



## Total Petroleum Hydrocarbons (TPHs), n-alkanes and Polynuclear Aromatic Hydrocarbons (PAHs) in water of Shatt Al-Arab River – part 1

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### Abstract

Water samples were collected monthly from five stations along the middle part of Shatt Al Arab river during the low tide period from December , 2012 to November , 2013 to determine the concentrations , distribution and sources of hydrocarbons compounds in water samples. TPH is range from 5.18  $\mu\text{g/l}$  to 37.59  $\mu\text{g/l}$  . The carbon chain length of aliphatic ( n-alkanes) in water were recorded from C7 to C31 dominated by C22-C25 , and the total n-alkanes was ranged from 8.81  $\mu\text{g/l}$  to 35.58  $\mu\text{g/l}$  . The range of PAHs compounds was ( 5.81 – 47.96)  $\text{ng/l}$  , dominated by carbazol and anthracene ( as light PAHs) and chrysene and floranthene (as heavy PAHs) . The LMW/HMW , CPI and Pristine/Phytane ratios indicated that the source of n-alkanes hydrocarbons was mainly biogenic and pyrogenic and at least petrogenic .Whereas the LMW/HMW , Phenanthrene /Anthracene , and Flouranthene / Pyrene ratios indicated that the source of PAHs compounds was mainly pyrogenic and petrogenic .

**Key words :** Shatt Al-Arab water, TPHs , n-alkanes , PAHs , hydrocarbon indices.

### Introduction

Tigris and the Euphrates rivers meet at Qurna town north of Basrah city and form the Shatt Al-Arab river with length of about 195 km , and width varies at different point from 0.35 km at Basrah city to 1.5 km at its mouth in Fao town . This river is the most important source of fresh water in Basrah city , and influenced by freshwater discharges from agricultural runoff , industrial activities , and untreated domestic sewage .

One of the most dangerous pollutant for water environment is petroleum hydrocarbons and it's derivatives . Hydrocarbons enter the aquatic environment either anthropogenic which occurred by discharge of petroleum products such as spillages , tanker operations , industrial effluents , refineries , transport of petroleum products , uncontrolled releases from power plants , accidental discharges , municipal waste discharges , or biogenic which occurred by decomposition of organisms containing biogenic hydrocarbons or by natural seepage (Al-Imarah *et al* ,2010; Farid *et al* ,2014)

Although many aquatic organisms of Shatt Al-Arab river including fish , plants , zooplankton , algae and bacteria are capable to synthesize biogenic hydrocarbons , a large proportion is derived from sources related to human activities ( Al- Saad ,1995 ).

Petroleum hydrocarbons are among the dangerous materials because they are potential carcinogenic materials especially PAHs compounds . Low molecular weight(LMW) PAHs, containing two or three fused rings, are more water soluble and volatile, therefore they are more available, than high molecular weight (HMW) PAHs ,containing four or more fused rings , hence (LMW) PAHs are more susceptible to various degradation processes (Bakhtiari *et al* , 2009) . Long term exposure to hydrocarbon compounds can cause various disturbances in human life in terms of comfort and health (Azhari *et al* , 2011). In aquatic environments , they float and prevent the oxygen exchange and reduce the penetration of sunshine from reaching the deep phytoplankton and consequently alter the production of oxygen (Barbooti , 2011). The effects of oil discharges vary enormously, because the characteristics of the receiving waters and the various types of oil are themselves very variable (Abel, 2002).

Petroleum hydrocarbons contains approximately equal amounts of n-alkanes with odd and even numbers of carbon atoms ; a large amount of aromatic and heavy asphaltenic substances , while organisms mostly contain n-alkanes with an odd number of carbon atoms , a least amount of aromatic compounds , and no asphaltenic substances (Ali *et al* ,2013) . Based on these distinctions, some authors suggest indices to assess the sources of hydrocarbons compounds in the aquatic environments . Guerra-García *et al* . ( 2003) showed that the dominance of unresolved complex mixture (UCM) in relation to the resolved alkanes , and the ratio of hydrocarbons with even and odd numbers of carbon atoms, carbon preference index (CPI) values close to the unity ( $\approx 1$ ), and pristine/phytane ratio indicated anthropogenic origins of the hydrocarbons . The phenanthrene/anthracene ratio below 10 refers to pyrogenic source ( Al-Khatib ,2008).

The aims of the present study are to determine the concentrations of different hydrocarbon fractions in water , and to identify the major sources of hydrocarbons compounds in water to give baseline data for further work, and to evaluate the water quality of Shatt Al-Arab river.

### Materials and Methods

This study was conducted during the period Dec. 2012 to Nov.,2013. The studied sites represented by 5 stations along the middle part of Shatt Al-Arab river from Al-Mohamadiyat (st.1) its water is a continuous flow from the confluence of Tigris and the Euphrates at Qurna about 59.2 km in the north of Basrah city center, Al-Sindibad (st.2) 3.35 km.to the south of the first station , Al-Maqal (st.3) about 2.87km. to the south of the second station and about 8

km to the north of Basrah city center , Al-Bradhiya (st.4) about 8.86 km. to the south of the third station, Abuflous (st.5) located about 19.9km.on the southern side of station four as shown in Figure 1.

