Journal of Basrah Researches (Sciences) **48**(2), 1 (2022)
DOI: https://doi.org/10.56714/bjrs.48.2.1

Presence and distribution of N - alkanes in the waters of some areas of the Shatt Al-Arab River, southern Iraq

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ARTICLE INFO

Received 02 November 2021
Accepted 06 February 2022
Published 30 December 2022

Keywords:

N – alkanes, Water, Shatt Al-Arab
Diagnostic evidence for hydrocarbons,
Seasonal variation.

Citation: M.F. Albidhani et al., J. Basrah Res. (Sci.) **48**(2), 1 (2022). DOI: https://doi.org/10.56714/bjrs.48.2.1

ABSTRACT

The study dealt with (4) stations distributed along the Shatt Al-Arab, namely Al-Mashab, Al-Ashar, Abu Al-Khasib and Al-Faw. Samples were collected monthly over a whole year, starting from January 2012 until December of the same year to estimate and diagnose the n - alkanes in them using Gas Chromatography (GC) . The highest recorded concentrations were (154.92 , 167.34 , 104.56 , 191.00) µg/l in the stations (Al - Mshab , Al - Ashar , Abu Al - Khasib and Al - Faw) respectively during the month of December . The lowest recorded concentrations were (4.79, 5.46, 3.34, 5.00) µg/l in the same stations, respectively. In terms of seasonal changes, the results showed that the highest rate of normal alkanes was recorded during the winter months and the lowest during the summer months. As for the results of the evidence of the Carbon Preference Index (CPI)and the ratio of Pr/Ph compounds (Pristan / Phytan) it was more than one in some months and less than one in other months, which indicates the common sources of hydrocarbons in the water.

1. Introduction

We The increasing dependence of different countries in their economy on oil and its derivatives has led to the expansion of exploration and extraction operations. As a result of these operations, from drilling wells, transporting, refining, storing and distributing, the circle of oil pollution expanded, in addition to human activities harmful to the environment, accidents, and weak environmental control, all of these reasons led to pumping huge quantities From oil pollutants to the environment [1] Iraq is one of the largest producers and exporters of crude oil in the world, and most of the production and export of oil is from Basrah Governorate[2] . Crude oil includes a very large group of hydrocarbons. It consists of a complex mixture of aliphatic hydrocarbons (alkanes), aromatic (aromatics) and heterocyclic hydrocarbons [3] and a large part of them are widely used in transportation, heating and industry, which leads to their release into the environment as pollutants. Through long-term leakage, accidental spills, or operational failure [4] Pollution with crude oil or one of its products is one of the most dangerous types of environmental pollution that spreads in oil-producing countries due to oil exploration, extraction and refining operations, which caused great destruction in the environment of these countries [5].

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ISSN: 1817-2695 (Print); 2411-524X (Online)
Online at: https://bjrs.uobasrah.edu.iq

The most important components of hydrocarbons in water are ordinary alkanes [6], which may come mainly from petroleum hydrocarbons and their products [7], or from biological sources such as terrestrial plants, phytoplankton and marine bacteria, in addition to genetic transformation of biological precursors, which also contributes to the presence of ordinary alkanes [8]. It is usually considered a classic indicator of organic geochemistry to distinguish between the biological and geological origin of petroleum pollutants [9] by using several indicators to identify the sources of common alkanes, such as CPI, ratio (Pr/Ph), Pr/C17, pH/C18, mixture Heterogeneous compound (UCM) and low molecular weight to high molecular weight (LMW/HMW) [10-12]. And because the Shatt al-Arab is the only source of fresh water in Basrah Governorate, as it depends on it in many daily vital activities, it suffers, like the rest of the world’s rivers, from pollution resulting from the dumping of industrial, agricultural and domestic waste, in addition to oil waste [13] and that what is happening in the Shatt al-Arab region is that some Small ships and tugboats that are present most of the time in this area empty their waste oils into the Shatt al-Arab waters, which leads to an increase in the problem of oil pollution [14]. Therefore, the current study aimed to diagnose the usual alkanes in selected areas of the Shatt al-Arab and to know the sources of these alkanes. Whether it is natural or caused by pollution.

2 . Materials and methods :

2.1. Study area:

The first site is located in Al-Mashab, which is a populated area where agriculture, livestock and fishing are practiced. It is characterized by shallow depths compared to other areas and by its dense aquatic plants . The second site is located in the Al-Ashar area, and the waters of this area are affected, in addition to the activity of the boats that dump their waste, including oil pollutants, in large quantities . It is also affected by the drainage of internal rivers, such as the Khandaq and Al-Khora rivers, especially those that are thrown directly into the river. The third site is located in the district of Abu al-Khasib near the port of Abu Flus, in which the movement of ships and boats for various purposes is active , this station is characterized as a deep water area and represents a waterway for merchant ships entering the Shatt al-Arab towards a port The fourth site is located in the Al-Faw area at the end of the Shatt Al-Arab, and is affected by marine waters during the tidal period and river waters during the low period. The depth of the river is about 14-12 m, and the movement of many boats is active in the fishing process. Table 1.

