



Total Petroleum Hydrocarbons (TPHs), n-alkanes and Polynuclear Aromatic Hydrocarbons (PAHs) in Sediments of Shatt Al-Arab River – part 2

Makia M. Al-Hejuje* ; H. T. Al-saad ** & N. A. Hussain*

*Department of Ecology , College of Sciences , University of Basrah, Iraq .

**Department of Marine Chemistry , Marine Science Center , University of Basrah, Iraq .

Abstract

Surface sediments samples were collected monthly during December , 2012 to November , 2013 from five stations located at the Shatt Al-Arab River to determine the concentrations , distribution and the sources of hydrocarbons compounds in sediments samples. Total Petroleum Hydrocarbons (TPH) concentrations in sediments was range from 4.76 µg/g dry weight to 45.24 µg/g dry weight . The carbon chain length of aliphatic (n-alkanes) were recorded from C7-C31 dominated by C22-C25 , and the total n-alkanes concentration in sediments was ranged from 4.76 µg/g dry weight to 10.09 µg/g dry weight . The range of PAHs was ranged from 4.318 ng/g dry weight to 28.48 ng/g dry weight dominated by carbazol and anthracene (as light PAHs) and indeno (1,2,3,c,d) pyrene and benzo(g,h,i)perylene (as heavy PAHs). The LMW/HMW , CPI index and Pristane/Phytane ratio 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 was pyrogenic only. non- significant correlation was found between hydrocarbons concentrations and each of TOC% or grain size of the sediments .

Key words : Shatt Al-Arab sediments, TPHs, n-alkanes ,PAHs , hydrocarbon indices

Introduction

Pollution of the aquatic ecosystems by petroleum hydrocarbons is a widespread problem . N-Alkane is a type of hydrocarbons which consists of odd and even carbon numbers which can be up to 64 carbons with no alkyl branch or substitutes . N-alkanes enter the aquatic environment sediments according to numerous sources , such as recent benthic biosynthesis , decomposition , geochemical processes , in addition to sinking compounds from the water column .

Polynuclear Aromatic Hydrocarbons (PAHs) is another large group of hydrocarbons materials with two or more fused aromatic rings . PAHs contamination is present in incomplete combustion of organic and fossil fuel as phenanthrene , fluorine , benzo[a]pyrene and pyrene as in car exhaust , while phenanthrene , fluorine , and pyrene as in diesel vehicles exhaust (Azhari *et al.* ,2011). Naphthalene and acenaphthalene have been reported to be present in fuel oil used extensively in Shatt Al-Arab region , and these compounds are not easily attacked by microorganisms , and numerous of these compounds as well as their derivatives are potential carcinogens (Al-Saad , 1995). Light oils are relatively volatile and disperse quickly , though they are extremely toxic and can cause severe local damage . Heavy oils are less toxic, but can have marked physical effects in the substratum and the banksides, which , of course ,will be reflected in changes to the biological community. Heavy oils may remain in situ for long periods ; they do, over time, decompose biologically and chemically, but in so doing impose a high BOD (Abel, 2002) . Although water analysis is useful in the assessment of river pollution , sediments can also serve as pollution indicator . Surficial sediments of the studied rivers represent a sink for hydrocarbons, and this accumulation of hydrocarbons in sediments could serve as a source of water pollution in case of environmental conditions changes.

Carbon Preference Index(CPI) is defined as ratio of concentration of odd to even carbon number n-alkanes , The " Odd "carbon numbers come mainly from the biogenic sources ,while "Even" carbon numbers are usually derived from the anthropogenic sources. 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) . For these reasons professionals submitted some indices as CPI , ratio of Pristane / Phytane , LMW/HM , Phenanthrene / Anthracene , Flouranthene / Pyrene to give an image about the sources of hydrocarbons compounds in the aquatic environments .

The objectives of this study were to assess the compositional patterns and sources of TPHs , n-alkanes and PAHs concentrations in surface sediment samples at the middle part of Shatt Al – Arab River .

