N- Alkanes in the southern part of Al – Hammar marsh , southern Iraq

*Mariam F. Al-Bidhani[1] , Salah Mahdi Saleh[2] , Abdalhussein A. Khwedem[3] , Hamid T. Al-Saad[4]

1,2,3 Marine science centre, University of Basrah, Iraq.

4 College of Marine science, University of Basrah, Iraq.

Mariam.hameed2005@yahoo.com

Abstract

Marshes are one of the oldest natural water bodies in the Middle East located in southern Iraq, where Tigris and Euphrates rivers meet . It represent natural sources of many food stuff such as fish, agricultural materials and cows . Also, it consider a shelter for hundreds of migratory birds in winter. The present study includes the collection of water samples from different areas of Al – Hammar marsh to estimate the concentration of normal alkanes which were analyzed by using capillary Gas Chromatography (GC) technique . The concentrations of normal alkanes were (0.039 , 0.002 , 0.002 , 0.001) µg/l in (Lusan Harer, Almusahab, Alnakara and Alburka) respectively . In addition the study included evaluating the Carbon Preference Index (CPI) for the same areas which were (0.083 , 0.263 , 0.312 , 0.086) respectively, which indicate that the hydrocarbons in these areas were from anthropogenic origin.

Key wards : Water, Al Hammar marsh ,normal alkanes , GC.

Introduction :

Rapid urbanization and extensive industrial activity in recent decades have led to increased consumption of oil and its products worldwide(Abila, 2015, Liu *et al*., 2019, Lotfalipour *et al*., 2010, Zambrano-Monserrate *et al*., 2018). Large amounts of petroleum hydrocarbons have been released into estuaries and coastal areas during the production, transportation and processing of petroleum on land or at sea, which has an adverse effect on the health of aquatic environments and organisms(Bo *et al*., 2017, Kamalakannan *et al*., 2017, Nicolaus *et al*., 2017, Yang *et al*., 2015) .

Petroleum is a complex mixture of alkanes, aromatics, natural gas and heterocyclic hydrocarbons, depending on their pressure , composition and temperature conditions (Mahjoubi *et a*l., 2018) . It represents a high risk of mutagenic and carcinogenic diseases as well as other toxic properties such as bioaccumulation and biomagnification (de Quadros *et al*., 2016, Kotzakoulakis and George, 2018).The most important constituents of hydrocarbons in waters are normal alkanes (Adeniji *et al*., 2017) and it comes mainly from petroleum hydrocarbons and its products (Vaezzadeh *et al*., 2017) . Biogenic input such as terrestrial plant waxes, phytoplankton , marine bacteria and the digenetic conversion of biogenic precursors also contributes to the presence of n-alkanes (Ficken *et al*., 2000). Even numbered n-alkanes generally come from various anthropogenic activities such as petrogenic input, fossil fuels and biomass combustion (Eckmeier and Wiesenberg, 2009, Sakari *et al*., 2008). Plankton, algae and higher land plants, however, are characterized by the presence of odd n-alkanes (Sakari *et al*., 2008) .

The differences in the characteristic chain lengths of n-alkanes, the distribution of the carbon numbers and the dominance of even / odd carbon numbers are effective biomarkers for the evaluation of the sources of organic substances in marine and freshwater sediments (Galoski *et al*., 2019). Several indices were used to identify the sources of n-alkanes(Rosell-Melé *et al*., 2018, Galoski *et al*., 2019, Lichtfouse *et al*., 1997) , such as CPI , Pristane to Phytane ratio (Pr/Ph) , Pr/C_{17} ,Ph /C_{18} , Unresolved Complex Mixture (UCM) ,and Low Molecular Weight to High Molecular Weight (LMW /HMW) .

The project aim is to estimate the total alkanes in the Al Hammar water and compare their levels with previous study, in addition to determining the source of these alkanes, whether they are biogenic or anthropogenic .

Description of the study area

Al – Hammar marsh located in the south of the Euphrates River and it extends from the city of Nasiriyah in the west, extending to the outskirts of Basrah on the Shatt al-Arab east to the south along the vast muddy coast until it reaches Arabian Gulf. It is surrounded by a belt of sand dunes of the southern desert . The area of this mound is approximately 2,800 to 4,500 km^2 during the period of seasonal flooding, the lake of Al – Hammar that forms the marshes is the largest water surface of the region in the south of Euphrates and has a length about 120 km and its width is approximately 25 km , the water characterized by low salinity (Slightly Brackish) due to its close proximity to the Arabian Gulf and a little deep with a depth of 1.8 meters in the least deep areas and 3 meters in the most depth (Maltby, 1994) .