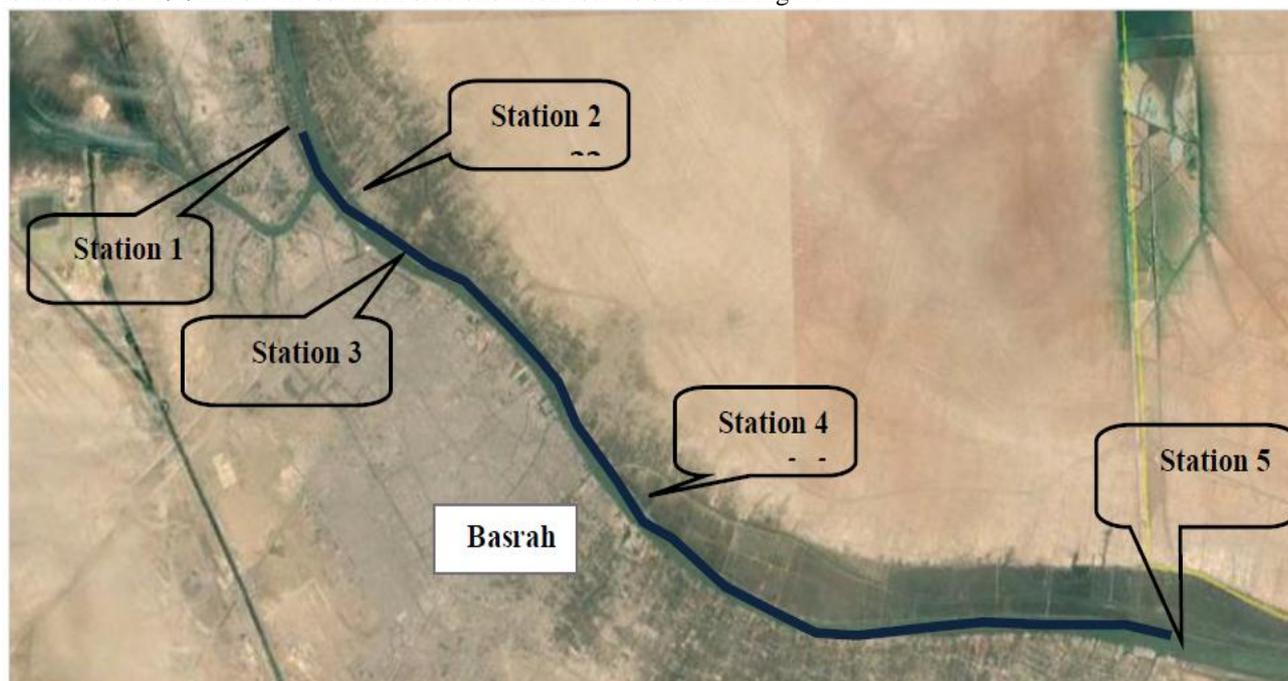


Fig.(1): The study stations .

Water samples were collected from the five stations at least 20 -30 cm under the water surface and whenever it was possible at the middle of the river using dark glass bottles and preserved *in situ* with 25 ml.  $\text{CCl}_4$ . Samples were never taken when it was raining. Hydrocarbons in water sample ( about 5L) were extracted according to (UNEP,1989) by mixing with another (25 ml )  $\text{CCl}_4$  for 20 min. using Water Mixer, the liquid fraction was drained , and the residual ( about 1L) was transferred into separator funnel . The organic (lower) phase was carefully poured into a glass column containing (5g) of anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), collected and dried . The residual was dissolved with n-hexane (25 ml ) , and passed through a 20 cm glass column ( packed with glass wool at the bottom , about 10 g deactivated silica gel (100-200 mesh), 10 g deactivated alumina ( 100-200 mesh) , and 5g anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) at the top ). The aliphatic fractions were eluted from the column with n- hexane (25 ml) , while the aromatics were eluted with benzene (25 ml) .The samples dried and stored until detection with spectrofluorometer (for total petroleum hydrocarbons(TPHs) ) and Gas-liquid chromatography (for aliphatic (n-alkanes) and polynuclear aromatic hydrocarbons (PAHs)) instruments .

Basrah Regular Crude Oil used as a standard. Spectrofluorometer was used at 360nm emission intensity , 310 nm excitation , and monochromatic slits of 10 nm, to quantify the total petroleum hydrocarbons in the extracted water samples.

Helium used as carrier gas in liquid Gas Chromatography with linear velocity of 1 ml./min and Flam Ionization Detector(FID). The operating temperatures for injector and detector were 280°C and 300°C , respectively ,was used for aliphatic separation. The column temperature was held at 35°C as initial temperature for 13 min. then 5°C/min to 280°C . Whereas for the PAHs separation, the operating temperatures for injector and detector were 300°C and 320°C , respectively , and the column temperature was held at 50°C as initial temperature for 8 min. then 8°C/min to 350° C.

### Hydrocarbons pollution indices:

The hydrocarbons pollution indices were used to determine the origin of hydrocarbons in the aquatic environments .

These indices were illustrated as below:

1- LMW/ HMW Ratio : Low Molecular Weight (LMW) n-alkanes are usually produced by marine biogenic sources , while High Molecular Weight (HMW) n-alkanes are usually produced from terrestrial vascular plant(Fagbote and Olanipekun , 2013).

LMW= Sum of concentrations of aliphatic hydrocarbons from c16 to c26.

HMW= Sum of concentrations of aliphatic hydrocarbons from c27- to c31.

Ratio below one show natural input from terrestrial biogenic sources , while values above one show natural input from biogenic sources , values around one is for petroleum sources .Whereas for PAHs compounds :

LMW= Sum of concentrations of light PAHs (2-3 rings) .