Materials and Methods

Surface sediments samples were collected monthly from five stations (Table 1) along the Shatt Al-Arab river during December , 2012 to November,2013 using an Ekman Grab sampler . After retrieval of the sampler, the water was allowed to drain off. To avoid disturbing , the surface layer of the samples was preserved using polyethylene bags ,then the samples were placed in an ice box until reaching the laboratory.

Table (1): The study stations coordinates:

Stations	GPS Coordinates	
Station 1	30 36.623 N	47 45.662 E
Station 2	30 34.915 N	47 46.368 E
Station 3	30 33.755 N	47 47.563 E
Station 4	30 30.376 N	47 51.328 E
Station 5	30 27.251 N	48 02.810 E

The sediment samples were dried, grinded finely and sieved through a 63 µm mesh sieve, stored in glasses containers until analysis. Twenty grams of sieved sediments were placed in cellulose thimble and Soxhlet extracted using Soxhlet intermittent extraction (Goutx and Saliot, 1980) with mixed solvents (120 ml) methanol : benzene (1:1 v/v) for 48 hrs. at temperature doesn't exceed 40°C. The combined extracts saponified for 2 hrs. by adding (15ml) 4M MeOH(KOH) at the same temperature and cooled to room temperature. The unsaponified matter was extracted with (50 ml) n-hexane using separator funnel. The upper unsaponified matter with hexane (hydrocarbons) was passed through open – chromatographic column separation column. 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 (0.3 mg/ml) was used as a standard. Spectrofluorometer type Shimadzu was used at 360 nm emission intensity and 310 nm excitation to quantify the TPHs in the extracted sediments samples.

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

Total organic carbon (TOC) concentrations in sediments were determined according to burning method (Ball, 1964). Two grams of sediments (dried and sieved <63µm) were put in pre-weighted crucible and burned at 550°C for 48 hrs. The difference in mass of crucible and sediments sample before and after burning was calculated as TOC.

Mean grain size analysis of the sediment was carried out using the combined dry sieve and pipet techniques according to Folk (1974). The grain size (sand, silt, and clay) was determined as percentage of sediments.

Results

TPHs in sediments : The concentrations of TPHs in sediments samples ranged from (4.76 µg/g) at station 3 in Winter to (45.24 µg/g) at station 4 in Autumn (Table 2). Significant differences ($P < 0.01$) were found among stations, the highest mean value (30.56 µg/g) was recorded at station 4, while the lowest mean value (6.89 µg/g) was recorded at station 1, whereas non- significant differences ($P > 0.05$) were found among seasons.

N-alkanes in sediments : The carbon chains length of n-alkanes in sediments samples were recorded from C7 - C31, the dominant of odd carbon chains were C7, C17, C19, C21, C23, C25, C27 and C29 specially C23, C25, while the dominant of even carbon chains were C16, C18, C20, C22, C24, C26 and C28 specially C22 and C24. Numbers of other hydrocarbons compounds were present in the aliphatic fraction, including pristane and phytane. Fig.(1) showed the percentage of n-alkanes in sediments. The total of n-alkanes concentrations in sediments, which was calculated by summing C7- C31 compounds, was illustrated in table (2). The highest mean concentrations of total n-alkanes in sediment (10.09 µg/g dry weight) was recorded at station 4 in Autumn, while the lowest mean concentrations (4.76 µg/g dry weight) was recorded at station 5 during Winter. Non-significant differences ($P > 0.05$) were found among stations or among seasons.

