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# Alkanes in the sediments of Al-Gharraf River, Southern Iraq

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**Abstract:** The study aimed to determine the concentrations of alkanes compounds using a gas chromatograph with high-precision separation techniques. Samples were collected from four stations in the Al-Gharraf River in southern Iraq during 2018-2019. A seasonal variation was observed in the concentrations of alkanes, which is the highest in the winter. The total alkanes concentrations were the lowest at 0.079 µg/g at station 1 in summer. The highest total concentration of alkanes was in station 3 in winter reaching 2.215 µg/g. There was a dominance of individual carbon compounds of C17, C19, and C21 indicating the source of hydrocarbon from phytoplankton, plant, and bacteria. The presence of carbon compounds higher than C25 reveals that organic matter is derived from land and aquatic plants. The results also indicate that the source of petroleum hydrocarbons in the sediments of the Al-Garraf River is a common biogenic and anthropogenic based CPI index and the pri/phy guide that was less than 1 in the second and third stations for all seasons, and greater than 1 in the first and fourth stations.

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## Introduction

One of the important pollutants in the aquatic environment is petroleum hydrocarbons which affect their living organisms (NRC, 1985). Hydrocarbons enter the aquatic environments through several sources and aquatic organisms absorb them during their feeding; however, the quantity of oil compounds is scare in the aquatic systems (Cajeravelli et al., 1995). The regular alkanes with carbon numbers of C15, C17, and C19 are formed from marine biological sources e.g. phytoplankton; while alkanes with carbon numbers of C33 and C25 are composed of terrestrial vascular plants (Sakari et al., 2008). The presence of high-chain carbon compounds (C25-C30) indicates the presence of flowering plants.

The most individual alkane compound found in the sediments of the marshes is C17, which is produced by the sulfur bacterium of *Desulfovibrio desulforicans* .(AL-Saad and Ali-Timari, 1993) Chromatography is used for detecting the type of pollution and its source, whether it is biogenic or anthropogenic by measuring the carbon preference coefficient (CPI). CPI is the sum of the odd-numbered carbon compounds to the sum of the concentrations of the even-numbered carbon compounds; if it is greater than one, indicating that the origin of the pollution is biogenic and if less than one, indicates the anthropogenic origin of the pollution, and if its values are close to one shows the common origin (Canton and Grimalt, 1992). The other source of hydrocarbons is oil and its derivatives are made up of a mixture of organic compounds constituting 50-98% of the total oil composition, in addition to other elements such as sulfur, nitrogen, and oxygen (Leighton, 2000). Oil also contains some trace elements such as cadmium (Cd), vanadium (V), nickel (Ni), and cobalt (Co) (Albagies, 1989). Therefore, this study aimed to investigate the pollution of petroleum hydrocarbons in the Al-Garraf River, a tributary of the Tigris River.

## Materials and Methods

The Al-Gharraf River, a tributary of the Tigris River, is located in the southeastern part of Iraq, within the alluvial plain area before the Kut Dam (Ghazi, 2004).

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Table 1. Total sum and type of n-alkanes (mg/L) in the sediment of the AL-Gharraf River in summer.

| N-alkane | S1 | S 2 | S 3 | S 4 |
|---|---|---|---|---|
| C13 | 0.003 | 0.02 | 0.004 | 0.003 |
| C14 | 0.002 | 0.01 | 0.005 | 0.002 |
| C15 | 0.03 | 0.002 | 0.007 | 0.006 |
| C16 | 0.002 | 0.003 | 0.006 | 0.004 |
| C17 | 0.006 | 0.002 | 0.013 | 0.021 |
| C18 | 0.004 | 0.083 | 0.032 | 0.011 |
| C19 | 0.005 | 0.024 | 0.012 | 0.042 |
| C20 | 0.006 | 0.038 | 0.035 | 0.046 |
| C21 | 0.005 | 0.003 | 0.062 | 0.053 |
| C22 | 0.003 | 0.049 | 0.025 | 0.032 |
| C23 | 0.002 | 0.002 | 0.024 | 0.028 |
| C24 | 0.004 | 0.032 | 0.093 | 0.002 |
| C25 | 0.002 | 0.015 | 0.071 | 0.043 |
| C26 | 0.008 | 0.061 | 0.102 | 0.025 |
| C27 | 0.007 | 0.052 | 0.025 | 0.136 |
| C28 | 0.004 | 0.064 | 0.064 | 0.102 |
| C29 | 0.002 | 0.02 | 0.092 | 0.006 |
| C30 | 0.005 | 0.025 | 0.21 | 0.063 |
| C31 | 0.007 | 0.003 | 0.043 | 0.003 |
| C32 | 0.002 | 0.002 | 0.009 | 0.005 |
| C33 | 0.001 | 0.002 | 0.016 | 0.003 |
| C34 | 0.002 | 0.001 | 0.006 | 0.002 |
| Sum | 0.079 | 0.513 | 0.956 | 0.638 |
| Pristine | 0.005 | 0.072 | 0.008 | 0.01 |
| Phytine | 0.004 | 0.095 | 0.04 | 0.01 |
| Prstine/phytine | 1.25 | 0.757 | 0.2 | 1 |
| Even | 0.042 | 0.368 | 0.587 | 0.304 |
| Odd | 0.043 | 0.145 | 0. 369 | 0.494 |
| Odd/even | 1.023 | 0.394 | 0.628 | 1.625 |

