

**DISTRIBUTION, SOURCES, AND SEASONAL VARIATIONS OF
HYDROCARBONS IN SHAT AL-ARAB RIVER WATER**

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ABSTRACT

The distribution and seasonal variations of hydrocarbons in the Shatt Al-Arab River water column were determined. Total hydrocarbons concentrations were found to vary between 16.77 $\mu\text{g l}^{-1}$ to 42.6 $\mu\text{g l}^{-1}$. N-alkanes carbon chain length ranged from C12 to C32 with total concentrations varied from 6.50 $\mu\text{g l}^{-1}$ to 14.23 $\mu\text{g l}^{-1}$. The bimodal distribution pattern of n-alkanes with two maxima around C19 to C32 suggested two different sources of hydrocarbons in Shatt Al-Arab River both biogenic and anthropogenic. Polycyclic aromatic hydrocarbons (PAH) appeared divisible into two groups, the low molecular weight (naphthalene, biphenyl, phenanthrene, acenaphthene, and anthracene) and the larger molecular weight (fluoranthene, pyrene, chrysene, benzo (a) pyrene and perylene) with total concentrations varied from 7.19 ng l⁻¹ to 22.47 ng l⁻¹. Their sources derived from different origins. The results indicated that there were distinct seasonal variations of hydrocarbons in Shatt Al-Arab River. The compounds tend to be highest in winter (averaged 31.46 $\mu\text{g l}^{-1}$) and lowest in summer (averaged 25.63 $\mu\text{g l}^{-1}$).

KEYWORDS: Shatt Al-Arab River, Total Hydrocarbons, Biogenic Hydrocarbons, N-Alkanes, Pahs, Hydrocarbons Pollution

INTRODUCTION

The Shatt Al-Arab River is the most important river and the only source of freshwater in the arid surroundings of southern Iraq. It is the prime freshwater source and pours about 5x10⁹ m³ nutrient rich water into the Arabian Gulf each year (DouAbul and Al-Saad, 1985). The Shatt Al-Arab River has an area of million km². Extensive areas are occupied by mangroves and aquatic grasses which are thought to be the major supporters of aquatic food web via detritus. The aquatic fauna and flora of the river are unique assemblages of subtropical and temperate representatives creating an exceedingly diverse and delicately balanced ecosystem.

The Shatt Al-Arab River region is with a large catchment area utilized for agriculture, grazing, and urban (Farid, 2007).

Development pressures to make Shatt Al-Arab River are mounting as the river provides easy access to small tankers. Many heavy industries are already located along the Shatt Al-Arab River shore, an oil refinery, electrical power stations, a paper mill, a fertilizers factory, a petrochemical complex, and iron and steel mills. The oil industries have established tanker unloading facilities. As yet, no large oil spills have occurred. Thus, even though the Shatt Al-Arab River is relatively unspoiled, it suffers constant threat of oil pollution from tanker activities as well as chronic inputs from sources such as boating, refinery and other industrial outfalls, and domestic sewage.

The Shatt Al-Arab River environmental studies were taken to gain knowledge of the physical, chemical, and biological systems in Shatt Al-Arab River and to identify man's impact on the ecosystem with a goal of water management policies. The hydrocarbons study described in this paper is part of these programmes.

To predict the impact of petroleum hydrocarbons pollution in Shatt Al-Arab River, an ecosystem approach was followed. It was necessary firstly to study hydrocarbons inputs into the river and then to establish the means by which the ecosystem dissipated these compounds. Hydrocarbons enter the aquatic environment either by loss and discharge of petroleum products or by the decomposition of organisms containing biogenic hydrocarbons. These compounds are readily transported in the form of dissolved and particulate adsorbed organic matter within the water column. The hydrocarbons contribution from the two sources (i.e. biogenic and anthropogenic) can be determined by chemical isolation of hydrocarbons constituents and their separation into components on a gas chromatography. Biogenic hydrocarbons are usually much different in chemical composition than petroleum. By comparing sample chromatograms with those from known sources one can compute the contribution of each in a sample ([Wang and Fingas, 2003](#)). Other techniques such as fluorescence provide information on types of hydrocarbons and are also useful in distinguishing petroleum sources.