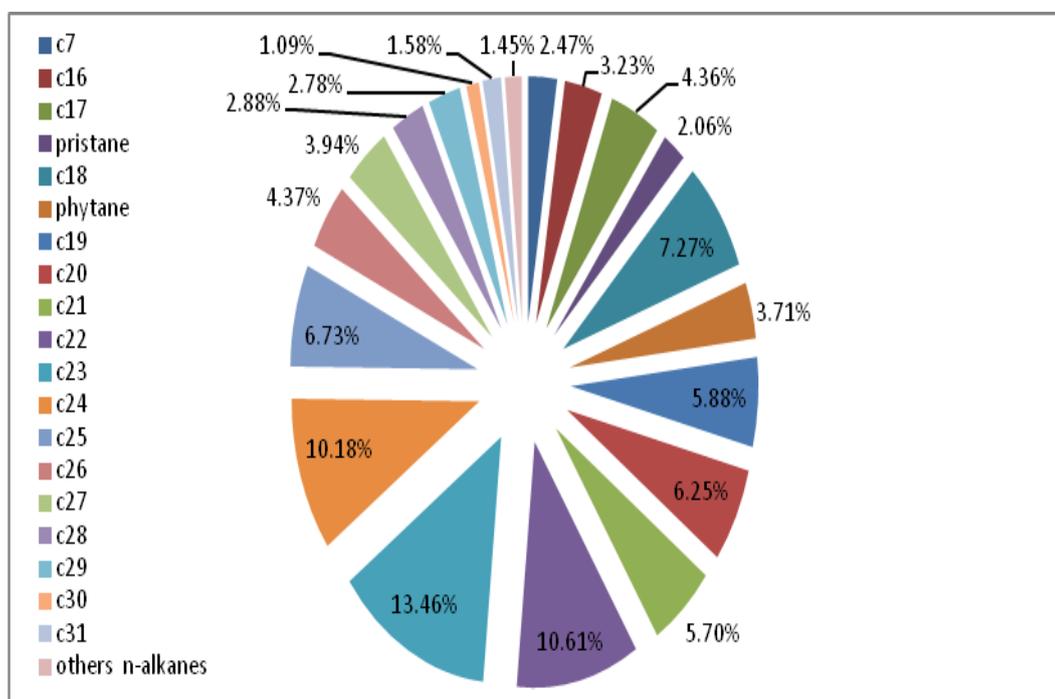


Fig. (1): The n-alkanes percentage at sediments during the studied periods.

PAHs in sediments : The dominant light PAHs compounds in sediments were Acenaphthylene, Acenaphthene, Fluorene, Dibenzofuran, Phenanthrene, Anthracene and Carbazol, specially Carbazol and Anthracene. Naphthalene was undetectable at the sediments samples along the study period. Whereas the dominant heavy PAHs compounds in sediments were Floranthene, Pyrene, Chrysene, Indeno (1,2,3,c,d) Pyrene, and Benzo(g,h,i) perylene, specially Indeno (1,2,3,c,d) Pyrene and Benzo(g,h,i) perylene. The percentage of PAHs compounds in sediments samples was shown in Fig.(2). The total PAHs concentrations in sediments was illustrated in table (2).