Table 1. Study areas and their coordinates.

NO.	Name of the site		
		N	E
Site 1	Al-Mashab,	:30° 38 33.4	47° 41 22.4
Site 2	Al-Ashar	30° 31 08.7	47° 50 44.5
Site 3	Abu al-Khasib	30° 27 47.5	48° 00 12.8
Site 4	Al-Faw	29° 58 40.2	48° 29 12.6

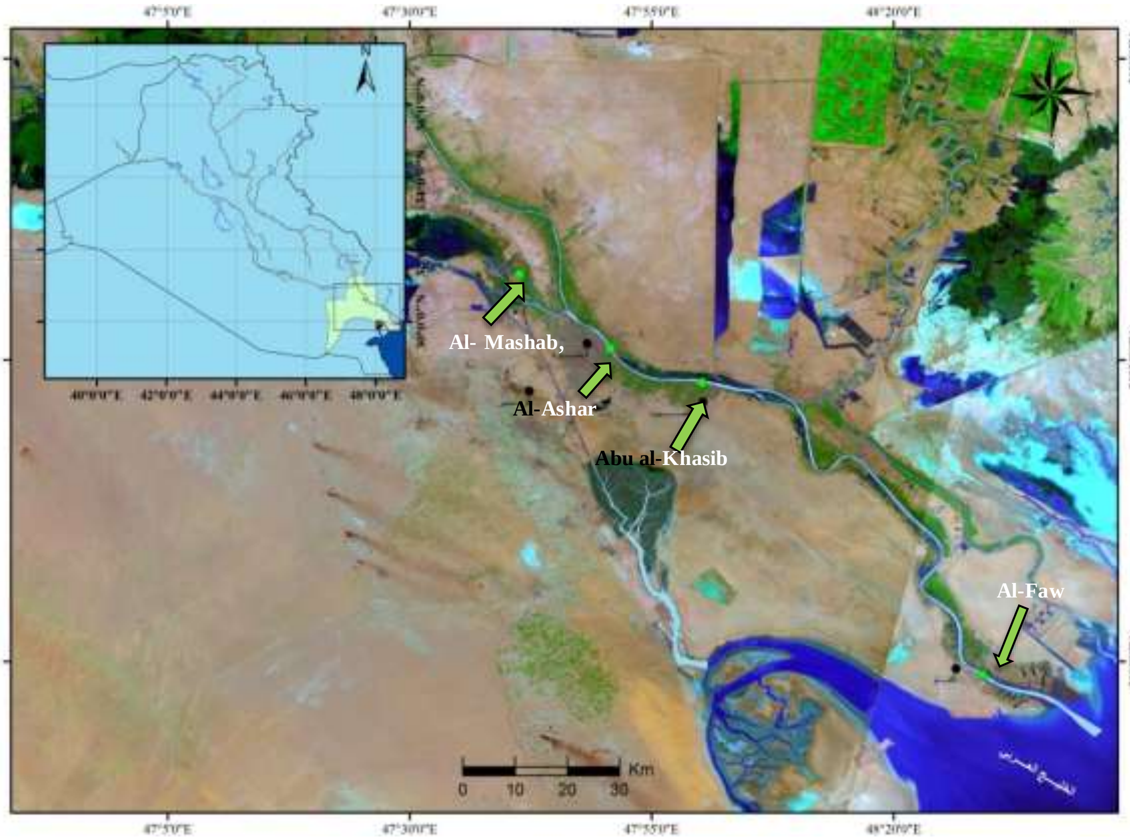

Image 1. A satellite image of the Landsat (8) satellite in 2013 showing the study stations

2.2. working methods

2.2.1. Sample collection

Water samples for hydrocarbons were collected monthly for the period from January 2012 to December 2012 from the study sites by using opaque glass bottles with a capacity of 4 liters and at a depth of 1 meter and they were field-fixed using carbon tetrachloride.

2.2.2. Extraction of hydrocarbons in water

The method approved by the United Nations Environmental Protection Program [15] was used to extract petroleum hydrocarbons from water samples. The concentrations of total petroleum hydrocarbons were measured after dissolving them with pure hexane using a Japanese-made Shimadzu RF 540 Spectrofluorometer, where the emission intensity was measured at a wavelength of 360. nanometer and excitation at a wavelength of 310 nanometers.

Then the total hydrocarbons were separated into aliphatic and aromatic compounds [15]. Then, the concentrations of aliphatic compounds were measured by a gas chromatography device in the Nahran Omar laboratories of the South Oil Company. The device is model 6890n, manufactured by the American company Agilent. It used a column of separation for aliphatic vehicles type J&W 123-1015 DB-1, length 15 m, diameter 320 µm, maximum temperature 280 ° C, and detector temperature 300 ° C. He used helium as a carrier gas, with a flow rate of 45 ml / min, and the temperature was The primary time is 60°C, the initial time is 5 minutes, the final temperature is 280°C, and the final time is 200 minutes.