The objectives of the present study are to determine the regional distributions of hydrocarbons, both in solution or dispersed through the Shatt Al-Arab River water column, in an attempt to identify major sources and estimate the seasonal variations of hydrocarbons to study the main ecological factors acting upon the weathering of hydrocarbons in Shatt Al-Arab River water.

MATERIALS AND METHODS

The Shatt Al-Arab River originates from the confluence of the two major rivers of Iraq (Tigris and Euphrates) at Qurna. 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. It's with 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.

Five sampling locations were selected along the Shatt Al-Arab River to represent different locations of north section of the River. The sampling programme was carried out during winter and summer seasons. Areas included in the present study and their positions are shown on the map. Replicate water samples were collected using water collector device at low tide from each location during 2012. After collecting water samples, the determination of hydrocarbons concentrations was carried out without delay.

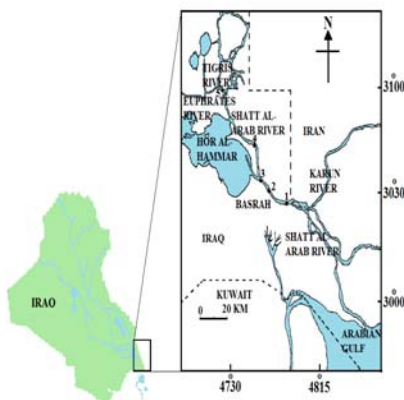


Figure 1. Map of Shatt Al-Arab River showing the position of stations

Hydrocarbons were extracted from water followed the procedure described by Grimalt and Olive (1993) and [Tuteja et al. \(2011\)](#) with some modification. The extracts were divided into two portions. The first portion was used to determine total petroleum hydrocarbons using a Shimadzu RF-540 spectrofluorometer. The extract volume was reduced using a rotary

evaporator to 10 ml and then saponified for 2 h with a solution of 4N KOH in 1:1 methanol: Benzene and then dried by anhydrous Na_2SO_4 and concentrated by a stream of nitrogen. Petroleum hydrocarbons were quantified by measuring the emission intensity at 360 nm, with excitation set at 310 nm and monochromatic slits of 10 nm. The second portion of the extract was used to determine the aliphatic (n-alkanes) and aromatic hydrocarbons using a Perkin-Elmer sigma 300 gas chromatograph. Prior to GC analysis the extracts were cleaned by passing them through column filled with 8g of 5% deactivated alumina (100-200 mesh) on the top and silica (100-200 mesh) in the bottom. The samples then were eluted by 50 ml n-hexane (aliphatic fraction) followed by 50 ml of benzene (aromatic fraction). Both fractions were reduced to suitable volume and subjected to GC analysis. Helium gas was used as a carrier gas with a linear velocity of 1.5 ml min^{-1} . The operating temperatures for detector and injector were 350°C and 320°C , respectively. The silica capillary column was operated under initial, final and rate temperatures that programmed as follows: Initial temperatures were 60°C for aliphatic fraction for 4 min and 70°C for aromatic fraction for 0 min, while final temperatures were 280°C for aliphatic fraction and 300°C for aromatic fraction for 30 min and rate was 4°C/min for both aliphatic and aromatic fractions. Quantification of peaks and identification of hydrocarbons were done by a Perkin-Elmer computing integrator model LC-100. The Unresolved Complex Mixture (UCM) was measured using planimetry. The Odd and Even n-alkane Predominance Index (OEPI) and the Carbon Preference Indices (CPI) were used to indicate the general source of hydrocarbons whether their origin was biogenic or anthropogenic (API, 2001; Zrafi et al., 2013). Pristane/Phytane ratio, Pristane/ C_{17} and Phytane/ C_{18} and the Unresolved Complex Mixture index (UCM) were used as indicators of petroleum contamination (API, 2001; Shi et al., 2008) and to estimate the degree of bacterial degradation (Wang et al., 2011).

