level	Probable effects level	Shatt Al-Arab River (Average)
Naphthalene	160	2100	30	390	2.03
Acenaphthylene	40	640	10	130	2.01
Acenaphthene	20	500	10	90	2.06
Fluorene	20	540	20	140	2.22
Phenanthrene	240	1500	90	540	3.68
Anthracene	90	1100	50	240	2.17
Fluoranthene	600	5100	110	1490	4.67
Pyrene	660	2600	150	1400	5.85
Benzo [a] Anthracene	260	1600	70	690	4.64
Chrysene	380	2800	110	850	6.20
Benzo [b] Fluoranthene	---	---	---	---	4.13
Benzo [k] Fluoranthene	---	---	---	---	3.69
Perylene	---	---	---	---	6.27
Benzo [a] Pyrene	430	1600	90	760	3.93
Indeno [1,2,3-cd] Pyrene	---	---	---	---	3.90
Benzo [g,h,i] Perylene	---	---	---	---	3.46

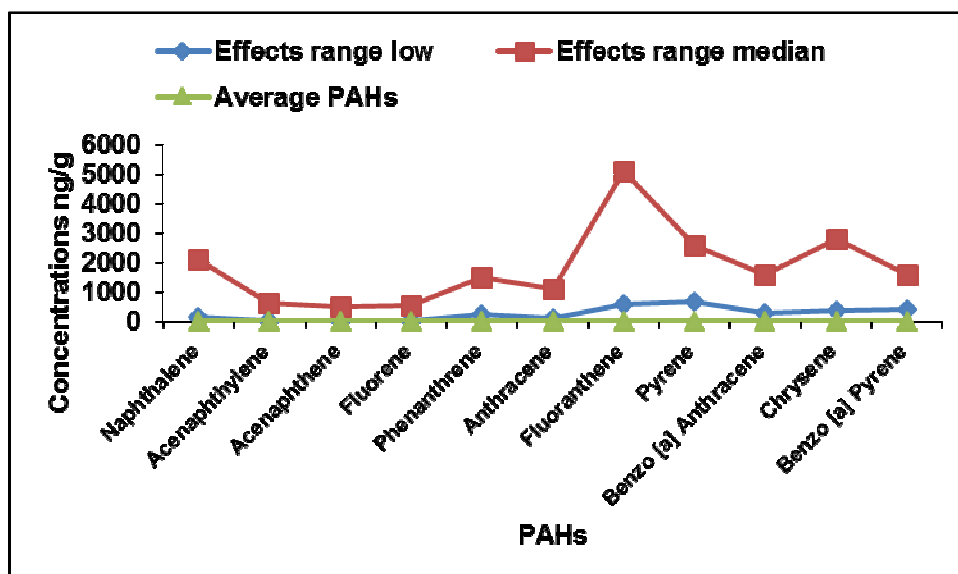


Figure 5. Average concentration of PAHs (ng/g) in Shatt Al-Arab River surface sediments relative to effects range low and effects range median.