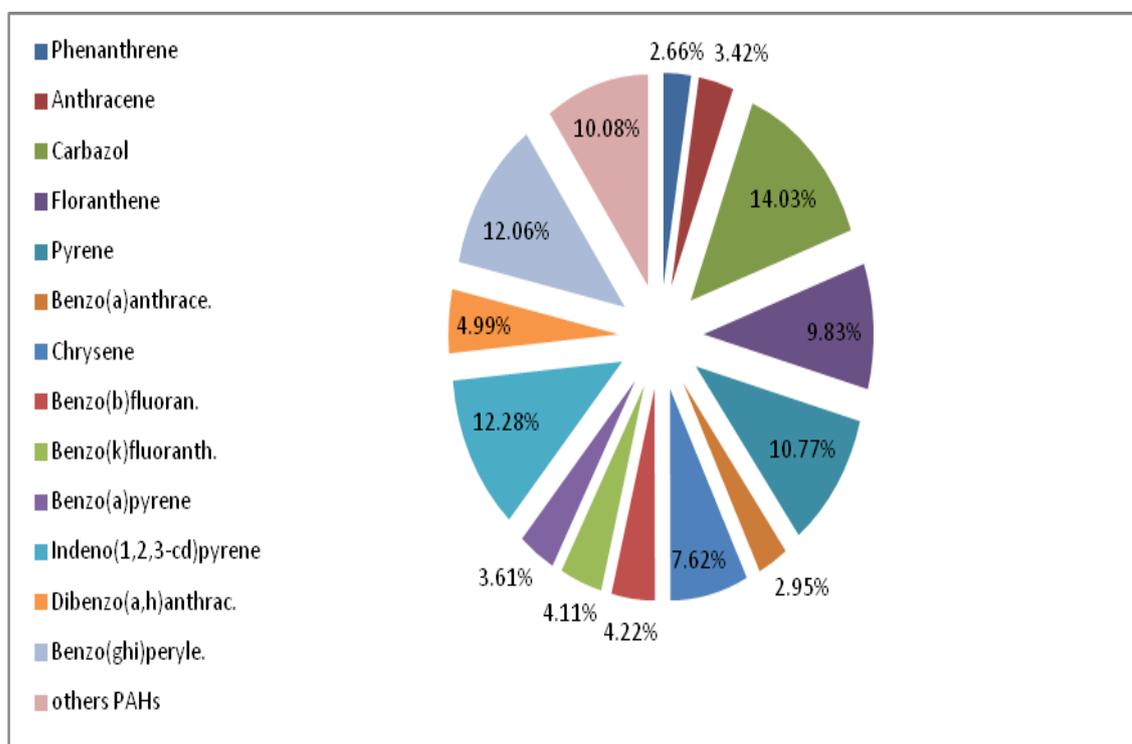


Fig.(2) : The PAHs compounds percentage in sediments samples during the studied periods.

Table(2): Total petroleum hydrocarbons (TPHs), n-alkanes ($\mu\text{g/g}$ dry weight) and PAHs compounds (ng/g dry weight) in sediments at the studied stations during the studied periods.

Stations	Seasons	TPHs ($\mu\text{g/g}$ dw.)	n-alkanes ($\mu\text{g/gdw.}$)	PAHs (ng/g dw.)
Station 1	Winter	7.86 ± 6.31	5.37 ± 3.35	7.33 ± 6.22
	Spring	7.71 ± 3.95	9.37 ± 1.06	10.39 ± 6.11
	Summer	6.50 ± 8.50	6.24 ± 1.21	5.52 ± 7.06
	Autumn	5.50 ± 2.40	6.15 ± 2.53	6.38 ± 5.09
Station 2	Winter	23.38 ± 28.69	7.30 ± 3.76	8.45 ± 1.61
	Spring	15.72 ± 5.88	7.91 ± 1.70	11.57 ± 5.31
	Summer	13.74 ± 6.36	6.75 ± 0.33	14.97 ± 8.35
	Autumn	19.01 ± 2.80	7.05 ± 0.75	13.72 ± 3.87
Station 3	Winter	4.76 ± 6.03	5.86 ± 5.59	9.11 ± 12.74
	Spring	31.56 ± 12.48	7.77 ± 1.00	20.15 ± 1.45
	Summer	5.90 ± 3.73	8.25 ± 2.79	4.32 ± 2.35
	Autumn	13.10 ± 7.48	7.88 ± 0.41	11.77 ± 3.62
Station 4	Winter	13.93 ± 5.72	6.47 ± 6.05	22.38 ± 25.19
	Spring	45.16 ± 2.17	9.14 ± 5.03	28.49 ± 13.24
	Summer	17.22 ± 21.01	9.46 ± 2.11	10.13 ± 10.84
	Autumn	45.24 ± 19.90	10.09 ± 2.13	27.83 ± 7.99
Station 5	Winter	25.10 ± 21.40	4.76 ± 2.54	8.08 ± 3.97
	Spring	17.65 ± 12.06	6.79 ± 1.64	11.35 ± 3.12
	Summer	6.87 ± 6.98	6.06 ± 1.31	5.00 ± 4.41
	Autumn	4.95 ± 2.79	5.92 ± 1.24	6.96 ± 2.51