HMW= Sum of concentrations of heavy PAHs(4 rings and more) .

Values below one show pyrogenic sources , while values above one show petrogenic (anthropogenic) sources .

2-Carbon Preference Index (CPI) : Carbon Preference Index is defined as ratio of concentration of odd to even carbon number n-alkanes .When CPI values are equal to 1 , this shows that the hydrocarbons are petrogenic in origin . CPI values less than 1 are commonly observed in bitumen and oils derived from carbonate or evaporate rocks(pyrogenic) (Fagbote and Olanipekun , 2013) . CPI value higher than 1 indicates a biogenic origin of alkanes .

3- Pristane / Phytane Ratio : The ratio values are equal to one show that the hydrocarbons are petrogenic in origin. The ratio value higher than one indicates biogenic origin of alkanes in the aquatic environments . Ratio below one indicates pyrogenic origin(Al-Saad ,1995)

4- Phenanthrene / Anthracene Ratio : The ratio values less than ten(10) show that the hydrocarbons are pyrogenic in origin .When the ratio values higher than ten , the hydrocarbons are petrogenic in origin (Kafilzadeh *et al.* , 2011, Al-Khion,2012) .

5-Flouranthene / Pyrene Ratio : When the ratio values are higher than one , the hydrocarbons are pyrogenic in origin , when the ratio values are less than one, the hydrocarbons are petrogenic in origin (Al-Khatib , 2008 ;Kafilzadeh *et al.* , 2011).

6-Unresolved Complex Mixture (UCM): The UCM appears as a hump in the baseline chromatograms and is generally considered to be a mixture of many structurally complex isomers and homologs of branched and cyclic hydrocarbons that cannot be resolved by capillary GC column (Bouloubassi and Saliot , 1993) . The UCM concentrations were not calculated but their presences suggested the presence of degraded petroleum hydrocarbons (Bakhtiari *et al.* , 2009) .

## Results

Results represented seasonally , three months make one season (Dec-Feb. represented Winter season ; March-May represented Spring season ; June-Aug. represented Summer season ; and Sep-Nov. represented Autumn season) .

**TPHs in water** : The concentrations of TPHs in water samples ranged from(5.18 $\mu\text{g/l}$ ) at station 4 in Winter to (37.59  $\mu\text{g/l}$ ) at station 2 in Summer (Table 1). Non – significant differences ( $P>0.05$ ) were found among stations, whereas significant differences ( $P<0.01$ ) were found among seasons , the highest mean value(32.83  $\mu\text{g/l}$ ) was recorded in Summer and the lowest mean value (6.14  $\mu\text{g/l}$ ) was recorded in Winter .

**N-alkanes in water** : The carbon chains length of n-alkanes in water samples were recorded from C7 to C31 , the dominant of odd carbon chains were C7, C17,C19 , C 21 , C23 ,C25 specially C23 , C25 , while the dominant of even carbon chains were C18 , C20 , C22 ,C24 and C26 specially C22 and C24 . Fig (2) showed the percentage of each n-alkane compound in water . Numbers of other hydrocarbons compounds were present in the aliphatic fraction , including pristane and phytane . The total of n-alkanes concentrations in water, which was calculated by summing C7-C31 compounds ,was illustrated in table (1). The highest mean concentrations of total n-alkanes in water ( 35.58 $\mu\text{g/l}$ ) was recorded at station 4 in Spring , while the lowest mean concentrations ( 8.81 $\mu\text{g/l}$ ) was recorded at station 1 during Summer (Table 1) . Non-significant differences ( $P>0.05$ ) were found among stations or among seasons.