2.2.3. Statistical analysis

The Package for Social Science (SPSS-19) program (ONE WAYANOVA test) was adopted in the statistical analysis of the results of this study under the level of significance $P>0.05$ and the Revised Least Significant Difference (LSD) test [16] .

3. Results and discussion :

Alkanes are an important part of petroleum hydrocarbons, and it was noted from the results of the current study that they are present in high and varying concentrations between the seasons in the studied sites. The highest concentrations were recorded during the autumn and winter months in the sites of Al-Mashab, Al-Ashar, Abu Al-Khasib and Al-Faw, where (see Tables 2, 3, 4 and 5) showed the highest Concentrations of total alkanes at these sites in December were (191.00, 104.56, 167.34, 154.92) µg/L, respectively. Perhaps the reason is due to the low temperatures in winter̋, which reduces the evaporation process and thus reduces the effectiveness of microorganisms in cracking hydrocarbon compounds [17], in addition to what precipitation from the air adds from hydrocarbon compounds, as the winter season witnesses more use of fuel for heating in homes, which increases concentrations Hydrocarbons in the Atmosphere[18]

Seasonal changes of the total aliphatic compounds showed that there are clear changes with the seasons. We find that the highest concentrations appeared in the winter season in Al-Mashab, Al-Ashar and Abu Al-Khasib stations, reaching 56.57, 59.50 and 43.80 µg/l, respectively, and in the Faw station, the highest concentration was in the autumn season. Recorded 73.95 µg/L and this may be due to local activities and environmental changes that lead to changes in the levels of normal alkanes [19], in addition to the use of boats for transportation and fishing, and what they add from the exhausts of their engines oils to that environment [20], while the lowest concentrations were recorded in the season The spring in the four sites, Al-Mashab, Al-Ashar, Abu Al-Khasib and Al-Faw, where it reached 6.43, 9.69, 9.08 and 8.49 µg/L, respectively (Fig.1, 2, 3 and 4), respectively. In general, the decrease in concentrations at all sites may be due to the effects of extreme weathering [21]. In addition to the processes of dissolution, chemical and optical oxidation and taking up by zooplankton or biodegradation [22]. Normally, lower molecular weight alkanes (C10 - C22) degrade faster than higher molecular weight compounds [23]. The mitigating factor may also have an important role in the lack of concentrations in the spring due to rainfall.

The presence of carbon compounds with odd numbers is due to the source of algae and phytoplankton, where many researchers indicated that the source of the compounds C15, C17 and C19 in the aquatic environment is phytoplankton and algae[24, 25] , and the study did not show the predominance of any of the carbon-numbered alkanes compounds As for alkanes with even numbers of carbon, compounds (C18, C20, and C22) were dominant, which may be sourced from zooplankton [26] , while Volkman et al. [27] indicated that diatoms in pure cultures produce alkanes compounds with the predominance of C18 and C20 compounds within Short and medium chains. As for the values of the carbon preference index (CPI), which is the ratio of odd to even carbon compounds, the results showed that it was less than one in the Al-Mashab site throughout the study period, which indicates the human source of hydrocarbons in that site [6]. As for the ratio of the two compounds, Alborstan to Vitan, was all below one except for one. In February and March, it was more than one, and this indicates the vital source of hydrocarbons. In the sites of Al-Ashar and Abu Al-Khasib, the values of the CPI and the ratio of Pristan to Phytan referred to the common sources of hydrocarbons, as some values are greater than the number (1) and others are smaller than the number (1) [28, 29] In the Faw site, the CPI values and the ratio of Pristan to Phytan were less than one, except in the months of May and June, which were higher than one, which indicates the common sources of hydrocarbons.