Hydrocarbons Pollution Indices :

N-Alkanes pollution indices: LMW/HMW ratio ranged from (4.77) at station 2 in Winter to (10.01) at station 5 in Spring. Ratio values which exceeded one indicated that the main source of n-alkanes in sediments was biogenic. CPI values ranged from (0.83) at station 4 in Autumn to (2.05) at station 3 in Winter, according to the CPI values which exceeded one at most stations, the main source of n-alkanes in the sediments was biogenic. Whereas few seasons showed CPI value lower than one or around one number indicated pyrogenic or petrogenic, respectively. Another important index is the ratio of Pristane / phytane which ranged from (0.30) at stations 1 and 2 in Winter and Summer, respectively, to (2.10) at station 3 in Autumn. Pristane / phytane ratio which was less than one number at most stations, indicated that the main source of n-alkanes in the sediments was pyrogenic. Whereas, only stations 3 and 4 in Autumn showed Pristane / phytane value exceed one number and indicated biogenic sources. Few sediments chromatograms showed UCM as a hump in the baseline chromatograms referred to anthropogenic or petrogenic sources of n-alkanes in sediments (Fig.3).

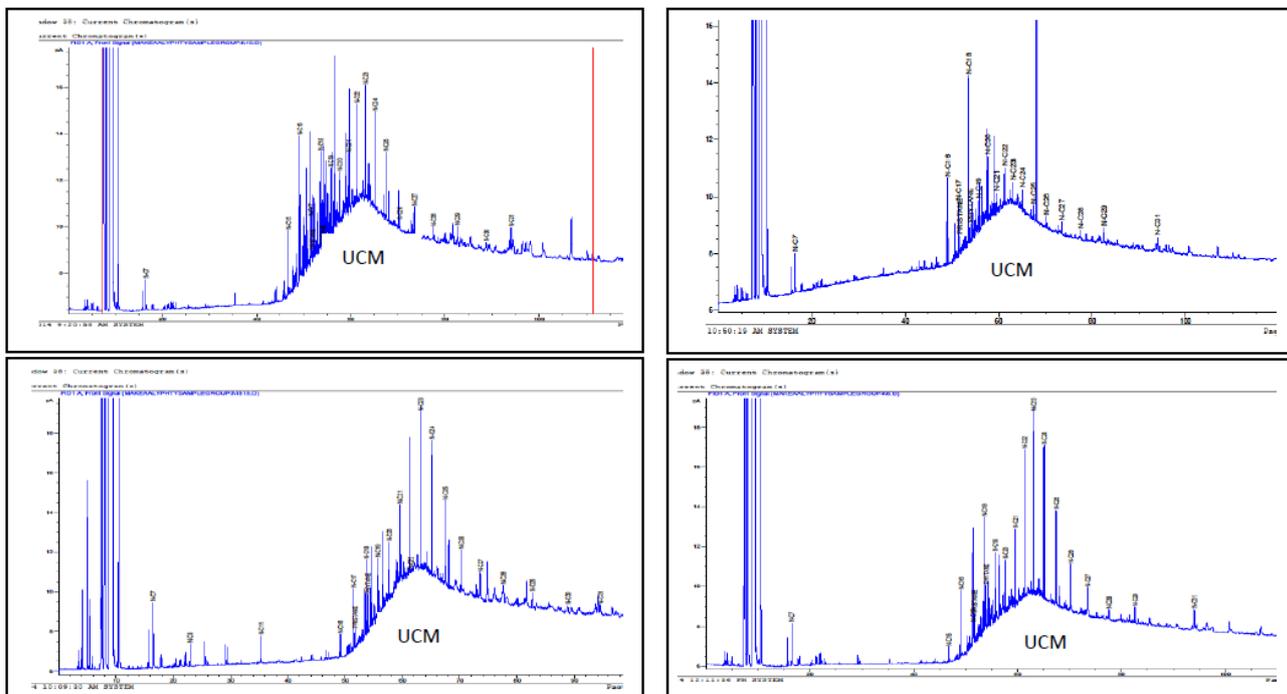


Fig.(3) : Chromatograms showed the UCM regions in some sediments samples at the stations during the studied periods