RESULTS AND DISCUSSION

The average concentrations of total hydrocarbons in the water of Shatt Al-Arab River were found to vary from $16.77 \mu\text{g l}^{-1}$ to $42.6 \mu\text{g l}^{-1}$ (Table 1). Our data indicated that the level of hydrocarbons observed in the Shatt Al-Arab River water lie within the range of values reported by DouAbul (1984) El-Samra et al. (1986) Marchand et al., (1988) Sen Gupta et al., (1993) Zanardi et al., (1999) Chouksey et al., (2004) Meepoka et al., (2007) Li et al., (2010) Wattayayakorn and Rungsupa (2012) and Tahrani et al. (2013). From the results presented here it is evident that all the studied locations were contaminated to some extent with hydrocarbons. The highest concentrations were always observed at location 2, while the

lowest were at location 5. This indicates that Shatt Al-Arab River hydrocarbons have possible originated from diverse sources.

The chromatographic distributions of carbon chain lengths of the average n-alkanes concentrations indicate different variations of peaks among the studied locations; however, these peaks exhibit a significant n-alkanes profile consisting of a bimodal distribution with two maxima around C₁₉ and C₃₂ (Figure 2). The distribution of total average n-alkanes concentrations in the water of Shatt Al-Arab River ranged from 6.50 µg l⁻¹ in location 5 to 14.23 µg l⁻¹ in location 2 (Table 2). The total average odd-even carbon numbers of n-alkanes

Table 1. Average concentrations of total hydrocarbons (µg l⁻¹ ±SD) and polynuclear aromatic hydrocarbons (ng l⁻¹ ±SD) in Shatt Al-Arab River locations during winter and summer 2012.

	Location 1	Location 2	Location 3	Location 4	Location 5
Total hydrocarbons	34.17 (±0.4)	42.6 (±0.3)	29.02 (±0.2)	20.15 (±0.4)	16.77 (±0.5)
Naphthalene	1.38 (±0.2)	1.62 (±0.3)	1.17 (±0.5)	0.83 (±0.1)	0.56 (±0.2)
Biphenyl	1.57 (±0.2)	1.86 (±0.2)	1.32 (±0.3)	0.85 (±0.4)	0.72 (±0.1)
Acenaphthene	1.56 (±0.0)	1.75 (±0.3)	1.25 (±0.2)	0.97 (±0.4)	0.54 (±0.3)
Phenanthrene	1.84 (±0.4)	2.23 (±0.4)	1.56 (±0.4)	0.85 (±0.4)	0.62 (±0.4)
Anthracene	1.38 (±0.3)	1.96 (±0.3)	1.00 (±0.3)	0.72 (±0.2)	0.42 (±0.2)
Fluoranthene	2.30 (±0.4)	2.98 (±0.4)	1.94 (±0.4)	0.79 (±0.4)	0.52 (±0.4)
Pyrene	1.47 (±0.4)	1.74 (±0.4)	0.92 (±0.4)	0.77 (±0.4)	0.53 (±0.4)
Chrysene	2.21 (±0.4)	2.59 (±0.4)	1.86 (±0.4)	1.62 (±0.4)	1.34 (±0.4)
Benzo(a) Pyrene	2.42 (±0.4)	2.86 (±0.4)	1.76 (±0.4)	1.43 (±0.4)	0.95 (±0.4)
Perylene	2.64 (±0.4)	2.88 (±0.4)	1.56 (±0.4)	1.25 (±0.4)	0.99 (±0.4)
Total PAH	18.77	22.47	14.34	10.08	7.19

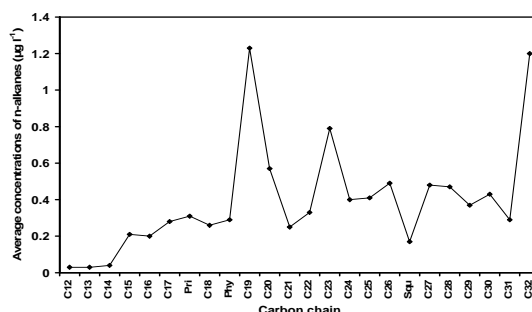


Figure 2. Chromatographic distributions of carbon chain lengths of the average n-alkanes concentrations (µg l⁻¹) in Shatt Al-Arab river locations during winter and summer 2012.