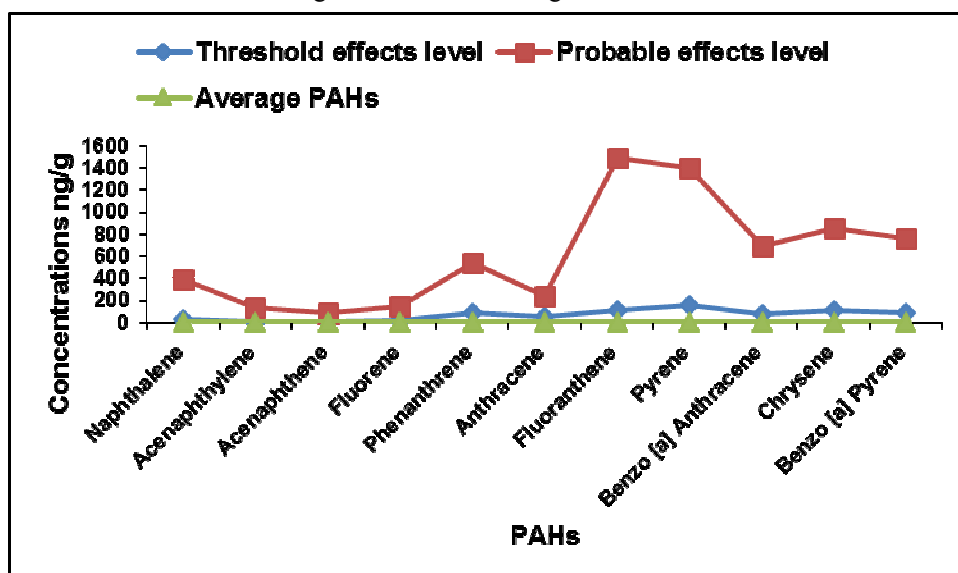


Figure 6. Average concentration of PAHs (ng/g) in Shatt Al-Arab River surface sediments relative to threshold effect level and probable effect level.

4. Conclusions

The surface sediments analysis of Shatt Al-Arab River provides valuable information to assess PAHs contamination levels and their probable sources in the river. The study showed that sixteen PAHs commonly found in the environment are present in the Shatt Al-Arab River sediments with dominance of PAHs characterized by high molecular weight (4–6 rings) over low molecular weight. The total concentrations of PAHs ranged from 30.86 to 87.79 ng/g dry weight with a mean value of 92.82 ng/g dry weight, indicating a moderate level of PAHs pollution compared with values reported for other studies and a heterogeneous distribution of these compounds in Shatt Al-Arab River sediments. The most contaminated sites of Shatt Al-Arab River sediments that were near potential oil pollution sources including Nahran-Omer-II, Basrah-IV, Abadan-VI, and Al-Fao-VIII. The concentrations of PAHs appear a consistent distribution trend with the sediment % TOC contents or grain size. Assessment of PAHs environmental risk suggested that the concentrations of PAHs will not cause any immediate adverse biological effects on Shatt Al-Arab river ecosystem. Based on the PAHs compounds profiles, the marked PAHs compounds, PAHs ratios and the PCA analysis, it can be concluded that the PAHs in the Shatt Al Arab River sediments were mainly from three different sources; pyrolytic, petrogenic, and biogenic. Pyrolytic sources of PAHs derived primarily from combustion of fossil fuels/petroleum (gasoline and crude oil) and vegetation fires. Whereas, refineries, port areas,

natural seep and tank shipping operation can be the potential sources of petrogenic PAHs. On the other hand degradation of organic matter and synthesis by certain organisms might represent the biogenic sources of PAHs. Further studies should be performed to investigate the effects of PAHs in the Shatt Al-Arab River in order to provide minimum acceptable levels of this compounds within this area to humans, fauna, and flora.