Materials and methods

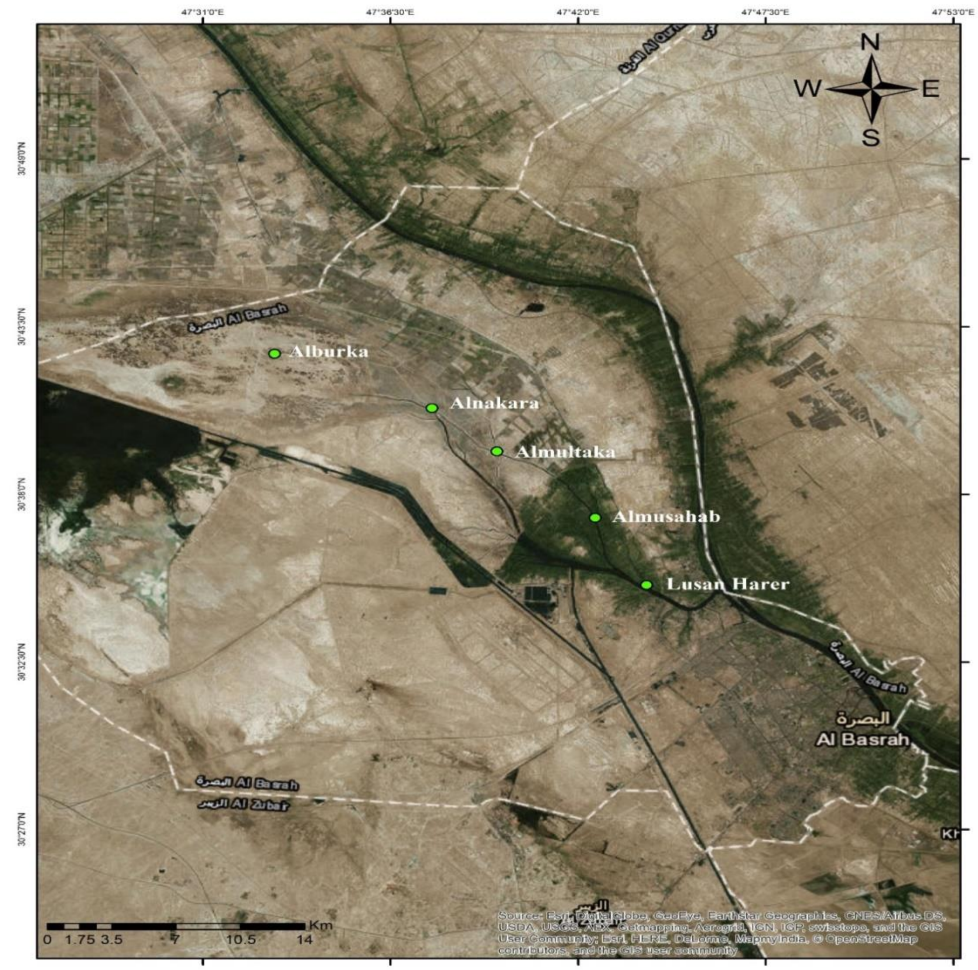
Water samples were collected by using a dark brown glass bottles of 5 liters capacity and 25 ml carbon tetrachloride (CCl_4) was added. Samples were collected from four stations along the al-Hammar marshes (Lusan

Harer, Almusahab, Alnakara and Alburka) through winter , as shown in fig (1)

The method used by the United Nations Environment Program (UNEP, 1989) was adopted for extracting hydrocarbons from water. 10 ml of carbon tetrachloride CCl_4 were added for every liter of water from the sample. The sample was shaken well by using an electric mixer for (30 minutes), the contents were transferred to a separation funnel , left to settle for a period of time, as the organic layer separated easily because it was heavier than water. The same process is repeated by adding 15 ml of CCl_4 and shaking with the mixer to extract the remaining petroleum hydrocarbons in the water.

The organic layer was collected , passed on a column containing glass wool at the bottom , topped with a layer of Anhydrous Sodium Sulphate (Na_2SO_4) to ensure that there was no water in the sample. The samples were then evaporated to dryness using the Rotary evaporator, to get rid of CCl_4. Then the petroleum hydrocarbons are dissolved in 50 mL of normal hexane and the sample is passed over a chromatographic separation column at the bottom of which is Glass wool and a layer of Silica gel topped with a layer of Na_2SO_4.