, CPI values, pristane/phytane ratio, pristane/C₁₇ ratio, phytane/C₁₈ ratio and UCM values of Shatt Al-Arab River are listed in Table (3). In general, the Indies suggest two different sources of hydrocarbons in the water of Shatt Al-Arab River both biogenic and anthropogenic. Biogenic sources of hydrocarbons were indicated by the dominance of the odd carbon n-alkanes, C₁₅, C₁₇, and C₁₉ which are commonly found in algae (Xue et al., 2012), C₂₀ to C₂₈ model n-alkanes without

Table 2. Mean n-alkanes concentrations (µg l⁻¹) and standard error in the water samples of the selected locations of Shatt Al-Arab River during the study period.

Carbon chain	Location 1	SE	Location 2	SE	Location 3	SE	Location 4	SE	Location 5	SE
C ₁₂	0.05	0.3	0.09	1.1	0.03	0.5	0.01	0.5	0.01	0.0
C ₁₃	0.04	0.4	0.08	1.6	0.01	1.3	0.01	1.5	0.01	0.7
C ₁₄	0.05	0.2	0.09	0.9	0.02	1.6	0.04	0.8	0.02	1.7
C ₁₅	0.26	0.5	0.36	0.7	0.20	0.8	0.07	1.6	0.20	1.5
C ₁₆	0.05	0.3	0.10	0.3	0.03	1.4	0.01	0.9	0.01	0.4
C ₁₇	0.36	0.2	0.45	0.5	0.26	0.6	0.15	0.7	0.18	0.8
Pristane	0.50	0.3	0.64	0.1	0.41	0.8	0.26	0.3	0.12	0.5
C ₁₈	0.18	0.6	0.28	0.6	0.17	0.9	0.10	0.5	0.11	0.1
Phytane	0.40	1.2	0.56	0.7	0.31	1.1	0.30	1.6	0.20	0.6
C ₁₉	1.28	0.7	1.48	0.3	1.20	0.3	1.11	0.0	1.12	0.7
C ₂₀	0.48	0.0	0.68	0.2	0.41	0.4	0.23	1.1	0.26	0.3
C ₂₁	0.42	1.2	0.57	0.1	0.30	0.5	0.21	0.5	0.25	0.2
C ₂₂	0.32	0.4	0.46	1.3	0.30	0.7	0.10	0.3	0.18	0.1
C ₂₃	0.9	1.5	0.99	0.5	0.75	0.9	0.62	0.8	0.70	0.5
C ₂₄	0.47	0.8	0.60	1.5	0.41	0.1	0.31	0.6	0.25	0.1
C ₂₅	0.59	0.1	0.72	0.5	0.51	0.3	0.41	1.2	0.32	1.8
C ₂₆	0.42	0.5	0.69	0.8	0.31	1.8	0.25	0.7	0.30	1.1
Squalane	0.20	0.6	0.36	0.4	0.17	1.1	0.11	0.3	0.02	0.5
C ₂₇	0.65	0.4	0.87	0.4	0.58	0.5	0.36	1.2	0.37	0.6
C ₂₈	0.42	0.3	0.64	0.3	0.32	0.6	0.21	0.4	0.26	0.2
C ₂₉	0.60	1.3	0.75	0.1	0.46	0.2	0.31	0.9	0.23	1.8
C ₃₀	0.30	1.9	0.48	1.1	0.23	0.3	0.25	0.9	0.10	1.1
C ₃₁	0.47	0.8	0.69	0.2	0.37	0.4	0.21	1.7	0.24	0.6
C ₃₂	1.20	0.2	1.40	0.6	1.20	1.4	1.16	1.0	1.04	0.0
Total n-alkanes	10.84		14.23		9.60		6.87		6.50	

Table 3. Odd and Even n-alkanes values, CPI values, Pristane/Phytane ratio, Pristane/C₁₇ ratio, Phytane/C₁₈ ratio and UCM values in the water samples of the selected locations of Shatt Al-Arab River during the study period.