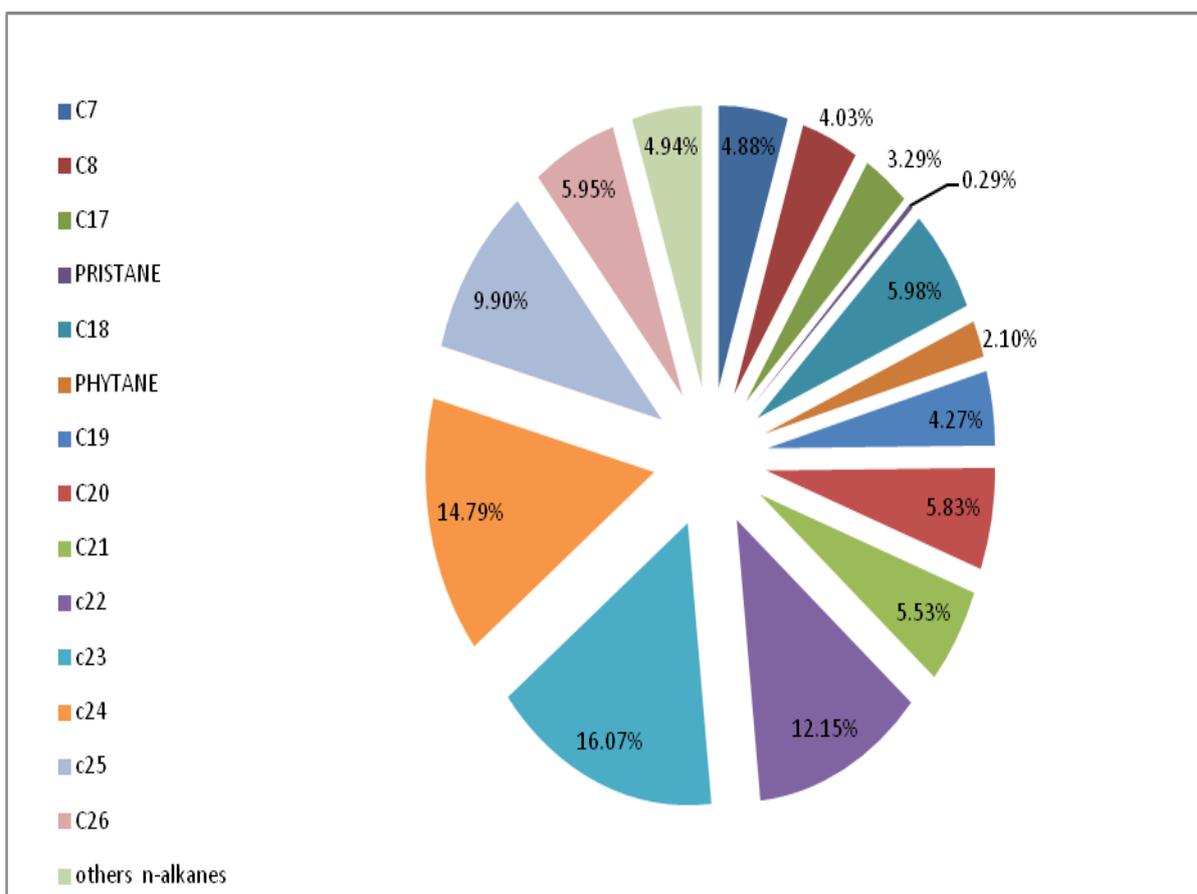


Fig .(2): The percentage of n-alkanes hydrocarbons in water samples during the studied periods.

**PAHs in water** : The dominant light PAHs compounds in water were Naphthalene , Fluorene , Dibenzofuran , Phenanthrene , Anthracene and Carbazole specially Carbazol and Anthracene. Whereas , the dominant heavy PAHs compounds were Floranthene , Pyrene , Benzo(a)anthracene , Chrysene, Benzo(a)Pyrene , specially Chrysene and Floranthene . Indeno (1,2,3,c,d) Pyrene , Dibenzo(a,h)anthracene and Benzo(g,h,i) perylene were undetectable in all water samples along the study period . Fig.(3) showed the percentage of PAHs compounds in water . The highest mean concentrations of total PAHs in water (47.96 ng/l) was recorded at station 1 in Summer season , while the lowest mean concentrations (5.81 ng/l ) was recorded at station 3 during Winter (Table 1). Non-significant differences (  $P>0.05$ ) were found among stations ,while significant differences ( $P<0.01$ )were found among seasons , the highest mean value (37.18 ng/l) was recorded in Summer , while the lowest mean value (12.09 ng/l) was recorded in Autumn .

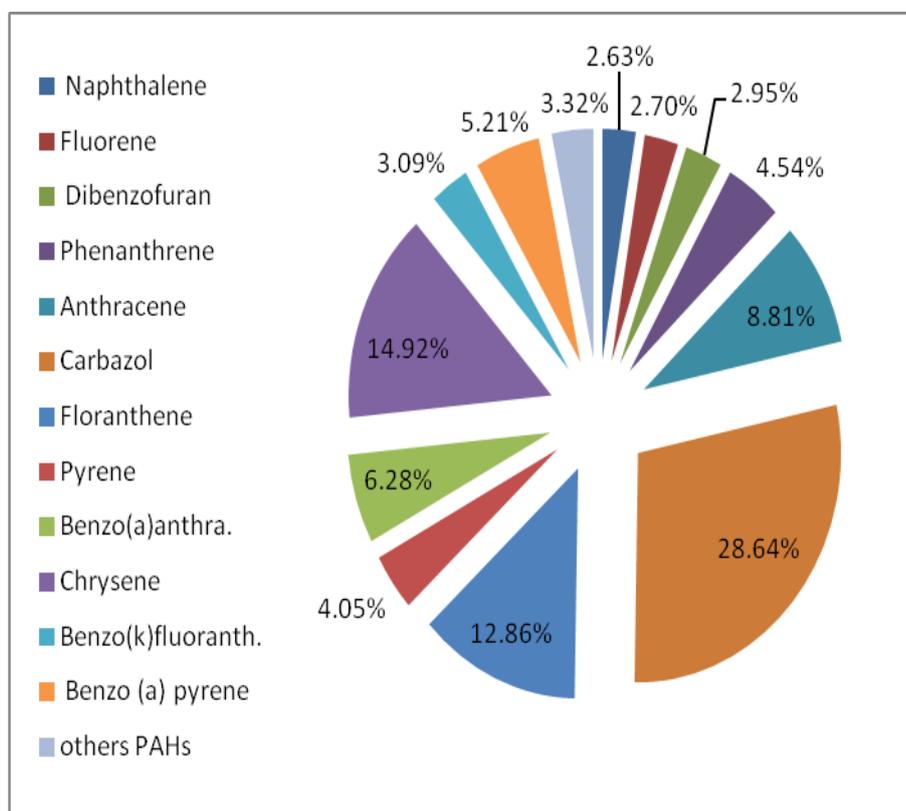


Fig.(3) : The PAHs compounds percentage in water samples during the studied periods.

Table(1): Total petroleum hydrocarbons (TPHs), n-alkanes ( $\mu\text{g/l}$ ) and PAHs compounds ( $\text{ng/l}$ ) in water at the studied stations during Dec., 2012 - Nov., 2013.

