

Original Research Paper

Assessment of Aliphatic Hydrocarbons in Sediments of Shatt Al-Arab River, Southern Iraq, North East Arabian Gulf

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Abstract: Shatt Al-Arab River is one of the important rivers for water supply, industry and irrigation in Basrah City, south of Iraq. It's also supply drinking water to users in the region. Despite the significance of this river, there is a lack of previous studies dealing with petroleum pollution especially for geochemical studies of organic matter in the river sediments using molecular tracer methods. Therefore, the identification and quantification of petroleum hydrocarbons in this river at the elemental and molecular levels will be of the utmost interest. Sediments were analyzed in nine Shatt Al-Arab River stations. Texture was silty clay or silty sand. TOC and TN ranged from 0.39-0.90 and 0.02-0.16%. OM varied from 17.43-34.36 $\mu\text{g g}^{-1}$ dw, representing 0.27-0.87% of TOC. AHs ranged from 3.19-10.27 $\mu\text{g g}^{-1}$ dw and constituted 16.07-29.88% of OM. Total n-alkanes concentrations ranged from 0.08-42.58 $\mu\text{g g}^{-1}$ dw with carbon numbers from C11-C34 were identified. N-alkanes content was relatively moderate compared to sites contaminated with oil worldwide. Dominance of even carbon number n-alkanes (C11-C20) with CPI and LMW/HMW values close to unity, indicated to oil-related n-alkanes. This was verified by the values of U/R (1.27-2.45), pri/phy (0.82-1.00), C17/pri (0.70-1.94) and C18/phy (0.95-1.56) ratios and the presence of UCM. Biogenic contributions were detected within the n-alkanes distribution of C17-C31 and CPI and LMW/HMW values of <1 that mainly related to terrestrial plants, phytoplankton, algae and bacteria sources, confirmed by TAR (0.79-2.15) and C31/C19 ratio (0.28-1.62) values. However, the contribution from biogenic hydrocarbons is overshadowed by petroleum origin n-alkanes. This was obvious by the presence of UCM. PCA showed concordant results with n-alkanes ratios indicating mixed n-alkanes sources in sediments. Hopanes and steranes in sediments displayed similar signatures that were characteristic of mature organic matter contribution from oil contaminations.

Keywords: Shatt Al-Arab River, n-alkanes, Sediments, UCM

Introduction

Pollution levels in the rivers and estuaries ecosystems are increasing mainly because of human activities (Wang *et al.*, 2011). Shatt Al-Arab River is one of the most important internal rivers in southern Iraq because of its economic, social and ecological importance. It is the Arabian gulf's main source of freshwater and therefore plays a major role for marine habitats in the gulf's north-eastern coastal areas (Al-Hejuje *et al.*, 2014). The river provides important commercial waterway to the Arabian gulf. It's water has also been used for various purposes in the region including potable water supply, irrigation, fisheries, tourism navigation and industrial uses. Moreover, It has numerous ports in

its lower parts (Farid *et al.*, 2016). Thus, the river is severely impacted by pollution from agricultural, industrial and domestic sources.

Petroleum hydrocarbons are one of the major organic contaminants in Shatt Al-Arab River. They can enter the river through accidental spills, normal tanker operations, offshore production, oil wastes disposal and atmospheric fallout. In addition, some hydrocarbons are derived from biogenic origins (Farid *et al.*, 2016). The oil contaminants causes serious pollution in water ecosystems and direct damage to living organisms and human health (El Nemr *et al.*, 2016). The fate of petroleum hydrocarbons in the aquatic environment is subject to complex and interrelated physical and chemical processes. These factors cause significant

modifications to hydrocarbons, making it difficult to detect and analyze (Zrafi *et al.*, 2013).

The hydrocarbons in water tend to associate with particulate organic matter due to their hydrophobic nature and they are subsequently to reach the sediments by adsorption and deposition processes. Therefore, the sediments can be considered as a major reservoirs of pollutants because of their ability to retain organic compounds (Zrafi *et al.*, 2013). The sediments analysis gives a lot of information about the pollutants sources, diagenetic processes and extent of pollution in the environment (Frena *et al.*, 2017). Hydrocarbons such as n-alkanes are commonly utilized to evaluate the oil pollution origins in the aquatic environment due to the ease of their analysis and most of it have specific sources (Punyu *et al.*, 2013).

Oil pollution in Shatt Al-Arab River sediments have been investigated through preliminary studies (DouAbul *et al.*, 1984; Grimalt *et al.*, 1985; Al-Saad 1987; Al-Saad and Al-Timari, 1989; 1993; Al-Saad *et al.*, 1995), which remain very incomplete and insufficient. The river is well known by receiving high inputs of organic matter from different sources. But the bulk of contamination is still not well known. After 2003 numerous operations by several international oil companies are carried out. However, few studies such as Al-Hejuje *et al.* (2015) and Mahdi (2005) have focused on the realization of a surveillance of hydrocarbons in Shatt Al-Arab River using the sediments as indicators. They were dealing with chemical analysis of pollutants. Nevertheless, their results remain relatively limited. There is still a lack of information specially with regard to using the molecular tracer methods to characterize of organic matter, particularly n-alkanes concentration and composition in the sediments of the Shatt Al-Arab River. Thus, the objective of the present study was to investigate the distribution, composition and sources of aliphatic hydrocarbons at the elemental and molecular levels. The study also provides an estimate of the background of hydrocarbons contamination in the river sediments. The bulk analysis and multi-biomarker data together will give a clear view of the sources of hydrocarbons in the river environment.

Materials and Methods

All the glassware used was well cleaned and stored in a clean place until used. Solvents were analytical grade and were distilled prior to use. Sodium sulphate ashed at 400°C and silica and alumina were washed using methanol and chloroform and dried before use.

Sediment samples were collected from nine Shatt Al-Arab River stations, southern Iraq, during July, 2017. The sampling stations were shown in Fig. 1 and were geo-located with Global Positioning System (GPS) (Table 1). The sediments were taken from the superficial

layer, 5-20 cm using Van-Veen grab sampler to form composite samples. The samples were transported to the laboratory in pre-cleaned ice box and stored frozen at -20°C. They were then sieved through stainless steel sieve with mesh size 62 µm and ground finely with mortar and pestle and kept at -20°C until further analysis.

Hydrocarbons were extracted from sediments followed the procedure described by Wang *et al.* (2011). 50 g of sediments were Soxhlet extracted for 24 h with 250 mL n-hexane: methylene chloride (1:1). Elemental sulfur was removed from the extracts using activated elemental copper. The extracts were then fractionated into aliphatic and aromatic hydrocarbons by chromatography column. The column was prepared by slurry packing 10 g of silica, followed by 10 g of alumina and finally 1 g of anhydrous sodium sulphate was added to the surface. The extract was then applied to the head of the column and eluted with 25 mL n-hexane to obtain on the aliphatic fraction and 25 mL of benzene to yield the aromatic once. The composition of only the aliphatic fraction will be discussed. The aliphatic fraction was concentrated on a rotary evaporator, transferred to a vial and the volume was adjusted to 1 mL exactly using a stream of nitrogen. An aliquot of 1 µL of extract of aliphatic hydrocarbons were subjected to analysis by Allegent capillary Gas Chromatography (GC). The 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 and 320°C, respectively. The silica capillary column was operated under initial, final and rate temperatures that programmed as follows: Initial temperature was 60°C for 4 min, while final temperature was 280°C for 30 min and rate was 4°C/min.