Table 2. Total sum and type of n-alkanes (mg/L) in the sediment of the AL-Gharraf River in autumn.

| N-alkane | S1 | S 2 | S 3 | S 4 |
|---|---|---|---|---|
| C13 | 0.002 | 0.034 | 0.005 | N.D |
| C14 | 0.002 | 0.025 | 0.004 | N.D |
| C15 | 0.001 | 0.043 | 0.007 | 0.021 |
| C16 | 0.005 | 0.062 | 0.003 | 0.034 |
| C17 | 0.001 | 0.093 | 0.082 | 0.042 |
| C18 | 0.071 | 0.154 | 0.081 | 0.032 |
| C19 | 0.028 | 0.054 | 0.095 | 0.068 |
| C20 | 0.001 | 0.012 | 0.092 | 0.041 |
| C21 | 0.011 | 0.047 | 0.12 | 0.052 |
| C22 | 0.002 | 0.068 | 0.098 | 0.021 |
| C23 | 0.032 | 0.084 | 0.11 | 0.092 |
| C24 | 0.003 | 0.054 | 0.125 | 0.074 |
| C25 | 0.001 | 0.082 | 0.095 | 0.062 |
| C26 | 0.016 | 0.074 | 0.182 | 0.052 |
| C27 | 0.085 | 0.042 | 0.121 | 0.063 |
| C28 | 0.012 | 0.098 | 0.21 | 0.082 |
| C29 | 0.052 | 0.024 | 0.071 | 0.054 |
| C30 | 0.001 | 0.032 | 0.092 | 0.023 |
| C31 | 0.062 | 0.011 | 0.021 | 0.021 |
| C32 | 0.002 | 0.021 | 0.043 | 0.02 |
| C33 | 0.041 | 0.003 | 0.002 | N.D |
| C34 | 0.003 | 0.009 | 0.003 | N.D |
| sum | 0.434 | 1.126 | 1.662 | 0.854 |
| Pristan | 0.084 | 0.07 | 0.03 | 0.062 |
| Phytan | 0.06 | 0.12 | 0.051 | 0.054 |
| Pristine/phytan | 1.4 | 0.583 | 0.588 | 1.1481 |
| Even | 0.118 | 0.609 | 0.933 | 0.379 |
| Odd | 0.316 | 0.517 | 0.729 | 0.475 |
| Odd/even | 2.6 | 0.848 | 0.83 | 1.253 |

It flows towards the southwest between the Tigris and Euphrates, passing through the Al-Hayy, Qalaat Sukar, Al-figer, Al-Nasr, and Al-Shatra towns. Then it splits into two branches, one of them i.e. Shatt al-Bid'ah ends in the marshes leading to Marsh al-Hammar (Directorate of Water Resources, 2008).

Four stations were selected for sampling: the first station (32°08'29.4"N 46°02'38.3"E) in an area characterized by the presence of villages and agricultural lands on both sides that were wide with the high water level, the second station (31°41'21.6"N 46°06'53.9"E) was about 50 km far from the first station, after the river exiting Al-Figer district in about 4 km. The river in this area is characterized by the abundance of water plants and with a narrow width, as well as the presence of villages and agricultural lands, the third station (31°22'50.8"N 46°10'51.0"E) is located after the river exits the city of Shatrah, at a distance of 40 km from the second station. On both sides of the river in this station, there are villages and agricultural lands, with the narrow course less than in the first and second stations, with a decrease in the water level. The fourth station (31°09'55.0"N 46°36'36.6"E) was located at the Islah area near the entrance of the river into the marshes (72 km away from the third station) and characterized by the presence of agricultural land and high water level.