Stations	Seasons	TPHs Con. Mean $\pm$ SD ( $\mu\text{g/l}$ )	n-alkanes Con. Mean $\pm$ SD ( $\mu\text{g/l}$ )	PAHs Con. Mean $\pm$ SD ( $\text{ng/l}$ )
Station 1	Winter	6.52 $\pm$ 2.98	15.73 $\pm$ 13.30	11.77 $\pm$ 8.32
	Spring	8.01 $\pm$ 2.91	21.36 $\pm$ 8.31	24.89 $\pm$ 11.53
	Summer	31.09 $\pm$ 9.22	8.81 $\pm$ 8.75	47.96 $\pm$ 13.21
	Autumn	8.99 $\pm$ 4.14	12.43 $\pm$ 3.02	16.04 $\pm$ 7.77
Station 2	Winter	5.92 $\pm$ 4.23	17.15 $\pm$ 22.98	9.62 $\pm$ 3.45
	Spring	8.43 $\pm$ 4.51	22.62 $\pm$ 3.12	11.38 $\pm$ 3.29
	Summer	37.59 $\pm$ 5.65	16.41 $\pm$ 1.89	41.23 $\pm$ 8.65
	Autumn	9.92 $\pm$ 7.82	14.08 $\pm$ 1.91	8.85 $\pm$ 0.93
Station 3	Winter	7.52 $\pm$ 2.74	10.51 $\pm$ 12.02	5.81 $\pm$ 3.16
	Spring	13.80 $\pm$ 9.07	21.20 $\pm$ 3.53	16.36 $\pm$ 7.31
	Summer	31.14 $\pm$ 3.91	14.52 $\pm$ 1.63	32.90 $\pm$ 13.67
	Autumn	7.62 $\pm$ 2.50	11.72 $\pm$ 3.02	13.65 $\pm$ 8.31
Station 4	Winter	5.18 $\pm$ 2.22	10.92 $\pm$ 14.31	27.13 $\pm$ 31.46
	Spring	7.35 $\pm$ 2.86	35.58 $\pm$ 26.37	20.28 $\pm$ 9.98
	Summer	34.83 $\pm$ 8.89	16.35 $\pm$ 3.44	38.85 $\pm$ 9.42
	Autumn	11.25 $\pm$ 8.15	12.50 $\pm$ 3.71	10.99 $\pm$ 3.07
Station 5	Winter	5.56 $\pm$ 2.72	9.98 $\pm$ 10.62	22.98 $\pm$ 25.48
	Spring	9.77 $\pm$ 3.31	11.50 $\pm$ 4.61	12.73 $\pm$ 2.43
	Summer	29.50 $\pm$ 4.71	17.38 $\pm$ 4.84	24.94 $\pm$ 6.30
	Autumn	8.07 $\pm$ 1.28	19.56 $\pm$ 13.91	10.93 $\pm$ 5.11

#### Hydrocarbons Pollution Indices :

**N-Alkanes pollution indices:** LMW/HMW ratio and CPI value were used to describe the origin source of n-alkanes in water samples (Table 2), while the Pristane / phytane ratio were disadvantageous because most water samples had undetectable pristane values and the other had undetectable phytane values, only few samples had pristane and phytane values together, because of that, the overall values (for all stations along the studied period) of pristane/phytane ratio (0.136) was calculated, it was less than one number and indicated pyrogenic source of n-alkanes in water samples. Few water chromatograms showed UCM as a hump in the baseline chromatograms (Fig.4)

Table(2):N-Alkanes pollution indices values and its origin source description in water samples at the studied stations during Dec.,2012 – Nov.,2013.

Stations	Seasons	LMW/HMW	Descriptions	CPI values	Descriptions
Station 1	Winter	25.54	Biogenic	0.88	Pyrogenic
	Spring	20.69	Biogenic	1.05	Petrogenic
	Summer	20.05	Biogenic	1.13	Biogenic
	Autumn	75.89	Biogenic	0.98	Petrogenic
Station 2	Winter	30.43	Biogenic	0.69	Pyrogenic
	Spring	30.57	Biogenic	1.13	Biogenic
	Summer	20.65	Biogenic	1.13	Biogenic
	Autumn	29.41	Biogenic	1.01	Petrogenic
Station 3	Winter	28.10	Biogenic	1.09	Biogenic
	Spring	29.08	Biogenic	1.08	Biogenic
	Summer	20.25	Biogenic	1.15	Biogenic
	Autumn	15.69	Biogenic	0.92	Pyrogenic
Station 4	Winter	24.91	Biogenic	1.19	Biogenic
	Spring	21.57	Biogenic	0.60	Pyrogenic
	Summer	20.63	Biogenic	1.23	Biogenic
	Autumn	54.10	Biogenic	0.99	Petrogenic
Station 5	Winter	20.08	Biogenic	0.72	Pyrogenic
	Spring	34.49	Biogenic	1.20	Biogenic
	Summer	20.66	Biogenic	1.17	Biogenic
	Autumn	24.10	Biogenic	1.00	Petrogenic

**PAHs pollution indices:** LMW/HMW and Flouranthen /Pyren ratios were used to describe the origin sources of PAHs compounds in water samples ( Table 3). The phenanthrene /Anthracen ratio was disadvantage because most water samples had undetectable phenanthrene values and the other had undetectable Anthracen values , only few samples had phenanthrene and anthracene values together , because that , the overall values(for all stations along the studied period) of phenanthrene /Anthracen ratio ( 0.52) was calculated , which was less than ten number , indicated pyrogenic source of PAHs in water samples.