The individual n-alkanes was identified based on the retention time of authentic n-alkanes standards (C11–C34). Their concentrations were calculated based on the standard calibration curves. Based on the areas of the internal standard and all n-alkanes in the sample, the UCM concentration was calculated. The recovery assays for standards aliphatic ranged from 80-92%. The standard deviation for the method was less than 10% based on replicate analysis. The method detection limits were 0.02-0.05 µg/g.

Table 1: Location of sampling stations

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

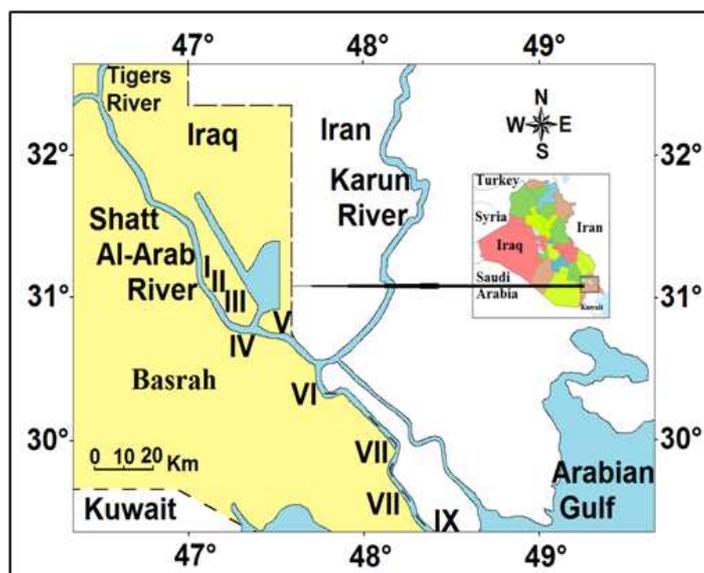


Fig. 1: Map of study area and sampling stations

Hopanes and steranes were analyzed using the Shimadzu QP-1000A Gas Chromatography-Mass Spectrometry (GC-MS). A fused silica capillary column (50 m \times 0.2 mm, inner diameter) coated with SE-30 of 0.25 μ m film thickness was used. Injector temperature was 60°C and source housing temperature was maintained at 250°C. Helium gas was used as the carrier gas with flow rate was maintained at 1.5 ml min⁻¹. The oven temperature was programmed to increase from 80-290°C at 4°C min⁻¹ and then kept constant for 30 min. The MS operating conditions were: EI ionization, ion source 230°C, electron energy 70 eV, interface temperature 280°C. The GC-MS operation was in full scan mode, scanning from m/z 50-500. The detection of hopanes and steranes was done using ions at m/z 191 and 217, respectively. The compounds identification was based on the comparison of relative GC retention times and mass spectra with those in the published literature.

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

Total Organic Carbon (TOC) was determined according the wet oxidation method of Walkey and Black (1934).

Kjeldahl method was used to determine the Total Nitrogen (TN) in sediment samples (Diniz *et al.*, 2013).

To determine the Organic Matter (OM) and Aliphatic Hydrocarbons (AHs) contents in sediments, the gravimetric method 5520E in Standard Methods was used (APHA, 1992). The OM relative to TOC (OM %) and AHs relative to OM (AHs %) were then calculated.

Data were statistically analyzed. Standard Errors (SE) were calculated between the repetitions of n-Alkane concentrations. The comparisons among samples were achieved by one way ANOVA. The statistical

significance was defined as $p < 0.05$. A simple correlation was also used to assess relationship between different parameters. The Principal Component Analysis (PCA) was applied to n-alkanes composition of sediments. A number of n-Alkane-based indexes were used to identify the hydrocarbon sources.

Results and Discussion

The characteristics of Shatt Al-Arab River sediments are shown in Table 2. The sediments texture of two stations I and II composed mainly of silty sand, while the other seven stations consisted fundamentally of silty clay texture.

The TOC and TN contents in the sediments are high in stations IV, VI and VIII and low in stations I, II, III, V, VII and IX. The fine grained sediments can easily accumulate and retain organic matter and nutrients (Lu *et al.*, 2005).

If the TOC to TN (C/N) ratio is between 5-8, the OM origin is aquatic plants and if the ratio is of 20 and greater, the source of sedimentary OM is terrestrial plants (Zaghdien *et al.*, 2017). The C/N ratio varies from 6.30-21.00%, indicating the OM in Shatt Al-Arab River sediments is originated of both aquatic and terrestrial plants.

The OM sediments content is close together for stations IV, V and II and is higher than stations I, III, VII and IX and lower than stations VII and VI. Different pattern of OM content was obtained after normalizing to TOC content which is higher for stations II, IV, VI, VII and VIII compared to stations I, III, V and IX. This provides evidence that OM has relatively shorter degradation processes in sediments of stations I, III, V and IX than the others (Gao *et al.*, 2007).

The AHs content is an essential part of OM content in Shatt Al-Arab River sediments, where it is represent 16.07-29.88% of the OM content.

The analysis of n-alkanes can use to detect the petroleum presence in the environment and provides information on hydrocarbons sources and degradation extent (Guo *et al.*, 2012). The total n-alkanes concentration in the sediments varies from 0.08-42.58 $\mu\text{g g}^{-1}$ dry weight (dw) (Table 3). The highest concentrations of n-alkanes are found near potential oil pollution sources, close to stations II, IV, VI and VII, while the lower concentrations are relatively recorded at stations I, III, V, VIII and IX (Fig. 2). Shatt Al-Arab River area is home to many industries and river activities, which may explain the difference can be observed between the n-alkanes 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 (Farid *et al.*, 2016). The concentrations of n-alkanes measured here are relatively within the range of many other worldwide oil contaminated sediments such as those reported by Bouloubassi *et al.* (2001), Yunker *et al.* (2003), Lee *et al.* (2005), Mille *et al.* (2007), Zaghden *et al.* (2007), Harji *et al.* (2008), Da Silva and Bicego (2010), Wang *et al.* (2011), Wagener *et al.* (2012), Punyu *et al.* (2013), Zrafi *et al.* (2013) and Frena *et al.* (2017). The comparison also reveal higher sedimentary concentrations of n-alkanes in Shatt Al-Arab River compared to those detected by Readman *et al.* (2002), Medeiros and Bicego (2004), Medeiros *et al.* (2005), Tolosa *et al.* (2005), Wang *et al.* (2006), Gao *et al.* (2007) and Harji *et al.* (2008). However, the concentrations of present n-alkanes were in the low range when compared with those reported by Commendatore *et al.* (2000), Sakari *et al.* (2008) and Yusoff *et al.* (2012) (Table 4).