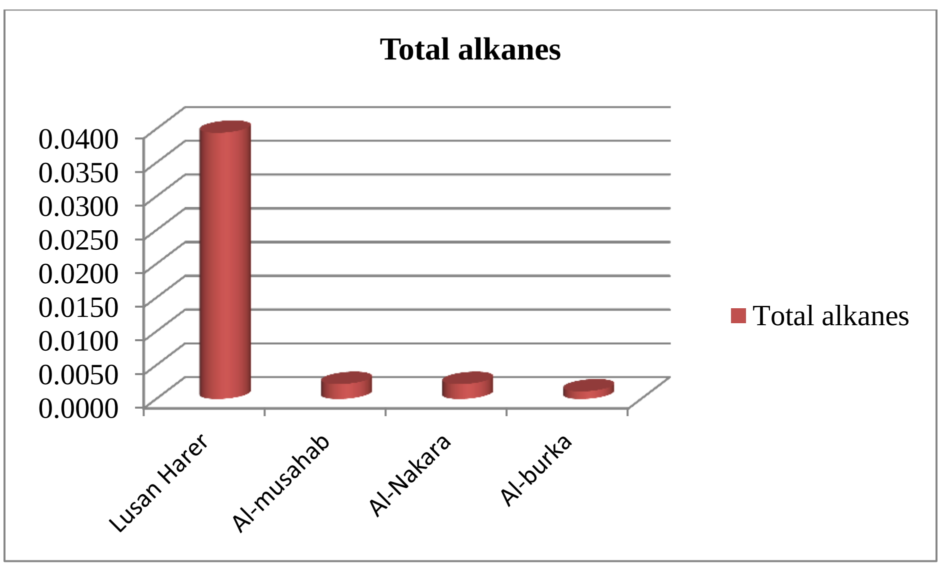
Adding 50 ml of regular n-hexane to obtain the aliphatic portion. . n-Alkanes were determined by gas chromatography-flame ionization detector (GC-FID; Shimadzu) with a capillary column (Methyl silicon) SE. 30 using splitless injection. The program was set at 290^{o}C for the injector, 330^{o}C for the detector, 60-280^{o}C for 90 minutes with rate 4^{o}C/Min for the column



(Figure 1) The study area

Result and Discussion

Concentrations of total alkans varied from 0.001 µg/L in Al-burka station to 0.39 µg/L in Lusan Harer , whereas at Al-musahab and Al-nakara was 0.002 µg/L fig (2) and table (1) . In general ,the decline in concentrations at all stations may be due to extensive weathering effects (Farid *et al.,* 2015). In addition to the processes of solubility, photochemical oxidation and taking by zooplankton or biodegradation (Talal, 2008). Usually, low molecular weight alkanes (C_{10} - C_{22}) are degraded first, then low molecular weight aromatic hydrocarbons (Duan et al., 2018). In addition to the sedimentation process, which plays an important role in the decrease of concentrations of alkanes in the water column, and this reached by (Salah *et al*., 2020) in his studies on the sediments of the marshes. . The results showed a significant difference between the stations at (P≤ 0.005)



(Figure 2) Total alkanes (µg/l) in water samples of Al-Hammar marsh stations

Table (1) Concentrations of n-alkanes (µg/l) in water samples of Al-Hammar marsh stations during 2018

Concentration	Lusan Harer	Al-musahab	Al-Nakara	Al-burka	mean	Std. Deviation
C20	0.00174	0.00031	0.00037	0.00016	.000645	.0007356
C21	0.00020	ND	0.00011	ND	.000076	.0000945
C22	0.01033	0.00044	0.00030	0.00023	.002827	.0050033
C23	0.00013	ND	0.00015	ND	.000071	.0000820
C24	0.00879	0.00035	0.00062	0.00025	.002501	.0041924
C25	0.00065	ND	0.00014	ND	.000197	.0003091
C26	0.00592	0.00037	0.00045	0.00037	.001778	.0027624
C27	0.00054	0.00019	0.00022	0.00012	.000265	.0001860
C28	0.00377	0.00028	0.00032	0.00022	.001149	.0017509
C29	0.00047	0.00013	0.00013	ND	.000183	.0001985
C30	0.00232	ND	0.00023	ND	.000638	.0011271
C31	0.00049	0.00014	ND	ND	.000158	.0002316
C32	0.00140	ND	0.00010	0.00016	.000555	.0007355
C33	0.00054	ND	ND	ND	.000542	
C34	0.00120	ND	ND	ND	.001204	
C35	ND	ND	ND	ND	0.000000	
C36	0.00095	ND	ND	ND	.000948	
TOTAL	**0.039**	**0.002**	**0.002**	**0.001**	**0.013737**	**.0019750**
odd	0.003	0.000	0.001	0.000		
even	0.036	0.002	0.002	0.001		
CPI	0.083	0.263	0.312	0.086		
LSD (stations)		**0.002079**				

Carbon preference Index (CPI), defined as the sum of odd numbered carbon alkanes to the sum of even numbered carbon alkanes and used to indicate the relative relationship between biogenic and anthropogenic origin (Farid *et al.,* 2015, Gong, 2005). CPI data in this study (table 1) was less than (1) 0.083 ,0.263 , 0.312, 0.086 in Lusan Harer , Al-musahab , Al-Nakara and Al-burka respectively which means that the origin of hydrocarbons were anthropogenic . There are abnormal sources of hydrocarbons produced from different human activities where fishing boats and air fall are added in addition to the oil compounds carried by rivers which are the presence of similar chains of normal alkanes between (C13 – C34) without the dominance of odd or even carbon numbers (figures 5 and 6) , is a characteristic of petroleum compounds and their derivatives (Law, 1994), while the dominance of some specific even numbered hydrocarbons over the odd ones (figures 3 and 4) suggest anthropogenic source pollution (Adeniji *et al*., 2017).