5. References

- Aizenshtat, Z. (1973). Perylene and its geochemical significance. *Geochimica et Cosmochimica Acta*, 37: 559-567.
- Ali, W.A.; Farid, W. A. and Al-Eed, A. A. (2013). Hydrocarbons distribution in Shatt Al-Arab River bacteria and fungi. *International Journal of Science and Modern Engineering (IJISME)*, 1(12): 5-9.
- Bin, J., Hai - Long, Z., Guo - Qiang, H., Hui, D., Xin - Gang, L., Hong, Tu. S. and Rui, L. (2007). Characterization and distribution of polycyclic aromatic hydrocarbon in sediments of Haihe River, Tianjin, China. *Journal of Environmental Sciences*, 19: 306 - 311.
- Cerniglia, C. E. (1992). Biodegradation of polycyclic aromatic hydrocarbons. *Biodegradation*, 3: 351 - 368.
- Chiou, C. T., McGroddy, S. E. and Kile, D. E. (1998). Partition characteristics of polycyclic aromatic hydrocarbons on soils and sediments. *Environmental Science and Technology*, 32: 264-269.
- De Luca, G., Furesi, A., Leardi, R., Micera, G., Panzanelli, A., Piu, P.C. and Sanna, G. (2004). Polycyclic aromatic hydrocarbons assessment in the sediments of the Porto Torres harbor (Northern Sardinia, Italy). *Marine Chemistry*, 86: 15-32.
- Dickhut, R. M., Canuel, E. M., Gustafson, K. E., Liu, K., Arzayus, K.M., Walker, S. E., Edgecombe, G., Gaylor, M. O. and Macdonald, E. H. (2000). Automotive sources of carcinogenic polycyclic aromatic hydrocarbons associated with particulate matter in the Chesapeake Bay Region. *Environmental Science and Technology*, 34: 4635-4640.
- El Nemr, A., Said, T. O., Khaled, A., El-Sikaily A. and Abd-Allah, A. M.A. (2007). The distribution and sources of polycyclic aromatic hydrocarbons in surface sediments along the Egyptian Mediterranean coast. *Environmental Monitoring and Assessment*, 124: 343-359.
- Farid, W. A., Al-Eed, A. A., Shihab, L. A. and Al-Saad, H. T. (2014). Distribution, sources, and seasonal variations of hydrocarbons in Shatt Al-Arab River water. *Journal of International Academic Research for Multidisciplinary*, 2(2): 729-739.
- Folk, R. L. (1974). *Petrology of sedimentary Rocks*. Hemphill publishing Co. Austin, Texas, USA, 182 pp.
- Grimalt, J.O. and Olive, J. (1993). Source input elucidation in aquatic systems by factor and principal component analysis of molecular marker data. *Analytica Chimica Acta*, 278: 159-176.
- Lee, C.; Hsieh, M. and Fang, M. (2005). Aliphatic and Polycyclic aromatic hydrocarbons in sediments of Kaohsiung harbor and adjacent coast, Taiwan. *Environmental Monitoring and Assessment*, 100: 217-234.
- Liu, A. X.; Lang, Y. H.; Xue, L. D. and Liu, J. (2009). Ecological risk analysis of polycyclic aromatic hydrocarbons (PAHs) in surface sediments from Laizhou Bay. *Environmental Monitoring and Assessment*, 159: 429-436.
- Liu, Y., Chen, L., Huang, Q. H., Li, W.Y., Tang, Y. J. and Zhao, J. F. (2009). Source apportionment of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of the Huangpu River, Shanghai, China. *Science of the Total Environment*, 407: 2931-2938.
- Long, E. R., Ingersoll, C. G. and MacDonald, D. D. (2006). Calculation and uses of mean sediment quality guideline quotient, a critical review. *Environmental Science & Technology*, 40: 1726-1736.
- Long, E. R., MacDonald, D. D., Smith, S. L. and Calder, F. D. (1995). Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management*, 19: 81-97.
- Mahmoodi, M., Safahieh, A., Nikpour, Y. and Ghanemi, K. (2012). Distribution and Sources of Polycyclic Aromatic Hydrocarbons in the Sediment of Bushehr Coastal Zone-Iran. *Iranica Journal of Energy and Environment*, 3(2): 173-179.
- Moyel, M. S. and Hussain, N. A. (2015). Water quality assessment of the Shatt Al-Arab River, Southern Iraq. *Journal of Coastal Life Medicine*, 3(6): 459-465.
- National Research Council (NRC) (2003). *Oil in the sea III. Input, fates and effects*, National Academic Press. Washington.
- Pereira, W. E., Hostettler, F. D., Luoma, S. N., Geen, A., Fuller, C. C. and Roberto J. A. (1999). Sedimentary record of anthropogenic and biogenic polycyclic aromatic hydrocarbons in San Francisco Bay, California. *Marine Chemistry*, 64: 99-113.
- Perra, Guido, Renzi, M., Guerranti, C. and Focardi, S. E. (2009). Polycyclic aromatic hydrocarbons pollution in sediments: distribution and sources in a lagoon system (Orbetello, Central Italy). *Transitional Waters Bulletin*, 3(1): 45-58.