Table 2: The sampling depth and some sedimentological parameters of Shatt Al-Arab River

	I	II	III	IV	V	VI	VII	VIII	IX
Depth (cm)	5-20	5-20	5-20	5-20	5-20	5-20	5-20	5-20	5-20
Clay (%)	14.34	23.65	13.12	27.72	23.55	30.83	35.34	34.19	30.74
Silt (%)	53.42	46.22	66.42	65.26	78.54	60.14	61.36	66.61	59.65
Sand (%)	31.68	11.65	33.88	14.45	2.54	6.87	4.22	5.78	4.93
Texture	Silty sand	Silty clay	Silty sand	Silty clay					
TOC (%)	0.41	0.69	0.39	0.82	0.58	0.90	0.89	0.58	0.47
TN (%)	0.02	0.04	0.02	0.10	0.04	0.16	0.14	0.09	0.06
C/N	21.00	20.10	20.50	10.02	16.32	6.30	7.16	7.25	8.65
OM ($\mu\text{g g}^{-1}$)	17.43	22.66	17.27	22.52	22.27	34.36	31.54	19.98	18.86
OM (%)	0.27	0.56	0.33	0.78	0.36	0.75	0.87	0.58	0.29
AHs ($\mu\text{g g}^{-1}$)	4.56	4.45	3.84	6.23	3.58	10.27	9.36	5.88	3.19
AHs (%)	26.16	19.63	22.23	27.66	16.07	29.88	29.67	29.42	16.91

Table 3: Concentration of n-alkanes ($\mu\text{g g}^{-1}$ dw) and standard error (SE) of Shatt Al-Arab River sediments

Carbon chain	I	SE	II	SE	III	SE	IV	SE	V	SE	VI	SE	VII	SE	VIII	SE	IX
C11	0.36	0.54	1.68	0.73	0.31	0.44	1.66	0.21	0.17	0.38	1.68	0.58	1.41	0.74	0.08	0.12	0.10
C12	0.45	0.26	3.15	0.45	0.32	0.25	2.72	0.34	0.85	0.56	3.25	0.32	3.24	0.93	0.06	0.50	0.07
C13	0.87	0.43	1.62	0.25	0.23	0.36	1.68	0.57	0.93	0.94	1.92	0.74	1.51	0.28	0.12	0.42	0.02
C14	0.45	0.41	2.25	0.75	0.34	0.68	2.66	0.93	0.45	0.92	4.28	0.85	3.32	0.66	0.17	0.44	0.08
C15	0.70	0.58	1.59	0.89	0.14	0.52	1.82	0.42	0.43	0.15	1.89	0.41	1.63	0.57	0.16	0.24	0.32
C16	0.30	0.71	2.63	0.74	0.25	0.81	3.17	0.64	0.36	0.26	4.33	0.17	2.84	0.17	0.23	0.76	0.29
C17	0.75	0.22	1.57	0.16	0.82	0.11	0.95	0.97	0.79	0.18	1.88	0.27	1.86	0.53	0.88	0.28	0.72
C18	0.67	0.46	2.42	0.24	0.73	0.10	1.12	0.55	0.62	0.83	3.33	0.43	2.24	0.54	0.77	0.56	0.66
C19	1.22	0.68	1.85	0.83	2.30	0.42	1.86	0.67	1.39	0.26	1.83	0.46	1.89	0.37	0.97	0.89	0.87
C20	0.22	0.67	3.37	0.23	0.39	0.26	2.73	0.42	0.58	0.32	3.49	0.19	3.93	0.56	0.10	0.19	0.07
C21	1.46	0.34	1.48	0.17	1.36	0.54	2.02	0.53	1.98	0.66	1.88	0.85	1.22	0.74	0.88	0.25	1.15
C22	0.47	0.28	0.56	0.54	0.45	0.53	0.44	0.74	0.22	0.50	0.93	0.50	0.65	0.62	0.12	0.67	0.46
C23	1.40	0.94	1.32	0.35	2.48	0.50	1.52	0.23	2.07	0.54	0.98	0.27	1.63	0.84	0.92	0.91	0.98
C24	0.26	0.56	0.69	0.67	0.39	0.64	0.31	0.18	0.50	0.44	0.35	0.12	0.39	0.19	0.31	0.25	0.03
C25	1.19	0.48	1.61	0.19	1.70	0.72	0.67	0.16	1.59	0.37	1.81	0.55	1.84	0.48	0.85	0.16	0.87
C26	0.23	0.27	0.78	0.56	0.28	0.88	0.62	0.52	0.40	0.83	0.63	0.74	0.45	0.15	0.27	0.77	0.06
C27	1.42	0.92	1.78	0.57	1.16	0.47	0.87	0.52	2.60	0.85	1.76	0.95	1.68	0.23	0.97	0.33	0.89
C28	0.97	0.47	0.49	0.17	0.22	0.53	0.65	0.33	0.66	0.73	0.60	0.34	0.62	0.66	0.17	0.45	0.04
C29	2.25	0.62	1.66	0.66	1.26	0.32	1.96	0.63	1.02	0.41	1.82	0.57	1.80	0.59	0.87	0.50	0.84
C30	0.85	0.18	0.53	0.84	0.23	0.63	0.68	0.28	0.46	0.73	0.38	0.32	0.36	0.46	0.15	0.43	0.13
C31	1.98	0.16	1.46	0.49	1.17	0.55	0.86	0.57	2.00	0.51	1.75	0.86	0.54	0.48	0.83	0.87	0.85
C32	0.45	0.55	0.46	0.22	0.38	0.74	0.53	0.37	0.35	0.34	0.72	0.50	0.32	0.50	0.05	0.38	0.14
C33	0.35	0.35	0.21	0.13	0.40	0.45	0.32	0.77	0.41	0.50	0.71	0.59	1.35	0.88	0.05	0.18	0.30
C34	0.33	0.75	0.48	0.63	0.16	0.85	0.43	0.50	0.3	0.73	0.38	0.15	0.29	0.75	0.03	0.65	0.04
Total	0.36		35.64		17.47		32.25		21.13		42.58		37.01		0.08		9.98

Table 4: Compaction of n-alkanes concentration in sediment of investigated river with other sites of the world

Location	Concentration ($\mu\text{g g}^{-1}$ dw)	References
Patagonia, Argentina	nd-1304.7	Commendatore <i>et al.</i> (2000)
Changjiang estuary, China	2.20-11.82	Bouloubassi <i>et al.</i> (2001)
Black Sea (Turkey, Russia and Ukraine)	0.10-3.40	Readman <i>et al.</i> (2002)
Fraser River Basin, Canada	1.60-20.60	Yunker <i>et al.</i> (2003)
Sao Sebastiao, Brazil	0.03-4.77	Medeiros and Bicego (2004)
Kaohsiung harbor and Adjacent coast, Taiwan	0.46-22.60	Lee <i>et al.</i> (2005)
Patos lagoon estuary, Brazil	0.20-7.50	Medeiros <i>et al.</i> (2005)
Arabian Gulf (Bahrain)	0.50-8.20	Tolosa <i>et al.</i> (2005)
Jiaozhou Bay, China	0.54-8.12	Wang <i>et al.</i> (2006)
Pearl River estuary, China	3.43-8.46	Gao <i>et al.</i> (2007)
Gulf of Fos, France	7.80-180	Mille <i>et al.</i> (2007)
Sfax coastal zone, Tunisia	2.18 to 429.5	Zaghden <i>et al.</i> (2007)
Mandovi estuary, India	0.80-3.20	Harji <i>et al.</i> (2008)
Marmugoa harbour, India	1.60-10.70	Harji <i>et al.</i> (2008)
Prai Strait, Penang Malaysia	421-3135	Sakari <i>et al.</i> (2008)
Sao Sebastiao (Brazil)	nd-28.8	Da Silva and Bicego (2010)
Yellow River Delta Nature Reserve, China	22.1-81.15	Wang <i>et al.</i> (2011)
Guanabara Bay	7.66-57.22	Wagener <i>et al.</i> (2012)
South China Sea off Kuching division, Sarawak	35.6-1466.1	Yusoff <i>et al.</i> (2012)
Visakhapatnam harbour, east coast of India	0.2-31	Punyu <i>et al.</i> (2013)
Khmiss coast, Tunisia	9.69-36.08	Zrafi <i>et al.</i> (2013)
Itajaí-Açu Estuarine System, Brazil	0.50-69.70	Frena <i>et al.</i> (2017)
Shatt Al-Arab River	0.08-42.58	Present study