	Location 1	Location 2	Location 3	Location 4	Location 5
Odd n-alkane	5.07	6.46	8.43	3.06	3.12
Even n-alkane	4.94	6.51	4.43	3.35	3.06
CPI	1.02	0.99	0.93	0.91	1.01
Pristane/Phytane	1.73	0.91	0.91	0.94	1.30
Pristane/C ₁₇	1.11	0.95	1.57	1.13	0.94
Phytane/C ₁₈	0.92	1.23	1.66	0.90	0.61
UCM	6.38	8.43	4.99	4.18	2.85

carbon number preference, maximizing around C₂₃ which may be produced by bacterial activity (Grimalt and Albaiges, 1990), and C₂₅ to C₃₂ odd carbon number n-alkanes which are synthesized by higher plants (Wang et al., 2011). The presence of the isoprenoids hydrocarbons, pristane and phytane in significant concentrations supported the biogenic origin of hydrocarbons in Shatt Al-Arab River. It has been reported that pristane synthesized from zooplankton, decomposition of algae, and chlorophyll of land-plant (Shi et al., 2008), and phytane originated from bacteria and deposition of algae (Simoneit, 1991). However, the weathered petroleum products could also include pristane and phytane as natural by-product (Al-Saad, 1995). The ratios of pristane/phytane, pristane/C₁₇, phytane/C₁₈ involved both biogenic and anthropogenic compounds, and confirm the strong biodegradation of hydrocarbons occurring in the Shatt Al-Arab River (Cripps, 1989). Squalane is also indicating in the river water, which may be originated from anthropogenic or living organisms (Al-Saad and Al-Timari, 1993). The study also show the presence of even-carbon numbered n-alkanes, which may be related to a contribution from artificial sources (Zrafi et al., 2013). The anthropogenic contribution of hydrocarbons is evident from the presence of a wide range of UCM in water. UCM represented components resistant to weathering and microbial degradation and its presence had frequently been taken as an evidence of recent petroleum contamination (Frysiner et al. 2003). However, the possible sources of UCM other than human activities were found like those synthesized by some bacteria (Han and Calvin, 1969). The UCM detected in the present study could be originated from a number of possible sources. CPI was an important parameter in relation to hydrocarbon sources, which may indicate biogenic and anthropogenic sources of hydrocarbons in water of Shatt Al-Arab River. Ehrhardt and Petrick (1993) reported that, if CPI was more than one, the sources of hydrocarbons are biogenic, and if it is smaller than one, the sources were anthropogenic. The suspected anthropogenic sources of hydrocarbons influencing each of the studied locations along the north section of the Shatt Al-Arab River water according Al-Saad (1995) suggestion include rural run-off (location 1 and 5), sewage discharges, transportation activities, and urban run-off (location 2), electrical generating station (location 3), and oil refinery (location 4).

The distribution of total average PAH concentrations in the Shatt Al-Arab River water ranged from 7.19 ng l⁻¹ to 22.47 ng l⁻¹. (Table 1) The PAH appears divisible into two groups, the low molecular weight PAH incorporating naphthalene; biphenyl; phenanthrene; acenaphthene; and anthracene, and the high molecular weight homologous PAH including fluoranthene; pyrene; chrysene; benzo (a) pyrene and perylene. The highest concentrations were found in location 2, while the lowest concentrations were at location 5 (Figure 2). This suggests that PAH has originated from different sources; the first is anthropogenic including refineries; and shipping activities and operations, and the second is probably from natural seep and biogenic origins. Similar conclusion were reached by Yunker et al. (2002), Zhang et al. (2004), and Yang et al. (2009).

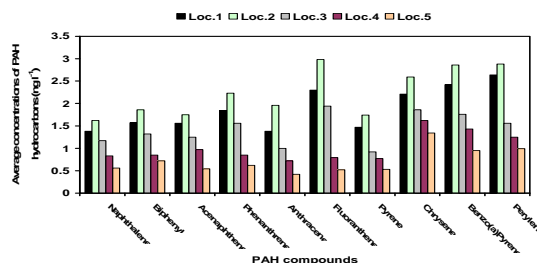


Figure 3. Average concentrations of polynuclear hydrocarbons (ng l^{-1}) at Shatt Al-Arab River locations during winter and summer 2012.