- Qiu, Y. W., Zhang, G., Liu, G. Q., Guo, L. L., Li, X. D. and Wai, O. (2009). Polycyclic aromatic hydrocarbons (PAHs) in the water column and sediment core of Deep Bay, South China. *Estuarine, Coastal and Shelf Science*, 83: 60–66.
- Quiroz, R., Grimalt, J. O. and Fernandez, P. (2010). Toxicity assessment of polycyclic aromatic hydrocarbons in sediments from European high mountain lakes. *Ecotoxicology and Environmental Safety*, 73: 559–564.
- Tolosa, I., De Mora, S., Sheikholeslami, M. R., Villeneuve, J. P., Bartocci, J. and Cattini, C. (2004). Aliphatic and aromatic hydrocarbons in coastal caspian Sea. *Marine Pollution Bulletin*, 48: 44 - 60.
- Trabelsi, S. and Driss, M. R. (2005). Polycyclic aromatic hydrocarbons in superficial coastal sediments from Bizerte Lagoon, Tunisia. *Marine Pollution Bulletin*, 50: 344 - 359.
- Venkatachalapathy, R., Veerasingam, S., Basavaiah, N., Ramkumar, T. and Deenadayalan, K. (2011). Environmental magnetic and petroleum hydrocarbons records in sediment cores from the north east coast of Tamilnadu, Bay of Bengal, India *Marine Pollution Bulletin*, 62: 681 - 690.
- Venkatesan, M. I. (1988). Occurrence and possible sources of perylene in marine sediments: a review. *Marine Chemistry*, 25: 1-27.
- Venkatesan, M. I., Sandstrom, M., Brenner, S., Ruth, E., Bonilla, J., Kaplan, I. R. and Reed, W. E. (1981). Organic geochemistry of surficial sediments from the Eastern Bering Sea. In: Hood, D.W., Calder, J. A. (Eds.), *The Eastern Bering Sea Shelf: Oceanography and Resources*, Vol. 1. US Department of Commerce, NOAA, *Oce of Marine Pollution Assessment*, pp. 389-409.
- Wakeham, S. G., Schafner, C. and Giger, W. (1979). Perylene in sediments from the Namibian Shelf. *Geochimica et Cosmochimica Acta* 43, 1141-1144.
- Walkey, A. and Black, I. A. (1934). An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil Science*, 34: 29–38.
- Wang, C., Wang, W., He, S., Due, J. and Sun, Z. (2011). Sources and distribution of aliphatic and polycyclic aromatic hydrocarbons in Yellow River Delta Nature Reserve, China *Applied Geochemistry*, 26: 1330-1336.
- Wang, Z. and Fingas, M. F. (2003). Development of oil hydrocarbon fingerprinting and identification techniques. *Marine Pollution Bulletin*, 47: 423 - 452.
- Yang, Z. F., Wang, L. L., Niu, J. F., Wang, J. Y. and Shen, Z. Y. (2009). Pollution assessment and source identifications of polycyclic aromatic hydrocarbons in sediments of the Yellow River Delta, a newly born wetland in China. *Environ. Environmental Monitoring and Assessment*. 158: 561–571.
- Yang, G. (2000). Polycyclic aromatic hydrocarbons in the sediments of the South China Sea. *Environmental Pollution*, 108: 163-171.
- Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, R. H., Goyette, D. and 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: 489–515.
- Zrafi, I., Hizem, L., Chalghmi, H., Ghrabi, A., Rouabhia, M. and Saidane - Mosbahi. D. (2013). Aliphatic and aromatic biomarkers for petroleum hydrocarbon investigation in marine sediment. *Journal of Petroleum Science Research (JPSR)*, 2(4): 146-155.
- Zrafi - Nouira, I., Khedir - Ghenim, Z., Zrafi, F., Bahri, R., Cheraief. I., Rouabhia, M., Saidane Mosbahi, D. (2008). Hydrocarbon pollution in the sediment from the Jarzouna - Bizerte coastal area of Tunisia (Mediterranean Sea). *Bulletin of Environmental Contamination and Toxicology*, 80: 566 - 572.