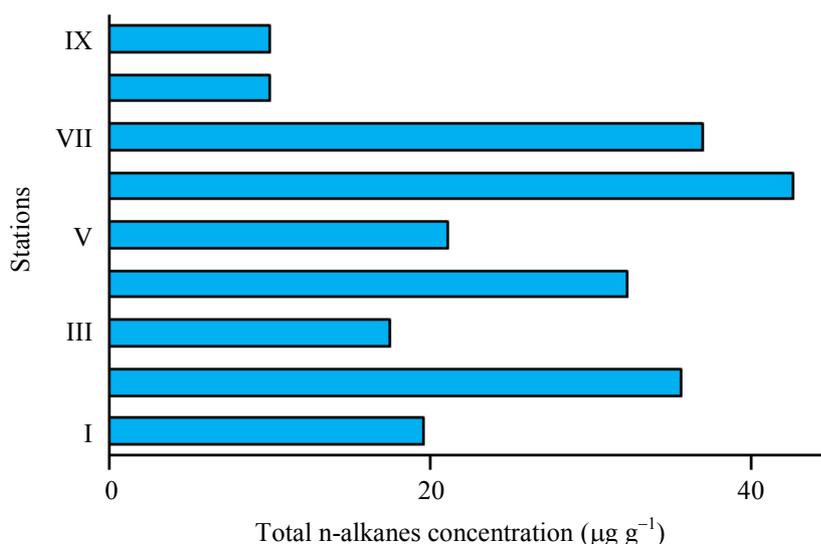


Fig. 2: Distribution of n-alkanes in the sediments of sampling stations

The distribution of carbon chain lengths of n-alkanes for sediments are shown in (Fig. 3). Generally, the range of recent carbon chain length of n-alkanes is C11-C34. Typically, the dominance of odd carbon number n-alkanes in the range C15-C33 is an indicator of biogenic inputs, the both phytoplankton (C15, C17 and C19) and terrestrial plants (C23, C25, C27, C29, C31 and C33) (Punyu *et al.*, 2013), whereas the dominance of the n-alkanes in the range C12-C24 without odd carbon number predominance suggests relatively the contribution from aquatic microorganisms

and petroleum inputs (Wang *et al.*, 2011). The n-alkanes profile of present study suggests two distinct sources at sediments are evident on the basis of their distribution pattern in the samples collected. Sediments of stations II, IV, VI and VII show a dominance of even carbon n-alkanes in the range C11-C20, suggesting the contribution of microorganisms and petroleum inputs. Whereas, sediments of stations I, III, V, VIII and IX show a predominance of odd-carbon number n-alkanes in the range C17-C31, indicating biogenic sources of n-alkanes.

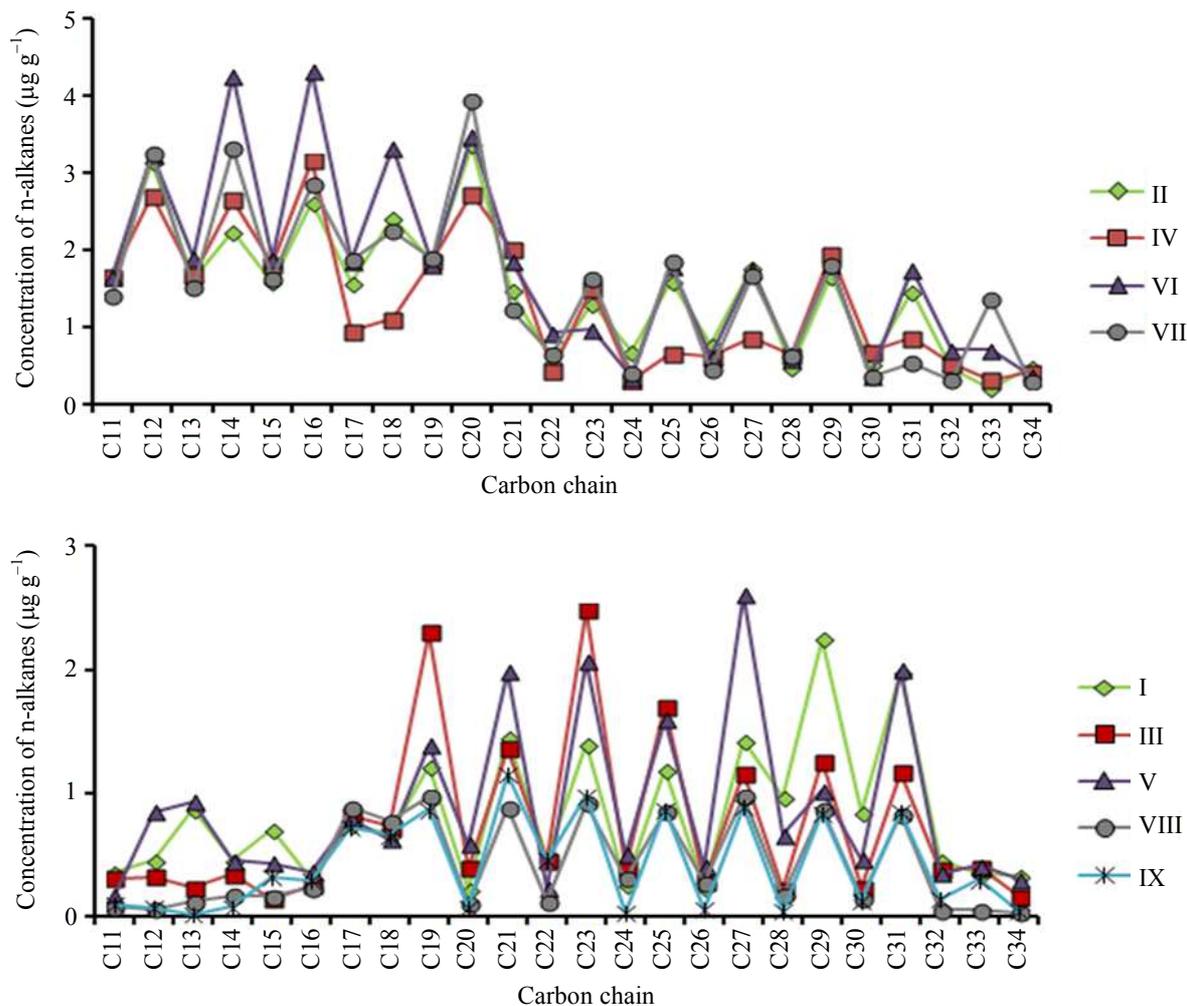


Fig. 3: Chromatographic distribution of n-alkanes carbon chain length for sediments of Shatt Al-Arab river