Sediment samples were collected from the four stations in four seasons using a Van veen grab and then kept in aluminum foil. Drying the sediment was done by freeze dryer and then they grind with a mechanical mortar and afterward sieved with a metal sieve with 63 µm diameter (Goutx and Saliot, 1982). A gas chromatography device (Hp-Hewlett Packard-5890, USA) was adopted to determine the concentrations of aliphatic hydrocarbons (alkanes) of the petroleum from sediments in the laboratories of the Marine Science Center, University of Basra. It is

Table 3. Total sum and type of n-alkanes (mg/L) in the sediment of the AL-Gharraf River in winter.

| N-alkane | S1 | S 2 | S 3 | S 4 |
|---|---|---|---|---|
| C13 | 0.002 | 0.004 | 0.004 | 0.008 |
| C14 | 0.003 | 0.005 | 0.002 | 0.009 |
| C15 | 0.023 | 0.007 | 0.074 | 0.019 |
| C16 | 0.018 | 0.006 | 0.002 | 0.063 |
| C17 | 0.082 | 0.002 | 0.102 | 0.232 |
| C18 | 0.096 | 0.003 | 0.126 | 0.181 |
| C19 | 0.092 | 0.012 | 0.075 | 0.173 |
| C20 | 0.082 | 0.027 | 0.097 | 0.123 |
| C21 | 0.065 | 0.042 | 0.041 | 0.176 |
| C22 | 0.043 | 0.052 | 0.095 | 0.092 |
| C23 | 0.086 | 0.026 | 0.086 | 0.163 |
| C24 | 0.094 | 0.092 | 0.178 | 0.102 |
| C25 | 0.092 | 0.071 | 0.093 | 0.103 |
| C26 | 0.043 | 0.182 | 0.162 | 0.098 |
| C27 | 0.096 | 0.178 | 0.086 | 0.146 |
| C28 | 0.085 | 0.043 | 0.198 | 0.088 |
| C29 | 0.0 89 | 0.064 | 0.093 | 0.096 |
| C30 | 0.083 | 0.143 | 0.173 | 0.073 |
| C31 | 0.032 | 0.013 | 0.063 | 0.022 |
| C32 | 0.021 | 0.001 | 0.172 | 0.01 |
| C33 | 0.032 | 0.112 | 0.021 | 0.003 |
| C34 | 0.021 | 0.002 | 0.031 | 0.006 |
| **sum** | 1.28 | 1.66 | 2.215 | 1.988 |
| Pristane | 0.046 | 0.012 | 0.062 | 0.062 |
| Phytane | 0.015 | 0.082 | 0.076 | 0.193 |
| pristane/phytane | 3.06 | 0.14 | 0.815 | 3.112 |
| Even | 0.589 | 0.55 | 1.236 | 0.839 |
| Odd | 1.091 | 0.531 | 0.738 | 1.138 |
| Odd/even | 1.85 | 0.96 | 0.597 | 1.356 |

Table 4. Total sum and type of n-alkanes (mg/L) in the sediment of the AL-Gharraf River in spring.

| N-alkane | S1 | S 2 | S 3 | S 4 |
|---|---|---|---|---|
| C13 | 0.002 | 0.004 | 0.004 | 0.008 |
| C14 | 0.003 | 0.005 | 0.002 | 0.009 |
| C15 | 0.023 | 0.007 | 0.074 | 0.019 |
| C16 | 0.018 | 0.006 | 0.002 | 0.063 |
| C17 | 0.082 | 0.002 | 0.102 | 0.232 |
| C18 | 0.096 | 0.003 | 0.126 | 0.181 |
| C19 | 0.092 | 0.012 | 0.075 | 0.173 |
| C20 | 0.082 | 0.027 | 0.097 | 0.123 |
| C21 | 0.065 | 0.042 | 0.041 | 0.176 |
| C22 | 0.043 | 0.052 | 0.095 | 0.092 |
| C23 | 0.086 | 0.026 | 0.086 | 0.163 |
| C24 | 0.094 | 0.092 | 0.178 | 0.102 |
| C25 | 0.092 | 0.071 | 0.093 | 0.103 |
| C26 | 0.043 | 0.182 | 0.162 | 0.098 |
| C27 | 0.096 | 0.178 | 0.086 | 0.146 |
| C28 | 0.085 | 0.043 | 0.198 | 0.088 |
| C29 | 0.0 89 | 0.064 | 0.093 | 0.096 |
| C30 | 0.083 | 0.143 | 0.173 | 0.073 |
| C31 | 0.032 | 0.013 | 0.063 | 0.022 |
| C32 | 0.021 | 0.001 | 0.172 | 0.01 |
| C33 | 0.032 | 0.112 | 0.021 | 0.003 |
| C34 | 0.021 | 0.002 | 0.031 | 0.006 |
| **sum** | 1.28 | 1.66 | 2.215 | 1.988 |
| Pristane | 0.046 | 0.012 | 0.062 | 0.062 |
| Phytane | 0.015 | 0.082 | 0.076 | 0.193 |
| pristane/phytane | 3.06 | 0.14 | 0.815 | 3.112 |
| Even | 0.589 | 0.55 | 1.236 | 0.839 |
| Odd | 1.091 | 0.531 | 0.738 | 1.138 |
| Odd/even | 1.85 | 0.96 | 0.597 | 1.356 |

equipped with a type Hp (3396A) Integrator with injection type of splitless. The type of separation shaft was capillary Column J+W DB5, with a diameter of 0.25 mm and a length of 30 meters.