Table 2. N - alkanes (µg/L) in water for Al-Mashab site

aliphatic compounds	January	February	March	April	May	June	July	August	September	October	November	December	SD
C8	–	–	–	–	–	–	–	–	.21	–	–	.15	.85
C9	–	–	–	–	–	–	1.28	.49	1.84	1.96	2.30	1.37	.91
C10	–	–	–	–	–	–	–	–	–	–	–	–	
C11	–	–	–	–	–	–	–	–	1.36	.35	.59		.20
C12	–	–	–	–	–	–	.33	–	–	.39	.47	.33	.19
C13	–	–	–	–	–	–	.51	–	1.57	.62	.79	.45	.31
C14	–	–	–	–	–	–	.34	–	.38	.39	.52	.29	.20
C15	.37	.35	–	–	.93	–	1.43	–	.64	.51	.59	.93	.24
C16	.66	3.21	2.44	1.67	1.55	1.34	1.02	1.03	1.02	1.47	4.52	1.33	1.35
C17	.39	2.63	2.06	1.50	1.96	1.88	2.72	.99	2.50	1.87	4.86	2.77	1.46
Pristan	.83	.80	.91	.61	.03	.50	.18	1.65	.16	.81	.67	.28	.20
C18	1.23	1.98	.83	1.04	.67	1.03	11.21	4.54	9.93	11.64	16.98	12.30	6.39
Phytan	.54	.12	.42	.50	.27	.41	.80	.26	.59	.62	1.14	.50	.27
C19	–	–	–	–	–	–	2.91	.40	2.96	1.75	2.59	2.73	1.03
C20	.77	.92	.71	.65	.55	.78	4.75	1.75	3.13	5.24	12.57	6.21	3.60
C21	–	–	–	–	–	–	2.73	.22	3.41	.40	1.10	2.90	.82
C22	–	–	–	–	–	–	6.22	1.46	2.65	4.58	8.12	8.91	3.43
C23	–	–	–	–	–	–	3.82	.69	2.80	.97	2.50	4.82	1.59
C24	–	–	–	–	–	–	7.51	–	2.12	1.52	6.17	12.47	4.10
C25	–	–	–	–	–	–	16.20	–	–	–	5.46	25.93	8.37
C26	–	–	–	–	–	–	5.99	–	–	–	–	34.30	10.54
C27	–	–	–	–	–	–	13.51	–	–	–	–	35.94	10.72
total	4.79	10.00	7.37	5.97	5.96	5.95	83.47	13.48	37.60	35.07	71.94	154.92	48.32
odd	.76	2.98	2.06	1.50	2.89	1.88	45.11	2.79	17.08	8.42	20.78	77.84	
even	2.66	6.11	3.98	3.36	2.77	3.15	37.37	8.78	19.77	25.22	49.35	76.30	
CPI	.29	.49	.52	.45	1.04	.60	1.21	.32	.86	.33	.42	1.02	
pri/phy	1.55	6.67	2.16	1.23	.10	1.21	.23	6.34	.26	1.32	.59	.57	
RLSD	monthes		5.81										

(-) not detected

Table 3. N - alkanes (µg/L) in water for Al - Ashar site

aliphatic compounds	**January**	**February**	**March**	**April**	**May**	**June**	**July**	**August**	**September**	**October**	**November**	**Decemb er**	**SD**
C8	–	–	–	–	–	–	–	3.05	2.72		2.83		1.30
C9	.36	.36	–	.25	–	.26	–	2.00	2.73	1.67	2.19	2.57	1.10
C10	–	–	–	–	–	–	–	–	–	–	–	–	
C11	–	–	–	–	–	–	–	.58	.62	1.56	.75	.65	.33
C12	–	–	–	–	–	–	–	.50	.63	.35	.47	.56	.27
C13	–	–	–	–	–	–	–	.77	1.14	1.61	.76	.88	.44
C14	–	–	–	–	–	–	–	.32	.94	.42	.49	.49	.31
C15	–	–	–	–	–	–	–	.71	1.02	1.56	.60	.66	.38
C16	1.88	1.88	.70	2.53	1.13	.82	1.56	2.80	1.20	5.02	2.14	1.60	1.14
C17	.75	.75	2.71	4.91	5.50	3.24	4.91	3.60	2.27	5.03	4.81	2.97	1.64
Pristan	.44	.19	.09	.08	.53	.12	.08	1.86	1.28	.90	2.31	.35	.44
C18	1.54	1.54	1.02	1.61	2.70	1.78	1.64	16.12	10.79	15.91	16.05	11.80	6.61
Phytan	.11	.11	.47	.84	1.22	.82	.10	1.05	.76	1.21	1.91	.75	.54
C19	.16	.16	.17	.18		.17	.16	3.22	2.74	3.65	3.15	2.19	1.53
C20	.46	.46	.72	.44	1.30	.53	1.15	5.35	4.57	4.73	19.66	5.72	5.44
C21	–	–	–	–	–	–	–	.41	.80	.61	3.92	2.01	1.19
C22	–	–	–	–	–	–	–	3.62	4.51	5.22	13.40	10.43	4.61
C23	–	–	–	–	–	–	–	1.20	1.09	2.48	2.48	6.12	1.85
C24	–	–	–	–	–	–	–	3.12	1.45	4.89	–	14.20	4.16
C25	–	–	–	–	–	–	–	–	–	7.69	–	30.04	8.76
C26	–	–	–	–	–	–	–	–	–	.00	–	37.25	10.75
C27	–	–	–	–	–	–	–	–	–	12.77	–	36.12	10.74
total	5.71	5.46	5.87	10.83	12.38	7.74	9.59	50.28	41.26	78.27	77.93	167.34	48.61
odd	1.27	1.27	2.88	5.33	5.50	3.68	5.07	12.49	12.41	39.64	18.67	84.21	
even	3.89	3.89	2.43	4.59	5.13	3.12	4.35	34.88	26.81	36.53	55.04	82.03	
CPI	.33	.33	1.18	1.16	1.07	1.18	1.17	.36	.46	1.09	.34	1.03	
pri/phy	4.05	1.76	.19	.09	.44	.15	.84	1.77	1.70	.74	1.21	.46	
RLSD	monthes		5.94										