Table 5: Indices of Shatt Al-Arab River sediments n-alkanes

	I	II	III	IV	V	VI	VII	VIII	IX
Odd	13.95	17.83	13.33	16.19	15.38	19.91	18.36	7.58	7.91
Even	5.65	17.81	4.14	16.06	5.75	22.67	18.65	2.43	2.07
UCM	25.64	87.54	28.76	76.45	26.88	98.45	81.98	14.36	17.67
U/R	1.30	2.45	1.64	2.37	1.27	2.31	2.21	1.43	1.77
Pri	0.62	2.32	0.64	1.64	0.59	3.65	2.38	0.62	0.58
Phy	0.62	2.58	0.67	1.75	0.60	3.78	2.63	0.75	0.63
Pris/Phy	1.00	0.89	0.95	0.93	0.98	0.96	0.90	0.82	0.92
C17/Pris	0.82	1.47	0.78	1.72	0.74	1.94	1.27	0.70	0.80
C18/Phy	0.92	1.06	0.91	1.56	0.96	1.13	1.17	0.97	0.95
CPI	2.46	1.00	3.21	1.00	2.67	0.88	0.98	3.11	3.82
LWH/HWH	0.44	1.63	0.50	1.73	0.45	1.89	1.81	0.54	0.47
TAR	2.11	0.97	1.10	0.79	2.15	0.98	0.98	1.32	1.35
C31/C19	1.62	0.78	0.50	0.46	1.43	0.95	0.28	0.85	0.97

The occurrence of the Unresolved Complex Mixture (UCM) in most recent samples with different range (14.36-98.45 $\mu\text{g g}^{-1}$ dw) (Table 5) suggests a petroleum inputs to the sediments. The UCM is mainly composed of branched alkanes, cycloalkanes and aromatic compounds.

Such compounds are resistant to biological degradation and have been considered as the environmental indicators of petroleum contamination and n-alkanes biodegradation (Harji *et al.*, 2008). The ratio of unresolved complex mixture/resolved n-alkanes (U/R) is used as a diagnostic

criterion for petroleum pollution. The U/R ratio > 2 suggests petroleum origin (Zaghden *et al.*, 2017). The ratio of U/R varies from 1.27-2.45 (Fig. 4) which confirms petroleum inputs to sediments.

The pristane (pri) and phytane (phy) are originated from geologic alteration of phytol and other isoprenoidyl products (Frena *et al.*, 2017). They are usually present in most petroleum as major constituents and are considered as common indicators for petroleum pollution. However, pri can also be derived from zooplanktons and other aquatic animals, while phy can be contributed by methanogenic and photosynthetic bacteria (Punyu *et al.*, 2013). These compounds are observed in all present sediments (Table 5). Typically, in uncontaminated sediments, the pri/phy ratio is ranged from 3-5, whereas it is ≤ 1 for petroleum contaminated sites (Wagener *et al.*, 2008). The pri/phy ratio varies from 0.82-1.00 (Fig. 4). The values are ≤ 1 at all stations indicating petroleum inputs to sediments. The C17/pri and C18/phy ratios are often used to evaluate the presence of freshly derived and degraded petroleum hydrocarbons in sediments (Harji *et al.*, 2008). The value is < 1 for degraded petroleum and > 1 for fresh petroleum input. The C17/pri and C18/phy ratios range from 0.70-1.94 and 0.95-1.56 respectively (Fig. 4). The ratios indicate that the fresh petroleum

input is present at stations II, IV, VI and VII and degrade petroleum at stations I, III, V, VIII and IX.

The Carbon Preference Index (CPI) is a measure of homologous odd over even n-alkanes in a specified range of carbon numbers. If CPI is > 1 , the hydrocarbons source is terrestrial plants and if it is 1 or close to 1, the source is petroleum input. If CPI is < 1 , the source is bacteria and diatoms (Punyu *et al.*, 2013). The CPI ranges from 0.88-3.82 (Table 5 and Fig. 4). The stations II, IV, VI and VII exhibit CPI values 1 or close to 1 indicating petrogenic inputs. At stations I, III, V, VIII and IX, the CPI are > 1 , suggesting the contribution from higher vascular plants.

The ratio of Low to High Molecular Weight hydrocarbons (LMW/HMW) < 1 indicates to the higher plants, aquatic animals and bacteria sources of n-alkanes and it suggests the sources of petroleum and plankton when close to 1. The LMW/HMW ratio > 2 often indicates the presence of fresh oil source (Wang *et al.*, 2011). The LMW/HMW ratio ranges from 0.44-1.89 (Table 5 and Fig. 4). The ratio is less than 1 at stations I, III, V, VIII and IX indicating higher plants, aquatic animals and bacteria inputs. However, the ratio of LMW/HMW is close to 1 at stations II, IV, VI and VII, suggesting petroleum and plankton sources of n-alkanes.

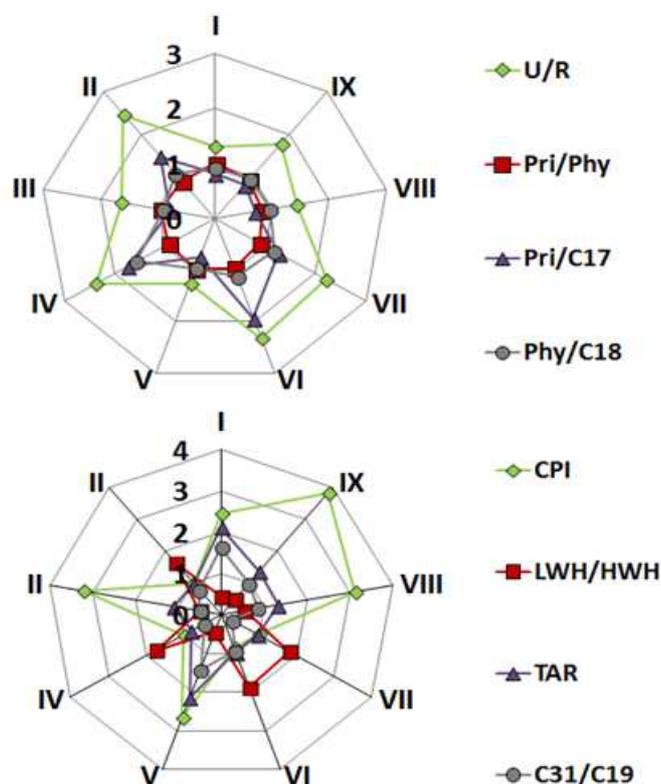


Fig. 4: Spatial trend of U/R, pri/phy, C17/pri, C18/phy, CPI, LMW/HMW, TAR and C31/C19 ratios of Shatt Al-Arab River sediments

The Terrigenous/Aquatic Ratio (TAR) is >1 for terrestrial input and <1 for aquatic input (El Nemr *et al.*, 2016). The ratio is higher than 1 at stations I, III, V, VIII and IX indicating terrestrial inputs over aquatic inputs. However, the ratio is less than 1 at stations II, IV, VI and VII, suggesting aquatic inputs over terrestrial inputs (Table 5 and Fig. 4).