PAHs pollution indices: Three PAHs pollution indices were used to assess the sources of PAHs in sediments: The LMW/HMW ratio which ranged from (0.14) at station 4 in Spring to (0.78) at station 1 in Summer . Ratio values which was less than one number at all stations indicated that the main source of PAHs in sediments was pyrogenic . Phenanthrene /Anthracene ratio which ranged from (0.07) at station 1 in Summer to(5.75) at station 3 in Winter . Ratio less than ten number at all stations indicated that the source of PAHs in sediments was pyrogenic .Flouranthene / Pyrene ratio is another index ranged from (0.33) at station 4 in Winter to (17.28) at station 4 in Autumn , which exceeded one number at most stations , indicated that the main source of PAHs in sediments was pyrogenic . Sediments collected from the studied station can be classified as silt-loam texture as illustrated in table (3).

Table(3): The Sediments texture and TOC% contains .

Stations	Sediments Texture			TOC%
	Sand %	Silt%	Clay%	
Station 1	8.39 ± 4.88	69.97 ± 8.63	21.65 ± 8.36	8.42 ± 2.59
Station 2	3.47 ± 2.14	71.01 ± 12.02	25.19 ± 12.63	8.65 ± 2.49
Station 3	3.17 ± 3.84	65.11 ± 15.44	31.72 ± 15.92	9.35 ± 3.29
Station 4	3.52 ± 3.68	68.75 ± 14.66	27.73 ± 14.88	10.17 ± 3.00
Station 5	3.89 ± 4.11	66.10 ± 16.46	30.01 ± 18.40	7.65 ± 2.17

Discussion

TPHs in sediments:

The distribution of petroleum hydrocarbons in surface sediments have an important role in oil pollution and in understanding temporal variations in the aquatic environments (Al-Saad , 1995). Highest TPHs at station 4 and lowest at station 1 may be a result of high quantities of diesel oil which commonly used in small recreation transport and fishing boats at station 4 as compared with station 1 .

The non-significant correlation (p>0.05) between the TPHs in sediments and each of the sediments texture compounds (sand , silt and clay) or TOC% was in agreement with Al-Khatib (1998) who found non-significant correlation between the TPHs in sediments and each of the sediments texture compounds (sand , silt and clay) or TOC% . This may be depend on other factors that have the greatest effects on the TPHs in sediments such as turbid domestic matter that precipitated high levels of TPHs through water column sinking to the sediments , or may due to the benthic algae and aquatic plant closed to sediment that released hydrocarbons to the sediments.

N-Alkanes in sediments:

N-alkanes enter the aquatic environment sediments according to numerous sources , such as recent benthic biosynthesis , decomposition , geochemical processes , in addition to sinking compounds from the water column.

The chromatograms of aliphatic hydrocarbons showed that sedimentary aliphatic hydrocarbons consisted of a series of solved compounds , mainly n-alkanes from C15– C31 and UCM . The present result was in agreement with Guerra-García *et al.* (2003) who found that sedimentary aliphatic hydrocarbons consisted of C12 to C33 and a UCM . Al-Khatib (1998) pointed that C17 , C18 and C19 were originated from algae and bacteria . Tala (2008) pointed that the high values of odd carbon number chains of C17 in sediments was a result of the presence of sulfuric reducer bacteria (*Desulfovibrio desulfuricans*) in the sediments, while the C19 indicating the algal origin . The high molecular weight n-alkanes (C25 , C27 and C29) in sediments may be a result of the higher plant tissues decomposition .