Generally, the recent results show that the total hydrocarbons concentrations in the water of Shatt Al-Arab River were significantly higher in winter and lower in summer (Figure 4). This indicates that the Shatt Al-Arab River water hydrocarbons undergo seasonal variations. Several factors could act to produce these seasonal variation in concentrations of hydrocarbons in water of Shatt Al – Arab river. It has been reported that the hydrocarbons concentrations vary inversely in relation to water temperature (NRC, 2003). Thus when the temperature was high during summer, the estimated hydrocarbons concentrations were lower than that when the temperature was low during winter. Wang et al. (2005) documented that temperature was the most important factor governing the removal of hydrocarbons in the environment by evaporation. In addition to the direct effect of temperature on the evaporation of hydrocarbons from water, temperature increase favors microbial degradation process (Coulon et al., 2007). The photo-oxidation may also degrade the components of oil in the waters (Garrett et al., 1998). The intense solar radiations coupled with relatively high water temperature were the characteristic features of the climate of the subtropical regions of Iraq. These two factors (i.e. temperature and photo-oxidation) could account for rather low levels of hydrocarbons encountered in the Shatt Al-Arab River water, particularly during summer. It is also postulated that petroleum hydrocarbons have a tendency to adsorb onto particular matter (Grimalt and Albaiges, 1990). Albaiges et al. (1984) have concluded that adsorption of hydrocarbons to estuarine sediments is the principle mechanism for the removal of these hydrocarbons. Douabul and Al-Saad (1985) observed pronounced seasonal variations in the average values of suspended matter along the Shatt Al-Arab River, being at minimum in summer. Accordingly lower concentrations of hydrocarbons concentrations in water of Shatt Al-Arab River during summer could be caused in part by the increased sedimentation of adsorbed hydrocarbons. The difference in the discharge of hydrocarbons into the aquatic environment during the different seasons could produce in seasonal variations in the

concentrations of hydrocarbons in water of Shatt Al-Arab River. Al-Saad (1995) showed that the possible explanation of higher concentrations during winter was that total hydrocarbons discharge was greater than in summer due to the wider occurrence of combustion processes with large amount of fossil fuel used in household heating during the cold season as well as the higher association of these hydrocarbons with atmospheric particles at lower ambient temperature. Accordingly, one expects that the levels of hydrocarbons that found in the Shatt Al-Arab River water will be considerably less in summer than in winter.

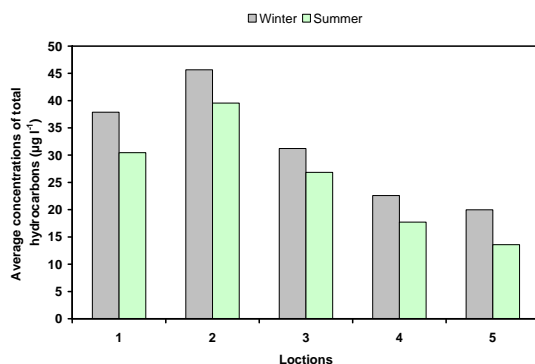


Figure 4. Average concentrations of total hydrocarbons ($\mu\text{g l}^{-1}$) at the selected locations in Shatt Al-Arab River during winter and summer 2012.

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CONCLUION

A measurable concentration of hydrocarbons were found in the Shatt Al-Arab River water which reflected the background levels. The concentrations were relatively higher in the locations near the sources of oil activities. The hydrocarbons in the Shatt Al-Arab River seem to be derived from both biogenic and anthropogenic sources. The rural run-off, sewage discharges, transportation activities, urban run-off, electrical generating stations, and oil refinery plants could be the possible sources of anthropogenic hydrocarbons in the sampled locations. On the other hand seeps from oil deposits, degradation of organic matter and synthesis by certain organisms might represent the natural sources. Several factors could produce the seasonal variations in hydrocarbons of Shatt Al-Arab River water. These factors include temperature, evaporation, biodegradation, photo-oxidation, sedimentation, and the difference in the discharge of hydrocarbons into the river. Every possible effort should be made to minimize petroleum plants wastes by applying outfall licenses to specify permissible

levels on the basis of the most toxic fractions of petroleum released into the environment. In addition, aromatic hydrocarbons should be carefully monitored in the water in order to provide their minimum and acceptable levels within the river environment to human, fauna and flora.