The C31/C19 ratio is a measure of the relative proportions of allochthonous and autochthonous hydrocarbon inputs. The C17/C19 ratio > 0.4 indicates to non-marine sources, while lower values suggest marine sources (Gao *et al.*, 2007). The C31/C19 ratio varies from 0.28-1.62 (Table 5 and Fig. 4), confirming the contribution of marine and non-marine sources in the sediments.

The two main components reorganize in the results of the PCA represent 70% of the total variance, 50% for the PC1 and 20% for PC2. The two groups of n-alkanes on the PCA loading scatter plot (Fig. 5) can be observed.

The first group loads on the positive part of PC1 and PC2 and form the main contributor to PC1 (50%). The group consist of low and medium molecular weight n-alkanes (C11-C21) as well as the pri and phy which fundamentally due to the sediments obtained from stations, II, IV, VI and VII, as shown on the score plot (Fig. 6). The high positive loading of the first group compounds suggest the petroleum, phytoplankton and microorganisms sources of n-alkanes in the sediments. The second group loads on the negative part of PC1 and PC2 and positive part of PC2. This group consist of C20-C34 n-alkanes which associate to sediments mainly collected from stations I, III, V, VII, VIII and IX (Fig. 5), suggesting the diagenic and biogenic (terrestrial plants) origin of n-alkanes in the sediments. However, since all the chromatograms of the sediments have a significant UCM, it is very likely that the origin of the hydrocarbons in these stations is also petrogenic.

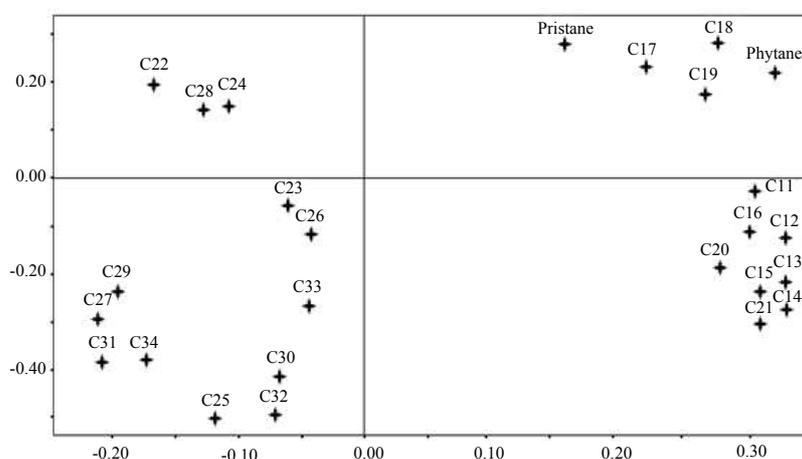


Fig. 5: PCA loading scatter plot showing composition of n-alkanes in sediments collected from Shatt Al-Arab River

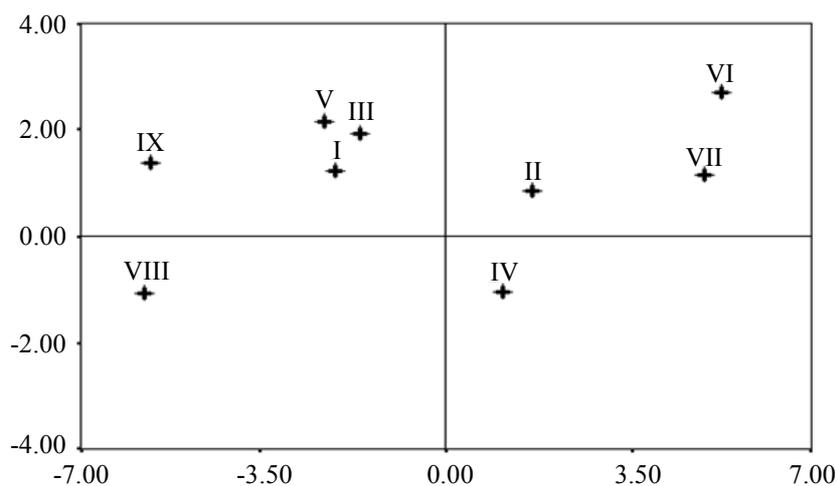


Fig. 6: PCA score plot showing Shatt Al-Arab River spatial clustering of n-alkanes corresponding to sediments

The presence of hopanes in all recent analyzed sediments in the concentration ranges from 4-995 ng g⁻¹ (Fig. 7, Table 6 and Fig. 8), confirm the presence of petroleum compounds. The hopanes mass fragmentograms ($m/z = 191$) indicate the presence of tricyclic terpanes (C19-C23), tetracyclic terpanes (C24) (7% of total hopanes) and pentacyclic triterpanes or hopanes (C27-C35) (93%). (Fig. 7, Table 6 and Fig. 9) The presence of 17 α (H),21 β (H) configurations (49%) and 18 α (H)-22,29,30-Trisnorneohopane (Ts) (4%) strongly supports the presence of petroleum compounds (Punyu *et al.*, 2013). The high concentrations of these compounds are detected at stations II, IV, VI and VII (Fig. 8). The tricyclic terpanes and tetracyclic terpanes are observed at all sediments which are found in crude oil and fossil fuel (Frena *et al.*, 2017). The extended 17 α ,21 β -hopane series (C31-C35) occur as 22S and 22R epimers (Fig. 7 and Table 6).

The ratio of Ts/(Ts + Tm) of C27 hopanes is dependent on maturity and source. It reach equilibrium at intermediate to later thermal maturity (Wang *et al.*,

2011). It was reported that the Ts/(Ts + Tm) ratio can reach to 0.28, 0.33, 0.6 and 0.39-0.5 of Kuwait crude oil, Arabian heavy crude oil, Arabian light crude oil and five representative lubricating oils respectively (Gao *et al.*, 2007). The Ts/(Ts + Tm) ratio varies from 0.39-0.57 (Table 7), indicating the presence of mature petroleum in sediments.

The steranes (73-530 ng g⁻¹) are detected at all stations. The mass fragmentograms of steranes ($m/z = 217$) showed the presence of many stereoisomers such as steranes C27-cholestane (23% of total steranes), C28-ergostane (17%) and C29- stigmastane (40%) with their 20S and 20R epimers. The diasteranes (11%) and C30 steranes (9%) are also detected (Fig. 7, Table 6, Fig. 8 and Fig. 9). The relative abundances of three regular steranes series are in an order of C29> C27> C28. The sterane compounds are strong indicators of petroleum input in sediments (Punyu *et al.*, 2013). The high concentrations of these compounds are presented at stations II, IV, VI and VII (Fig. 8).