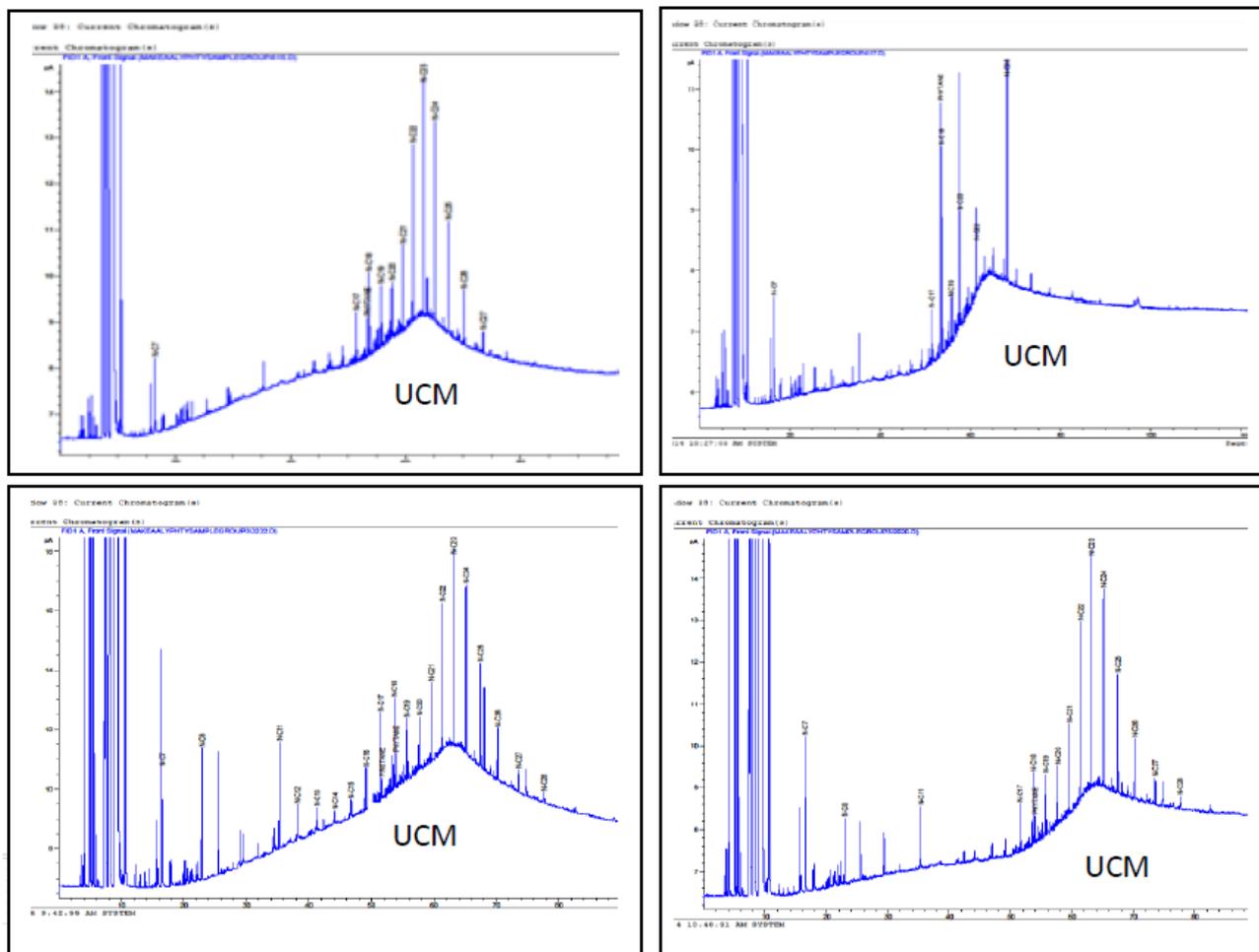


Fig.(4) : Chromatograms showed the UCM regions in some water samples.

Table(3):PAHs pollution indices values and its origin source description in water samples at the studied stations during the studied periods.

Stations	Seasons	LMW/HMW	Descriptions	Floura/Pyren	Descriptions
Station 1	Winter	0.54	Pyrogenic	1.80	Pyrogenic
	Spring	0.99	Pyrogenic	1.68	Pyrogenic
	Summer	2.21	Petrogenic	3.42	Pyrogenic
	Autumn	0.74	Pyrogenic	2.04	Pyrogenic
Station 2	Winter	0.33	Pyrogenic	1.13	Pyrogenic
	Spring	0.70	Pyrogenic	1.81	Pyrogenic
	Summer	1.75	Petrogenic	5.05	Pyrogenic
	Autumn	0.31	Pyrogenic	ND	-
Station 3	Winter	0.80	Pyrogenic	1.18	Pyrogenic
	Spring	1.09	Petrogenic	2.40	Pyrogenic
	Summer	1.63	Petrogenic	2.51	Pyrogenic
	Autumn	1.07	Petrogenic	2.61	Pyrogenic
Station 4	Winter	1.29	Petrogenic	1.71	Pyrogenic
	Spring	1.68	Petrogenic	1.28	Pyrogenic
	Summer	1.75	Petrogenic	4.22	Pyrogenic
	Autumn	0.25	Pyrogenic	2.59	Pyrogenic
Station 5	Winter	3.01	Petrogenic	1.52	Pyrogenic
	Spring	1.40	Petrogenic	1.01	Pyrogenic
	Summer	1.48	Petrogenic	2.51	Pyrogenic
	Autumn	0.84	Pyrogenic	3.16	Pyrogenic