REFERENCES

1. Albaiges, J.; Grimalt, J.; Bayona, M.; Risebrough, R.; Delappe, B. and Walker, H. W. (1984). Dissolved particulate and sedimentary hydrocarbons in a deltic environment. *Organic Geochemistry*, 6: 237-248.
2. Al-Saad, H. T. (1995). Distribution and sources of hydrocarbons in Shatt Al-Arab estuary and North West Arabian Gulf. Ph.D. thesis, Biology department, Basrah University, Iraq, 186 p.
3. Al-Saad, H. T. and Al-Timari, A. K. (1993). Sources of hydrocarbons and fatty acids in sediment of Hor Al-Hammar, Shatt Al-Arab river, and North-west Arabian Gulf. *Marine Pollution Bulletin*, 26: 207-212.
4. API (2001). Risk-based methodologies for evaluating petroleum hydrocarbon impacts at oil and natural gas E&P Sites. American Petroleum Institute.
5. Chouksey, M. K.; Kadam, A. N. and Zingde, M. D. (2004). Petroleum hydrocarbon residues in marine environment of Bassen-Mumbai, *Marine Pollution Bulletin*, 49: 637-647.
6. Coulon, F.; McKew, B. A.; Osborn, A. M.; McGenity, T. J. and Timmis, K. N. (2007). Effects of temperature and biostimulation on oil-degrading microbial communities in temperate estuarine waters. *Environmental Microbiology*, 9: 177-186.
7. Cripps, G. C. (1989). Problems in the identification of anthropogenic hydrocarbons against natural background levels in the Antarctic. *Antarctic Science*, 1: 307-312.
8. DouAbul, A. A. Z. (1984). Petroleum residues in the waters of the Shatt Al-Arab River and the North-West region of the Arabian Gulf. *Environment International*, 10: 265-267.
9. DouAbul, A.A.Z. and Al-Saad, H. T. (1985). Seasonal variations of oil residues in water of Shatt Al-Arab River, Iraq. *Water, Air, and Soil Pollution*, 24: 237-246.
10. Ehrhardt, M. and Petrick, G. (1993). On the composition of dissolved and particulate-association fossil fuel residues in Mediterranean surface water. *Marine Chemistry*, 42: 57-70.
11. El-Samra, M. I.; Emara, H. I. and Shunbo, E. (1986). Dissolved petroleum hydrocarbons in the Northwestern Arabian Gulf, *Marine Pollution Bulletin*, 17:65-68.
12. Farid, W. A. A. (2007) The use of some species of molluscs of the Shatt Al-Arab River in the toxicity tests, bioaccumulation and monitoring of oil pollution. Ph.D. thesis, Biology department, Basrah University, Iraq, 198 p.
13. Frysinger, G. S.; Gaines, R. B.; Xu, L. and Reddy, C. M. (2003). Resolving the unresolved complex mixture in petroleum contaminated sediments. *Environmental Science and Technology*, 37: 1653-1662.
14. Garrett, R. M.; Pickering, I. J.; Haith, C. E. and Prince, R. C. (1998). Photooxidation of crude oils. *Environmental Science and Technology*, 32: 3719-3723.
15. Grimalt, J. O. and Olive, J. (1993). Source elucidation in aquatic systems by factor and principal component analysis of molecular marker data. *Analytica Chimica Acta*, 278:159-176.
16. Grimalt, J.O. and Albaiges, J. (1990). Characterization of depositional environments of the Erbo Delta (western Mediterranean) by the study of sedimentary lipid markers. *Marine Geology*, 95: 207-224.
17. Han, J. and Calvin, M. (1969). Hydrocarbon distribution of algae and bacteria, and microbiological activity in sediments. *Proceeding of the National Academy of Sciences*, 64: 436-443.
18. Li, Y.; Zhao, Y.; Peng, S.; Zhou, Q. and Ma L. Q. (2010). Temporal and spatial trends of total petroleum hydrocarbons in the seawater of Bohai Bay, China from 1996 to 2005. *Marine Pollution Bulletin*, 60: 238-243.