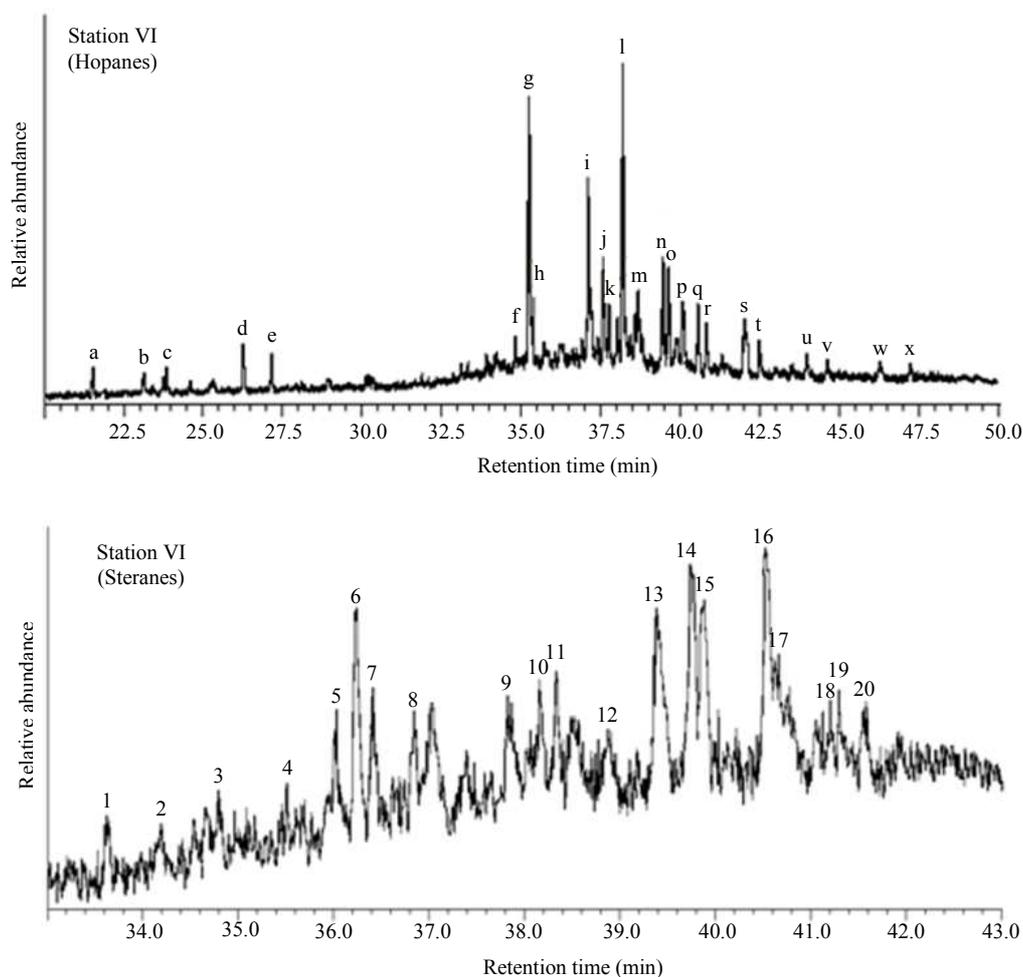


Fig. 7: Mass fragmentogram of hopanes (m/z 191) and steranes (m/z 217) of the Shatt Al-Arab river sediments at station VI (the symbols of the compounds identified are shown in Table 6)

The composition of C27, C28 and C29 steranes indicates a mixed source of the constituent oils origin. Generally, the dominance of C27 over C29 steranes suggest marine sources of petroleum origin, while a predominance of C29 over C27 steranes indicate petroleum input derived from terrestrial sources (Harji *et al.*, 2008). It is also known that higher abundance of C29 steranes could

possibly indicate microbial activity in the environment as C27 and C28 steranes are more susceptible to microbial degradation (Ollivier and Magot, 2005). The ratio of C27/C29 steranes varies from 0.39-0.89 (Table 7), indicating that the source of petroleum is terrestrial plants in stations I, III, V and VIII and marine algae in stations II, IV, VI and VII.

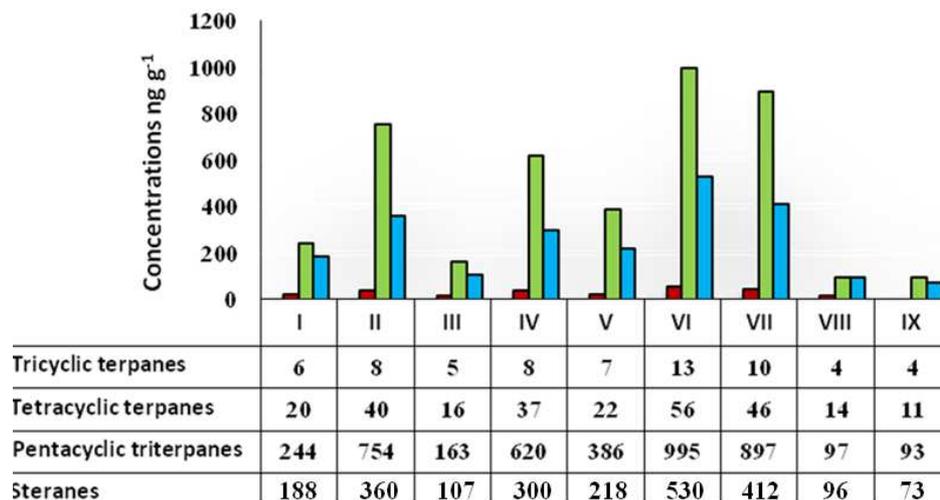


Fig. 8: Concentrations of hopanes and steranes (ng g⁻¹) in sediments of sampling stations

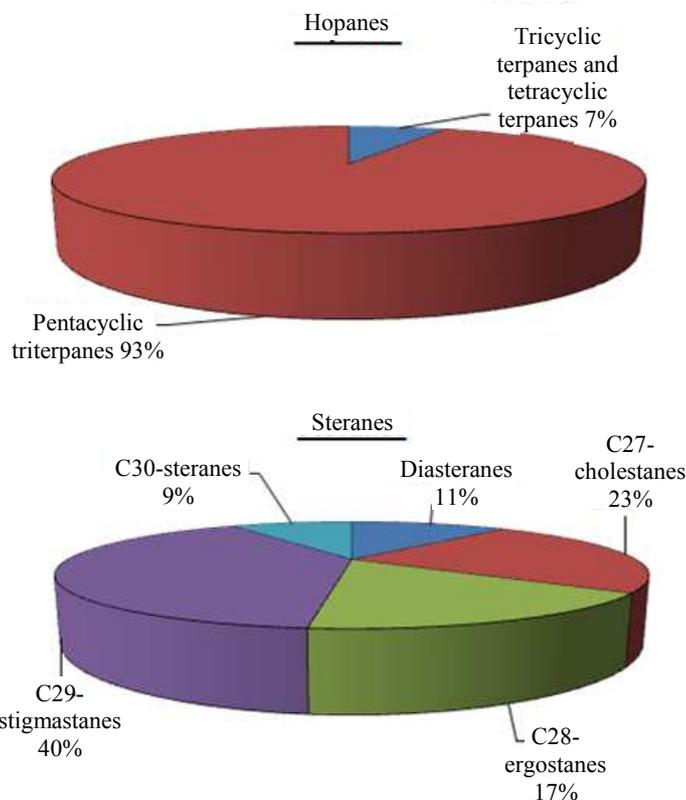


Fig. 9: Percentage of hopane and sterane compounds in the sediments of Shatt Al-Arab River