The high values of n-alkanes in the sediments of Shatt Al-Arab river may be due to the biodiversity and prevalence of phytoplankton, zooplankton, and aquatic plants which have the ability for scavenging dissolved compounds from water and upon sinking to the sediments. Also, the highest turbid matters in water column may have the ability to scavenge some of n-alkanes then sinking to the sediments. Al-Saad (1995) showed that higher molecular weight aliphatic hydrocarbons in water adsorbed to suspended particles due to their low water solubility, while low molecular weight aliphatic hydrocarbons remain as dissolved in water. Benthic algae was expected to form another source for organic matter including n-alkanes in sediments. Al-Saad (1995) concluded that Diatoms are the most likely source for n-alkanes with even-to-odd carbon predominance encountered in aquatic sediments. Al-Khatib (2008) showed that high molecular n-alkanes which have C23-C31 in sediments was the wax of higher terrestrial plants, while the source of C24, C26, and C28 was the activities of bacteria.

The non-significant correlation ($p > 0.05$) between the n-alkanes in sediments and each of the sediments texture compounds (sand, silt and clay) or TOC% was in agreement with Al-Khatib (1998) who found non-significant correlation between the n-alkanes in sediments and each of the sediments texture compounds (sand, silt and clay) or TOC%. The explanation for this status may be due to another important factor such as uncontrolled domestic sewage and agricultural effluents which discharged, without any pretreatment, directly to the river.

PAHs in sediments:

PAHs are lipophilic compounds with very low water solubility and therefore, their concentrations in water were very low and rapidly tended to become associated to the particulate matters ending in sediments (Kafilzaadeh *et al.*, 2011).

Al-Saad *et al.* (2009) showed that the sediments texture play a major role in the distribution of hydrocarbons, it was observed that sediments having silt-clay texture contain more higher capacity of area loading of small particles. In the present study non-significant correlation ($p > 0.05$) was found between the silt-loam sediments and its containing of PAHs, this may be due to another factors that play a main role in the distributions of PAHs in the present sediments such as the bacteria and fungi (Ali *et al.*, 2013) benthic organisms; Mollusca, Diatoms or turbid inorganic matters.

Al-Khion (2012) found that the sources of PAHs in sediment of the Iraqi Coast region were Pyrogenic and Petrogenic with predominance of Carbazole and Anthracene in high concentration indicating a pyrogenic origin, and present naphthalene with 1+2 methyl naphthalene and Fluorene and Phenanthrene indicating a petrogenic origin.

Comparison of the total n-alkanes and PAHs concentration in the sediments of the present study with those reported by other studies listed in Table (4) showed that the present value was located within the previous ranges, and the present area was classified as unpolluted with petroleum hydrocarbons according to US-EPA (2012) criteria values which is in 'unpolluted' sediments, TPHs concentrations generally ranged from <1 ppm to approximately 10 ppm. Also, sediments can be considered as unpolluted with PAHs compounds according to the CCME (1999) limiting permissible values in sediments.

Table (4): Comparison between the levels of total hydrocarbons, n-alkanes ($\mu\text{g/g}$ dry weight), and PAHs (ng/g dry weight) in sediments for the present study with the other previously studied ones.

Studied Areas	Total Hydrocarbons ($\mu\text{g/g}$)	n-alkane ($\mu\text{g/g}$)	PAHs (ng/g)	References
Shatt Al-Arab River & NW Arabian Gulf	2.46 - 38.33	6.97 - 55.67	8.42 - 70.56	Al-Saad (1995)
Shatt Al-Arab River & NW Arabian Gulf	0.108 - 37.02	3.470 - 18.952	-	Al-Khatib (1998)
Al-Howaiza Marsh	4.057 - 47.335	3.43 - 42.38	0.1 - 145.8	Al-Khatib (2008)
Al-Hammar Marsh	0.458 - 1.250	6.53 - 31.46	-	Talal (2008)
Shatt Al-Arab River, Northern	7.37 - 24.41			Al-Imarah <i>et al.</i> (2010)
Iraqi Coast Region	2.39 - 30.88	-	12.15 - 47.38	Al-Khion (2012)
Shatt Al-Arab River	4.76 - 45.24	4.76 - 10.09	4.318 - 28.48	Present study