(-) not detected

Table 4. N - alkanes (µg/L) in water for Abu Al-Khasib site

aliphatic compounds	January	February	March	April	May	June	July	August	September	October	November	December	SD
C8	–	–	–	–	–	–	–	–	–	–	–	–	
C9	.24	–	–	.25	–	–	.66	1.33	1.00	2.42	1.21	1.99	.86
C10	–	–	–	–	–	–	–	–	.37	–	–	–	.11
C11	–	–	–	–	–	–	.38	.76	–	.61	–	.39	.28
C12	–	–	–	–	–	–	–	–	–	.53	–	.41	.18
C13	.37	–	–	–	–	–	.23	.46	–	.84	.53	.73	.33
C14	–	–	–	–	–	–	.15	.30	–	.61	–	.42	.21
C15	–	–	–	–	–	–	.22	.43	.62	.98	.42	.65	.35
C16	–	1.06	.99	.81	.93	.68	.59	.49	1.45	1.88	1.16	1.66	.69
C17	.26	2.78	2.60	2.90	2.41	1.72	1.41	1.09	2.17	3.16	1.57	2.96	1.28
Pristan	.38	.40	.23	.08	.45	.26	.21	.61	.91	.64	.93	.63	.22
C18	1.13	.99	1.01	1.31	1.04	.59	3.23	5.88	13.45	13.26	7.58	12.14	5.45
Phytan	.13	.42	.47	.45	.51	.28	.32	.35	.71	.58	.66	.81	.29
C19	–	17.03	8.51	–	–	1.75	.49	.97	2.18	2.06	1.46	4.39	4.82
C20	.81	.82	.78	.75	.73	.55	1.40	2.25	5.02	4.57	9.71	5.88	3.05
C21	–	–	–	–	–	–	–	–	.35	2.01	.82	2.22	.82
C22	–	–	–	–	–	–	1.38	2.76	3.60	3.73	7.53	7.92	3.01
C23	–	–	–	–	–	–	–	–	1.02	1.95	1.44	7.28	2.10
C24	–	–	–	–	–	–	–	–	3.26	4.30	4.10	17.50	5.06
C25	–	–	–	–	–	–	–	–	–	3.57	–	36.58	10.52
C26	–	–	–	–	–	–	–	–	–	–	–	–	
C27	–	–	–	–	–	–	–	–	–	–	–	–	
total	3.34	23.50	14.59	6.56	6.08	5.84	10.67	17.69	36.12	47.72	39.11	104.56	30.42
odd	.88	19.81	11.11	3.15	2.41	3.47	3.38	5.05	7.34	17.61	7.45	57.18	
even	1.95	2.86	2.78	2.88	2.70	1.83	6.75	11.68	27.16	28.89	30.07	45.93	
CPI	.45	6.92	4.00	1.10	.89	1.90	.50	.43	.27	.61	.25	1.24	
pri/phy	2.98	.95	.49	.17	.88	.92	.66	1.74	1.28	1.10	1.41	.78	
RLSD	monthes												