## Results and Discussions

The total concentrations of total alkanes in the study stations ranged between 0.079 µg/g in the first station in summer and 2.215 µg/g in the third station in winter (Tables 1-4; Fig. 1). There were two types of regular alkanes, first with low molecular weights and others with high molecular weights, and their sources are multiple. Compounds with double carbon atoms such as C16, C18, and C20 indicates the presence of plant and animal plankton and bacteria (Volkmon, 1980) and the presence of carbon compounds more than C25 e.g. C31, C25, C27, and C29 evidence the organic matter is derived from land and aquatic plants (Simoneit, 1993). The results showed that the concentrations of total alkanes in the winter are higher than in summer in all stations since the high evaporation reduces alkanes as well as microorganisms break them into normal alkanes (Al-Saad, 1996). Microorganisms are less active and effective in winter (Douabul et al., 2012). Al-Imarah et al. (2006) studied the seasonal changes in the content of total petroleum hydrocarbons in the water and sediments of the southern Iraqi marshes showing the concentrations ranging 29.12-48.14 µg/g dry weight in its sediment samples and those of ranged 0.6-17.41 µg/L. The concentrations of hydrocarbons also were 0.012 µg/g dry weight in the sediments of Al-Baraka to 0.96 µg/g dry weight in the Al-Baghdadiya sediments (Nasir 2007) and it was also found that the concentrations of hydrocarbons in the water were lower than sediments.

The results indicate that most of the CPI values are

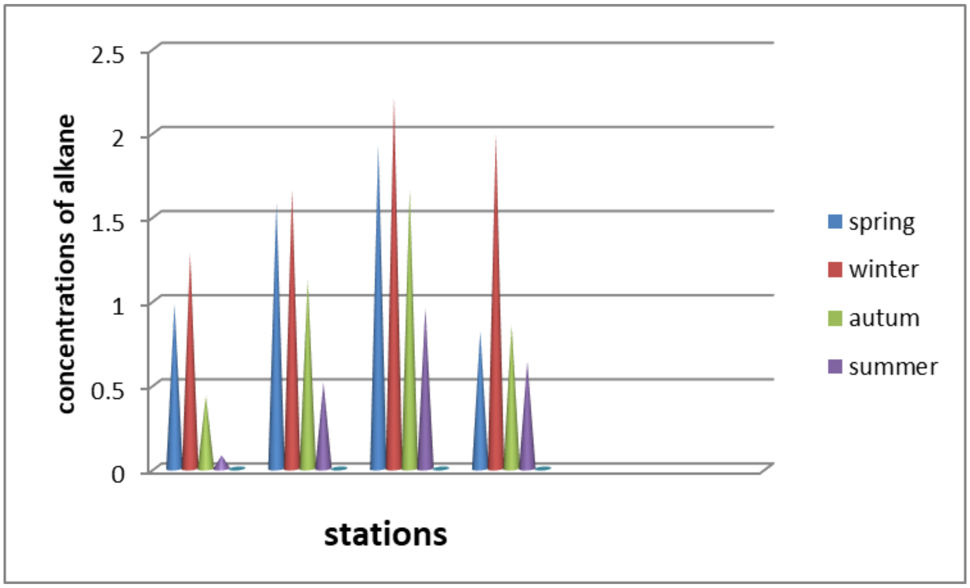


Figure 1. Seasonal variation of n-alkanes in the sediments of the Al-Gharaf River.

greater than 1 showing that the main source of the hydrocarbons in the sediments of the Al-Gharrrf River is biological, and there is little contribution from human sources with the values of CPI less than 1 in the second and third stations. These pollutants can originate from different sources, including household waste, untreated heavy waters, atmospheric deposits carrying hydrocarbon atoms, and vehicle exhaust. The results also indicated that the values of pri/phy are less than 1 in the second and third stations for all seasons and greater than one in the first and fourth stations indicating the source of hydrocarbons in the sediments of the Al-Gharraf River from anthropogenic origin.

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