19. Marchand, J. C.; Caprais, J. C. and Pignet, P. (1988). Hydrocarbons and halogenated hydrocarbons in coastal water of the western Mediterranean (France). *Marine Environmental Research*, 25: 131-159.
20. Meepoka, T. (2007). Petroleum hydrocarbon concentrations in seawater and sediments around fishing piers in Chanburi Province. Senior Project, Department of Marine Science, Chulalongkorn University.
21. National Research Council (NRC) (2003). Oil in the sea III. Input, fates and effects, National Academic Press. Washington.
22. Sen Gupta, R.; Fondekari, S. P. and Alagarsamy, R. (1993). State of oil pollution in the northern Arabian sea after the 1991 Gulf oil spill. *Marine Pollution Bulletin*, 21: 85-91.
23. Shi, H.; Zhang, L.; Yue L. and Zheng, G. (2008). Petroleum hydrocarbon contamination in surface sediments of Beiluohe Basins, China. *Bulletin Environmental Contamination and Toxicology*, 81: 416-421.
24. Simoneit, B. R. T. (1991). Organic geochemistry of deep sea drilling project sediments from Legs 63-66: A synthesis of sources, preservation and maturation of organic matter in the Quaternary and Neogene sediments from an active continental margin. in: *The Gulf and Peninsular Province of the Californias*. (Dauphin, J.P. and Simoneit, B.R.T. eds.), American Association Petroleum Geologists, Memoir 47, Chapter 32, pp. 667-706.
25. Tahrani, G. M.; Hashim, R.; Sulaiman, A. H.; Sany, B. T.; Salleh, A.; Jazani, R. K.; Savari, A. and Barandoust, R. F. (2013). Distribution of total petroleum hydrocarbons and of polycyclic aromatic hydrocarbons in Musa Bay sediments (Northwest of the Persian Gulf). *Environment Protection Engineering*, 39(1): 115-128.
26. Tuteja, G.; Rout C. and Bishhnoi, N. R. (2011). Quantification of polycyclic aromatic hydrocarbons in and underground vegetables: A case study around Panipat City, Haryana, India. *Journal of Environmental Science and Technology*, 4: 611-620.
27. Wang, C.; Wang, W.; He, S.; Du, 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.
28. Wang, X. L.; Li, K. Q.; Zhu, C. J.; Han, X. R.; Deng, N. N. and Cheng, H. (2005). Pollution condition of petroleum hydrocarbon pollutant and estimation of its environmental capacities in summer in the Bohai Sea. *Marine Science Bulletin*, 7: 21-29.
29. Wang, Z. and Fringas, M. F. (2003). Development of oil hydrocarbon fingerprinting and identification techniques. *Marine Pollution Bulletin*, 47: 423-452.
30. Wanttayyakorn, G. and Rungsupha, S. (2012). Petroleum hydrocarbon residues in the marine environment of Koh Sichang-Sriracha, Thailand. *Coastal Marine Science*, 35(1): 122-128.
31. Xue, H.; Qimin, M.; Hua, Z. and Haiou, C. (2012). Normal alkanes characteristic in surface sediments from typical Bohai sea areas. *Environment Chemistry*, 31(9): 1315-1320.
32. 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. *Environmental Monitoring and Assessment*, 158: 561-571.
33. 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.
34. Zanardi, E.; Bicego, M. C.; Miranda, L. B. and Weber, R. R. (1999). Distribution and origin of hydrocarbons in water and sediment in Sao Sebastiao, SP, Brazil. *Marine Pollution Bulletin*, 38: 261-267.
35. Zhang, Z. L.; Hong, H. S.; Zhou, J. L. and Yu, G. (2004). Phase association of polycyclic aromatic hydrocarbons in the Minjiang River Estuary, China. *Science of The Total Environment*, 323: 71-86.
36. Zrafi, I.; Hizem, L.; Chalhmi, H.; Ghrabi, A.; Rouabhia, M. and Saidance-Mosbahi, D. (2013). Aliphatic and aromatic biomarkers for Petroleum Hydrocarbon Investigation in Marine Sediment. *Journal of Petroleum Science Research*, 2(4): 144-155.