ND: undetectable values

## Discussion

Based on elicitation of numerous expert opinions, the variations in the total hydrocarbons in Shatt Al-Arab river were due to many factors mainly: the discharging of hydrocarbons compounds to the environment, uncontrolled releases from power plants, petroleum tanker traffic, temperature changes, evaporation, photo-oxidation, biosynthesis, biodegradation, adsorption and absorption by suspended matters and organisms, and sedimentation. The intense solar radiation coupled with relatively high water temperature are the characteristic features of the climate of subtropical region of Basrah city. These two factors could account for rather low level of dissolved hydrocarbons in water. Total hydrocarbons tend to be the highest in Summer and the lowest in Winter, this result was in agreement with Al-Bidhani (2014) in her study at Al-Faw station in Shatt Al-Arab river, and this may be mainly due to the uncontrolled emission from the local electricity power generators especially in Summer. Another explanation of this could be due to the enhanced phytoplankton and aquatic plants growth in Summer, which synthesized most of hydrocarbons compounds and released them to the aquatic environments. Al-Saad (1995) found that many species of biota have the ability to synthesize some of hydrocarbon compounds in their bodies and then release them to the aquatic environments.

### - n-alkanes in water:

The range of carbon chain length of n-alkanes in the water samples was C7-C31 with abundance of odd carbon number chains C17, C19, C21 originated mainly from photo-synthesis organisms (Al-Bidhani, 2014) and C23, C25, C27 carbon number chains originated mainly from higher plant wax layer (Al-Khatib, 2008; and Talal, 2008). While the even carbon number chains in water samples were from C18-C26, the C22, C24 were considered mainly as bacterial activities origin (Al-Saad, 1995; Al-Khatib, 2008; and Talal, 2008). Other evidence on the aquatic biogenic source of n-alkanes was derived from diatoms populations, which found to be the most dominant group of phytoplankton in Shatt Al-Arab river (Al-Bidhani, 2014), that contain a range of n-alkanes from C15- C31 (Al-Saad, 1995).

The undetectable values of C9, C10, and the low values of C11-C16 and C28-C31 in the present study may be due to the fact that the low molecular weight n-alkanes such as C9-C16 in water has the ability to decompose by microorganisms or evaporate easily, while the high molecular weight n-alkanes (C28-C31) has the ability to precipitate to the sediments.

### -PAHs in water:

The surface water receives direct PAHs inputs, such as shipping, dry and wet atmospheric deposition, air-water exchange, most of which contribute PAHs derived from pyrolysis and combustion activities.

Low levels of PAHs in water may be a result of photo-oxidation, and sedimentation of PAHs from the water column. These factors collectively reduce the concentration of PAHs compounds, this made the low molecular weight PAHs predominant in surface water. Another possible explanation for this may be due to degradation of low molecular weight PAHs in water column (Bakhtiari *et al.*, 2009).

The disappearance of some heavy PAHs compounds such as Indeno(1,2,3, c,d)pyrene, Dibenzo(a,h)anthracene and Benzo(g,h,i)perylene in water samples could be a result of high particle affinity according to their high molecular weight that made them finally sink to the sediments.

Comparison of total petroleum hydrocarbons, n-alkanes and PAHs concentrations with the previous studies (Table 4) indicated that Shatt Al-Arab river still unpolluted with hydrocarbons compounds.

Table(4) : Comparison between the concentrations of total hydrocarbons , n-alkanes ( $\mu\text{g/l}$ ) , and PAHs (ng/l) in water (Dissolved.+particulate) for the present study with the other previously studied ones .

Studied Areas	Total Hydrocarbons ( $\mu\text{g/l}$ ) (Dissol.+partic.)	n-alkane ( $\mu\text{g/l}$ ) (Dissol.+partic.)	PAHs (ng/l) (Dissol.+partic.)	References
Shatt Al-Arab river &NW Arabian Gulf	3.25-25.33	4.12 - 19.52	5.94 -35.41	Al-Saad (1995)
Al-Howaiza Marsh	1.005-11.965	1.143 – 34.461	1- 50.8	Al-Khatib(2008)
Al-Hammar Marsh	0.411-0.824	3.64- 4.40	-	Talal (2008)
Shatt Al Arab Northern	5.67-9.48	-	-	Al-Imarah <i>et al</i> (2010)
Iraqi Coast Region	1.51-18.14	-	0.59-12.7	Al-Khion(2012)
Shatt Al-Arab river	16.77-42.6	6.50-14.23	7.19-22.47	Farid <i>et al</i> (2014)
Shatt Al-Arabriver	0.22 - 17.78	6.43 - 73.95	0.14 -31.91	Al-Bidhani (2014)
Shatt Al-Arab river	5.18 – 37.58	8.81 - 35.58	5.81 -47.96	Present study

### Hydrocarbon source indices:

LMW/HMW ratio indicated biogenic sources of n- alkanes . most CPI ratio ,which is used to determined the degree of biogenic versus petrogenic n-alkanes in aquatic environments, indicated biogenic origin of n-alkanes in Shatt Al-Arab river. This result may be due to the present of aquatic plants and phytoplankton at the study area.

Another useful indicator of the n-alkanes origin is the ratio of the isoprenoids pristane and phytane . Pristane (2, 6,10,14-tetramethylpentadecane) is usually found in zooplankton and other marine animals, while phytane (2,6,10,14 tetramethylhexadecane) is reported as a normal component of oil (Guerra-García *et al*, 2003).