Hydrocarbons Pollution Indices :

According to the LMW/HMW ratio, the main source of n-alkanes in sediments of Shatt Al-Arab was biogenic origin, this may be due to many species of organisms such as mollusca which have the ability to produce n-alkanes. Fagbote and Olanipekun (2013) showed that LMW n-alkanes are usually produced by marine biogenic sources. While the main source of PAHs compound in sediments was pyrogenic as a result of fuel combustion. High CPI values (> 1), together with a dominance of n-alkanes with more than 25 carbons, indicate that the major source of n-alkanes is from terrestrial plants (Guerra-García *et al.*, 2003).

Pristane in aquatic environments result mainly and directly from zooplankton and from decomposition of algae, while phytane originated from several types of bacteria and from deposition of algae. Also these isoprenoid (pristane and phytane) came indirectly from aquatic biomolecules such as chlorophyll. When pristane/phytane ratio < 1 referred to an oxic conditions (pyrogenic origin), and the ratio > 1 referred to a reducing conditions (biogenic origin) the main source of PAHs in water and sediment was pyrogenic origin depending on high flouranthene values as compared with pyrene.

values . The origin of UCM in sediments samples could be a result of microbial oxidation for the dead aquatic organisms.

Conclusion

The carbons chain length of n-alkanes in the sediments of Shatt Al-Arab river were from C7-C31 dominant with C22-C25 , while the PAHs compounds can be divided into two major groups (Low Molecular Weight (LMW) that consist of 2-3 fused rings , and High Molecular Weight(HMW) that consist of 4 and more fused rings. From the LMW/HMW ,CPI index and Pristane/Phytane values , the source of n-alkanes hydrocarbons in thesediments Shatt Al-Arab river was mainly biogenic and pyrogenic and at least petrogenic.

From the LMW/HMW , Phenanthrene/Anthracene ,and Flouranthene / Pyrene ratios , the source of PAHs compounds in in the sediments was only pyrogenic .

Generally , the hydrocarbons concentrations were within the permissible values and Shatt Al-Arab river was considered as unpolluted river.

References

- Abel , P.D. (2002) ." Water Pollution Biology ". 2nd ed. Copyright © Taylor & Francis Ltd .
- 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. (1998)."Distribution of hydrocarbons compound and their sources in sediment cores from Shatt Al-Arab Estuary and North-West Arabian Gulf". M.Sc. Thesis . University of Basrah, college of science , biology department , 95 pp.
- 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.
- Al-Saad , H. T. ;Al-Taein , S. M. ; Al-Hello , M A. R. ; and DouAbul , A .A.Z.(2009)." Hydrocarbons and trace elements in the waters and sediments of the marshlands of southern Iraq". Mesop. J. Mar. Sci. , 24(2):126-139.
- 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.
- Ball , F.D. (1964)."Loss on ignition as an estimate of organic matter and organic carbon in non-calcareous soils ". J. Soil Sci. , 15 : 84-92.
- CCME: Canadian Council of Ministers of the Environment. (1999). "Canadian sediment quality guideline for the protection of aquatic life" .
- 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.
- Folk , R.L. (1974)."Petrology of Sedimentary Rocks". Hemphill Publishing Co. Austin , Texas . USA , 182 pp.
- Goutx, M. and Saliot , A. (1980). " Relationship between dissolved and particulate fatty acid and hydrocarbons , chlorophyll (a) and zooplankton biomass in Ville Franche Bay , Mediterranean Sea" .Mar. Chem., 8:299-318.
- 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.
- US-EPA :United States –Environmental Protection Agency .(2012)." Edition of the Drinking Water Standards and Health Advisories EPA 822-S-12-001 Office of Water U.S. Environmental Protection Agency Washington, DC Spring 2012.