Table 6: Hopanes and steranes compounds identified in the sediment samples of Shatt Al-Arab River stations

Biomarker	I	II	III	IV	V	VI	VII	VIII	IX
Hopanes									
Tricyclic terpanes									
C19 (a), C20 (b), C21 (c) and C23 (d)	+	+	+	+	+	+	+	+	+
Tetracyclic terpanes									
C24 (e)	+	+	+	+	+	+	+	+	+
Pentacyclic triterpanes or hopanes									
18 α (H)-22,29,30-trisnorhopane (Ts) (f)	+	+	+	+	+	+	+	+	+
Hopene (g)									
17 α (H)-22,29,30-trisnorhopane (Tm) (h)	+	+	+	+	+	+	+	+	+
17 α (H),21 β (H)-30-norhopane (i)	+	+	+	+	+	+	+	+	+
lupine (j)									
17 α (H),21 β (H)-hopane (l)	+	+	+	+	+	+	+	+	+
17 β (H),21 α (H)-hopane (m)	+	+	+	+	+	+	+	+	+
17 α (H),21 β (H)-30-homohopane(22S) (n)	+	+	+	+	+	+	+	+	+
17 α (H),21 β (H)-30-homohopane(22R) (o)	+	+	+	+	+	+	+	+	+
17 β (H),21 β (H)-hopane (p)	+	+	+	+	+	+	+	+	+
17 α (H),21 β (H)-30,31-bishomohopane(22S) (q)	+	+	+	+	+	+	+	+	+
17 α (H),21 β (H)-30,31-bishomohopane(22R) (r)	+	+	+	+	+	+	+	+	+
17 α (H),21 β (H)-30,31,32-trishomohopane(22S) (s)	+	+	+	+	+	+	+	+	+
17 α (H),21 β (H)-30,31,32-trishomohopane(22R) (t)	+	+	+	+	+	+	+	+	+
17 α (H),21 β (H)-30,31,32,33-tetrakishomohopane(22S) (u)	+	+	+	+	+	+	+	+	+
17 α (H),21 β (H)-30,31,32,33-tetrakishomohopane(22R) (v)	+	+	+	+	+	+	+	+	+
17 α (H),21 β (H)-30,31,32,33,34-pentakishomohopane(22S) (w)	+	+	+	+	+	+	+	+	+
17 α (H),21 β (H)-30,31,32,33,34-pentakishomohopane(22R) (x)	+	+	+	+	+	+	+	+	+
Steranes									
Diasteranes: (1), (2), (3) and (4)									
C27 5 α (H),14 α (H),17 α (H)-cholestane(20S) (5)	+	+	+	+	+	+	+	+	+
C 27 5 α (H),14 β (H),17 β (H)-cholestane(20R) (6)	+	+	+	+	+	+	+	+	+
C27 5 α (H),14 β (H),17 β (H)-cholestane(20S) (7)	+	+	+	+	+	+	+	+	+
C27 5 α (H),14 α (H),17 α (H)-cholestane(20R) (8)	+	+	+	+	+	+	+	+	+
C28 5 α (H),14 α (H),17 α (H)-ergostane(20S) (9)	+	+	+	+	+	+	+	+	+
C28 5 α (H),14 β (H),17 β (H)-ergostane(20R) (10)	+	+	+	+	+	+	+	+	+
C28 5 α (H),14 β (H),17 β (H)-ergostane(20S) (11)	+	+	+	+	+	+	+	+	+
C28 5 α (H),14 α (H),17 α (H)-ergostane(20R) (12)	+	+	+	+	+	+	+	+	+
C29 5 α (H),14 α (H),17 α (H)-stigmastane(20S) (13)	+	+	+	+	+	+	+	+	+
C29 5 α (H),14 β (H),17 β (H)-stigmastane(20R) (14)	+	+	+	+	+	+	+	+	+
C29 5 α (H),14 β (H),17 β (H)-stigmastane(20S) (15)	+	+	+	+	+	+	+	+	+
C29 5 α (H),14 α (H),17 α (H)-stigmastane(20R) (16)	+	+	+	+	+	+	+	+	+
C30-steranes: (17), (18), (19) and (20)	+	+	+	+	+	+	+	+	+

+ present

Table 7: Hopane and sterane biomarkers ratios

	I	II	III	IV	V	VI	VII	VIII	IX
Ts/(Ts + Tm)	0.43	0.48	0.51	0.44	0.44	0.46	0.39	0.40	0.57
C31 22S/(22S+22R)	0.57	0.59	0.59	0.58	0.58	0.58	0.59	0.60	0.60
C27/C29	0.41	0.62	0.48	0.89	0.40	0.68	0.39	0.74	0.44
C29 20S/(20S+20R)	0.51	0.54	0.51	0.50	0.55	0.53	0.54	0.51	0.52

The biological configurations of 22R C31-C35 hopanes and 20R C27-C29 steranes decrease in favor of their thermodynamically more stable epimers, 22S and 20S respectively which reach a known equilibrium point that is used as a measure of organic matter maturation (Wang *et al.*, 2011). This equilibrium point are varied for the hopane 22S/(22S+22R) and sterane 20S/(20S+20R) ratios where reach the equilibrium of 0.57-0.62 and 0.52-0.55 respectively during early oil generation and low

thermal maturity. This ratios show only minor variations among the analyzed sediments. The hopane C31 22S/(22S+22R) ratio varies from 0.57-0.60 and the sterane C29 20S/(20S+20R) ratio ranges from 0.50-0.55 (Table 7), which confirm the presence of mature petroleum in the sediments.

The lupine is thermodynamically more stable configuration isomer which suggests the lubricating oil input in sediments (Gao *et al.*, 2007) (Fig. 7 and Table 6).

Conclusion

This investigation provided useful information on the geochemical parameters and hydrocarbons contamination of Shatt Al-Arab River, which is an important economic area in southern Iraq due to activities related to the port, fishing, agriculture, industry and tourism. The OM in surface sediments is derived from the aquatic and terrestrial sources. The stations I, III, V reflect the short time degradation of OM than stations II, IV, VI, VII and VIII. The n-alkanes with total concentrations of 0.08-42.58 $\mu\text{g g}^{-1}$ dw and carbon numbers from C11-C34 are identified. In comparison with other sites, the n-alkanes concentrations fall within the range of areas considered to be mildly polluted. Two main sources of n-alkanes in the sediments are detected, the petrogenic sources from shipping and harbors activities and urban wastes from nearby river-borne communities and the biogenic sources associated with living organisms. This is supported by the UCM, n-alkanes ratios and biomarkers and PCA. The recent results can be used as baseline information for future source studies of n-alkanes and can promote the management of river environment. Long-time monitoring of hydrocarbons contamination in studied river is needed with the rapid economic development in Iraq.

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Ethics

This article is original and contains information and results that have not been previously researched and published for the study area.

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