LMW/HMW , Flouranthen /Pyren , and phenanthrene /Anthracen ratios indicated that most of PAHs is result from pyrogenic origin as fuel composition and petrogenic ,while undetectable biogenic source .

### Conclusion

There are many factors affecting the distribution of hydrocarbons compounds in Shatt Al – Arab river , such as volatilization ,adsorption to suspended particles , syntheses and released occurred by aquatic organisms , photo – oxidation , sedimentation , and biodegradation and direct release of waste materials by ships and boats .

The main source of n-alkanes in water is biogenic while the main source of PAHs compounds is pyrogenic . In general the concentrations of petroleum hydrocarbons in Shatt Al-Arab river were within unpolluted area in the world.

### References

- Abel , P.D. ( 2002) ." Water Pollution Biology ". 2<sup>nd</sup> ed. Copyright © Taylor & Francis Ltd .
- Al-Bidhani , Mariam F.H. (2014)." Qualitative composition of phytoplankton in the Shatt Al-Arab and the impact of environmental factors on the extent ofto which some of the production and accumulation of hydrocarbon compounds ". Ph.D. Thesis ,Univ. Basrah, College of Education for Pure Science , Biology Department , 165pp.
- Ali , W.A. ; Farid , W.A. ; and Al-Eed , A. A.(2013)." Hydrocarbons Distribution in Shatt Al-Arab River Bacteria And Fungi ". Intern. J. Sci. Modern Engineering (IJISME) , 1(12):5-9.
- Al-Imarah , F. J. M. ; Ali , S.A. ; and Ali , A. A. (2010)."Temporal and special variations of petroleum hydrocarbons in water and sediments from Northern part of Shatt Al-Arab River , Iraq ". Mesopot. J. Mar.Sci. , 25(1):65-74.
- Al-Khatib , F. M. (2008)." Determination the concentrations , origin and distribution of hydrocarbon compounds in water , sediments and some biota of Hor Al-Howaiza ,south of Iraq and their sources ". Ph.D. Thesis . University of Basrah, college of science , biology department , 228 pp.
- Al-Khion , D.D. (2012)." Sources and distribution of polycyclic aromatic hydrocarbons compounds in water , sediments and some biota of Iraqi coast regions " Ph.D. Thesis , College of Agriculture ,University of Basrah , 171 pp.
- Al-Saad , H. T. ( 1995 )." Distribution and sources of hydrocarbons in Shatt Al-Arab estuary and NW Arabian Gulf ". Ph. D. thesis , Basrah University , 186 pp.
- Azhari , A. ; Dalimin , M.N. ; and Wee , S. T. ( 2011)."Polycyclic Aromatic Hydrocarbons(PAHs) from Vehicle Emission in Vegetation of Highway Roadside in Johor , Malaysia ". Inter. J. Env. Sci. Develo. , 2(6): 465-468.
- Bakhtiari , A.R. ; Zakaria , M. P. ; Yaziz , M.I. ; Lajis , M.N.H. ; and Bi, X(2009)."Polycyclic Aromatic Hydrocarbons and n-alkanes in Suspended Particulate Matter and Sediments from the Langat River , Peninsular Malaysia ". Enviro.Asia , 2 :1-10.
- Barbooti , M. M. (2011). " Turbidimetric Determination of Hydrocarbon Contamination in Passaic River Sediments and Refinery Polluted Soil ". J. Enviro. Prot. , 2: 915-922 .
- Bouloubassi , I. and Saliot ,A. (1993)."Investigation of anthropogenic and natural organic inputs in estuarine sediments using hydrocarbon markers(NAH , LAB,PAH). Oceanol. Acta , 16(2):145-161.
- Fagbote , O. E. and Olanipekun , E.O.(2013)."Characterization and sources of Aliphatic Hydrocarbons of the Sediments of River Oluwa at Agbabu Bitumen Deposit Area , Western Nigeria ". J . Sci .Res.& Repo. , 2(1):228-248.
- Farid , W.A. ; Al-Eed , A. A. ; Shihab , L.A. ; and Al-Saad , H.T. (2014). Distribution , sources , and seasonal variations of hydrocarbons in Shat Al-Arab river water . J.Inter.Acadi.Rese.Multi. , 2(2): 729-739.
- Guerra-García , J. M. ; González-Vila , F.J. ; and García-Gómez , J.C.(2003). "Aliphatic hydrocarbon pollution and macrobenthic assemblages in Ceuta harbor : a multivariate approach ".Mar. Eco. Prog . Ser. , 263 : 127-138.
- Kafilzadeh .F. ; Shiva , A.H. ; and Malekpour , R. ( 2011). "Determination of Polycyclic Aromatic Hydrocarbons ( PAHs) in Water and Sediments of the Kor River , Iran ".Middle-East J. Sci. Res. , 10(1) : 1-7.
- Talal , A. A .(2008) ." A Study for the Seasonal and Regional Variations of Hydrocarbon Levels and Origin of n–alkanes in Water, Sediments and Some Species of Biota Iraqi Southern Marshes ". Ph.D. Thesis . University of Basrah, college of science , biology department , 143 pp.
- UNEP:United Nation Environmental Program (1989)." Comparative toxicity test of water accommodated fraction of oils and oil dispersant's to marine organisms. Reference methods for marine pollution" No. 45, 21PP.