(-) not detected

Table 5. N - alkanes (µg/L) in water for Abu Al-Faw site

aliphatic compounds	January	February	March	April	May	June	July	August	September	October	November	December	SD
C8	–	–	–	–	–	–	–	–	–	–	–	–	
C9	1.43	.71	–	.27	–	–	1.24	2.47	2.23	2.14	1.82	2.23	1.08
C10	–	–	–	–	–	–	–	–	–	–	–	–	
C11	–	–	–	–	–	–	.23	.47	.47	2.40	–	.49	.24
C12	–	–	–	–	–	–	.24	.47	.46	.39	.36	.49	.23
C13	–	–	–	–	–	–	.36	.72	.79	1.68	.59	.79	.38
C14	–	–	–	–	–	–	.26	.52	.39	.44	.40	.55	.24
C15	–	–	–	–	–	–	.26	.53	.55	1.56	.64	.58	.30
C16	–	.37	.75	3.20	1.31	–	.46	.92	1.34	1.14	7.38	2.23	2.09
C17	1.35	1.57	1.78	2.62	4.35	2.53	2.12	1.71	2.61	3.28	7.50	3.54	2.20
Pristan	.15	.14	.14	.66	.40	.60	.83	.71	.23	.32	2.04	1.50	.51
C18	1.19	1.08	.96	3.34	1.47	.87	7.19	13.52	14.53	11.32	23.47	15.31	8.13
Phytan	.58	.59	.60	.45	.59	.48	.58	.69	.77	.73	1.70	.83	.97
C19	–	–	–	.21	–	0.03	1.03	2.04	2.54	3.68	7.58	2.63	2.48
C20	.86	.82	.77	.63	.97	53.08	29.28	5.48	6.27	5.13	28.59	7.20	72.02
C21	–	–	–	–	–	0.40	.34	.28	.77	2.43	3.85	2.03	1.42
C22	–	–	–	–	–	–	1.78	3.57	6.73	3.84	9.03	8.99	3.82
C23	–	–	–	–	–	–	–	–	2.85	3.59	2.56	6.27	2.33
C24	–	–	–	–	–	–	–	–	6.62	4.42	8.82	16.14	6.09
C25	–	–	–	–	–	–	–	–	6.13	5.90	4.74	33.82	12.74
C26	–	–	–	–	–	–	–	–	7.61	–	–	45.86	21.96
C27	–	–	–	–	–	–	–	–	–	–	–	40.52	23.39
total	5.56	5.38	5.00	11.39	9.09	57.98	46.22	34.10	63.89	54.37	111.07	191.00	83.60
odd	2.78	2.28	1.78	3.11	4.35	2.96	5.59	8.22	18.94	26.66	29.28	92.90	
even	2.05	2.27	2.48	7.18	3.75	53.94	39.21	24.48	43.95	26.66	78.04	96.77	
CPI	1.35	1.00	.72	.43	1.16	.05	.14	.34	.43	1.00	.38	.96	
pri/phy	.26	.25	.23	1.46	.67	1.26	1.42	1.03	.30	.43	1.20	1.82	
RLSD	monthes		5.81										

(-) not detected

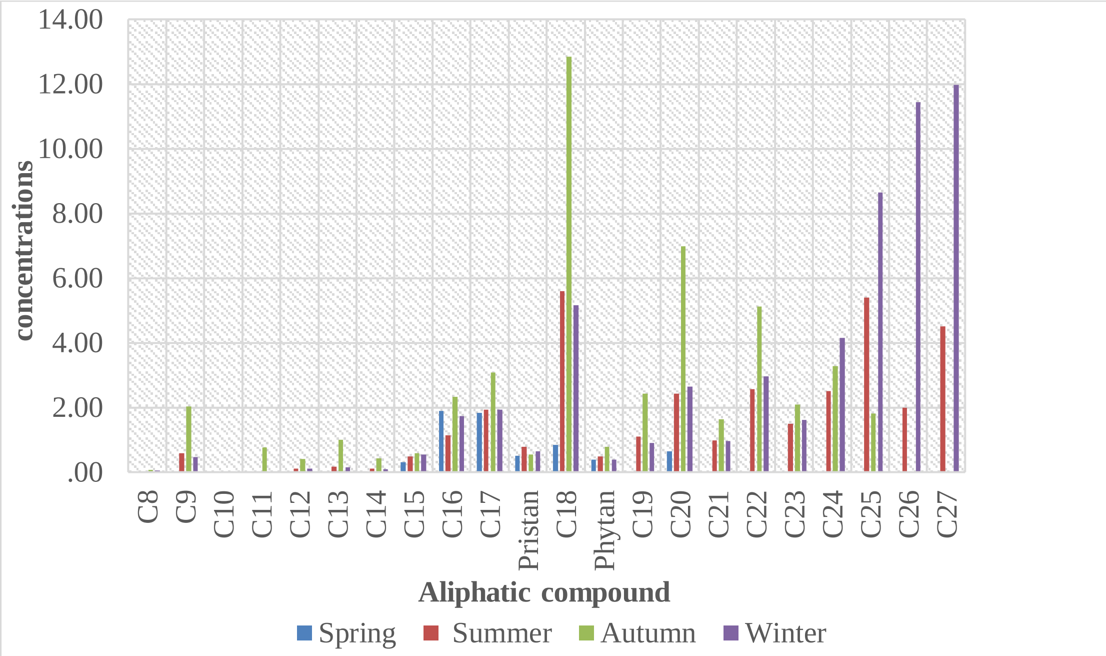

Fig. 1. N - alkanes (μg/L) in water for Al-Mashab site

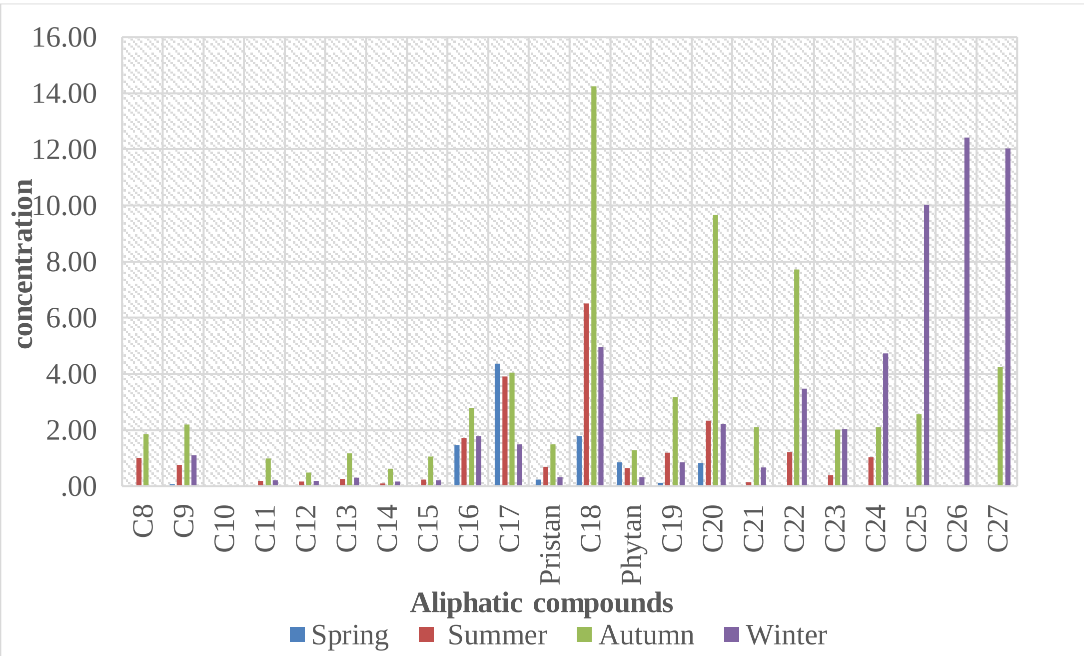

Fig. 2. N - alkanes (μg/L) in water for Al- Ashar site

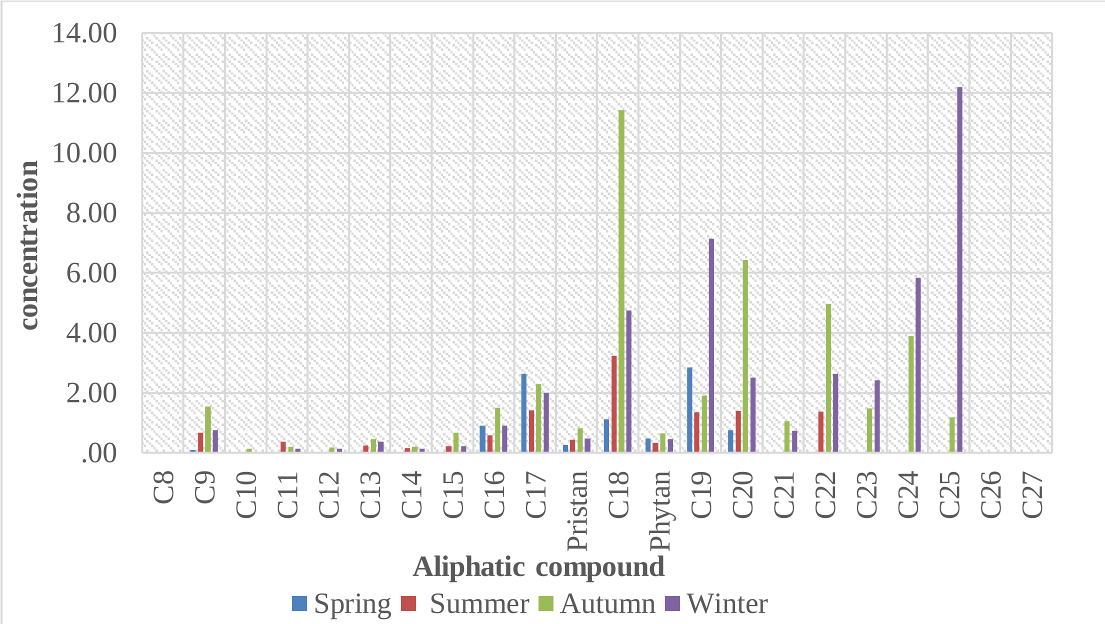

Fig. 3. N - alkanes (µg/L) in water for Abu Al-Khasib site

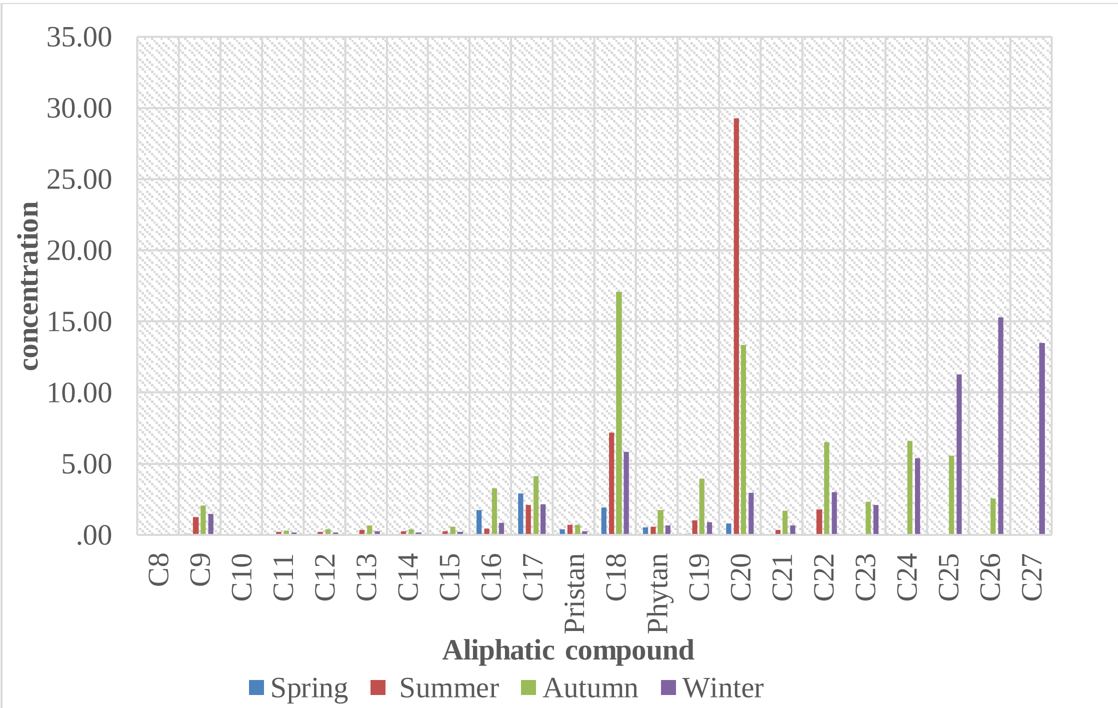

Fig. 4. N - alkanes (µg/L) in water for Abu Al-Faw site

3. Conclusions

The high concentrations of total alkanes were found mostly during the winter and autumn months, while the low concentrations were in the summer and spring, and the dominance of any of the compounds was not observed for either the odd number of carbon atoms or the even number. According to the results of the indicators of carbon preference index values (CPI) and the ratio of pristan to phytans, it was found that the sources of hydrocarbons in Shatt al-Arab waters are shared between biogenic from organisms, including algae, and anthropogenic sources of oil and industrial pollutants

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Journal of Basrah Researches (Sciences) **48**(2), 1 (2022)
DOI: https://doi.org/10.56714/bjrs.48.2.1

تواجد وتوزيع واصل الالكانات الاعتيادية في المياه لبعض مناطق نهر شط العرب ، جنوب العراق

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معلومات البحث

الاستلام	02 تشرين الثاني 2021
القبول	06 شباط 2022
النشر	30 كانون الاول 2022

الكلمات المفتاحية

الالكانات الاعتيادية، المياه، شط العرب ادلة تشخيص الهيدروكاربونات، التباين الفصلي.

Citation: M.F. Albidhani et al., J. Basrah Res. (Sci.) **48**(2), 1 (2022). DOI: https://doi.org/10.56714/bjrs.48.2.1

الملخص

تناولت الدراسة اربع مواقع توزعت على طول شط العرب وهي المسحب والعشار وابو الخصيب والفاو حيث جمعت العينات شهرياً على مدى عام كامل ابتداءاً من شهر كانون الثاني 2012 ولغاية شهر كانون الأول من العام نفسه لتقدير وتشخيص الالكانات الاعتيادية فيها باستخدام جهاز Gas Chromatography (GC) فكانت اعلى التراكيز المسجلة هي (154.92 ، 167.34 ، 104.56 ، 191.00) مايكروغرام / لتر في محطات المسحب والعشار وابو الخصيب والفاوعلى التوالي خلال شهر كانون الاول ،اما اقل التراكيز المسجلة فكانت (4.79 ، 5.46 ، 3.34 ، 5.00) مايكروغرام / لتر في المحطات نفسها على التوالي . ومن ناحية التغيرات الفصلية اظهرت النتائج ان اعلى معدل للالكانات الاعتيادية سجلت خلال اشهر الشتاء وادناها خلال اشهر الصيف . اما نتائج االادلة (CPI Carbon Preference Index) ونسبة مركبات Pr/Ph (Pristan / Phytan) فكانت اكثر من واحد في بعض الاشهر واقل من واحد في اشهر اخرى مما يدل على المصادر المشتركة للمركبات الهيدروكاربونية في الماء .

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ISSN: 1817-2695 (Print); 2411-524X (Online)
Online at: https://bjrs.uobasrah.edu.iq