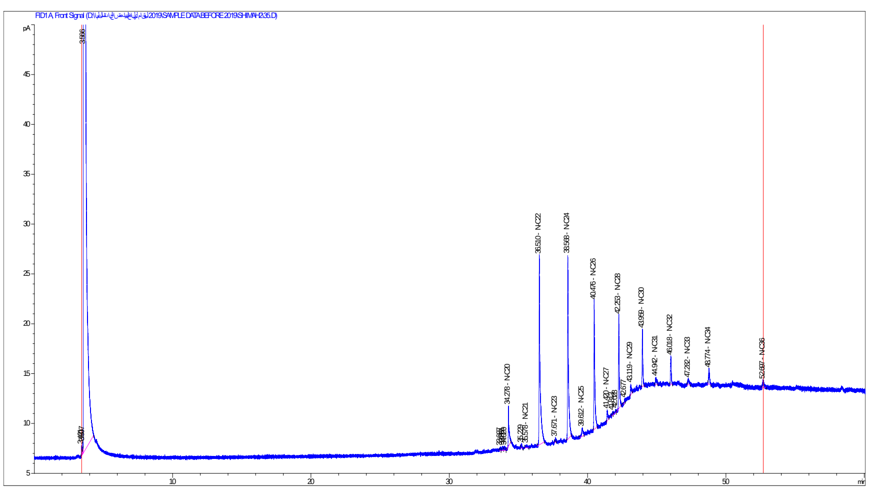


Figure (3) normal alkanes in Lusan Harer

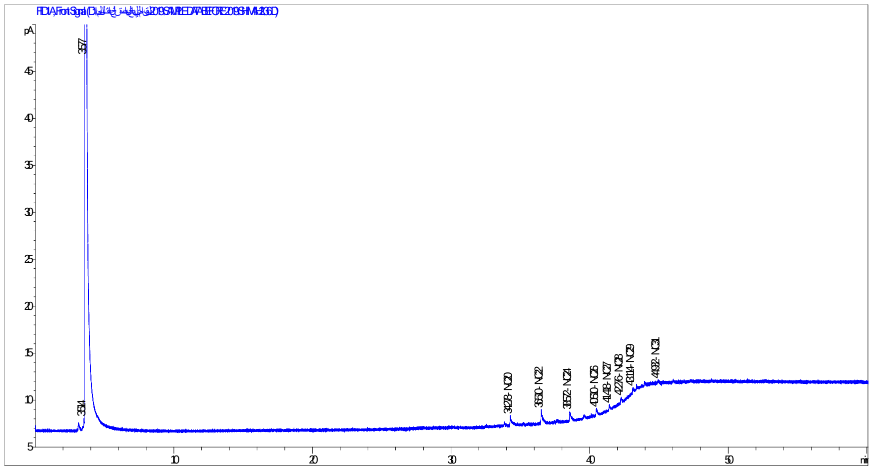


Figure (4) normal alkanes in Almusahab

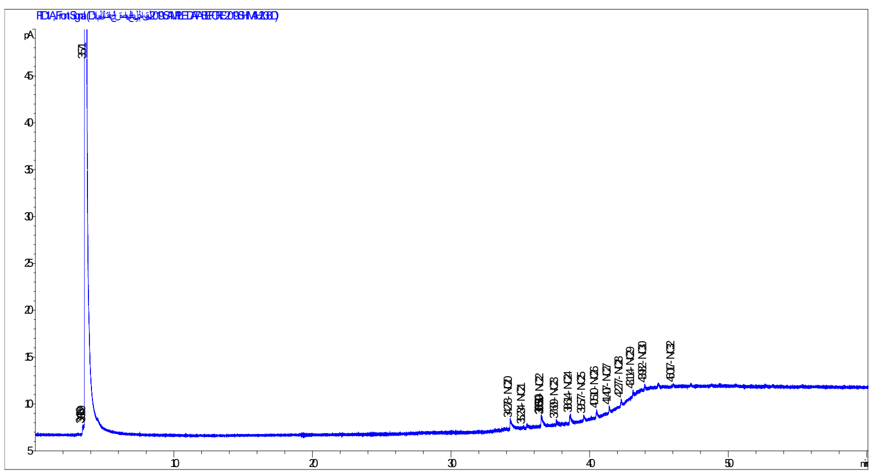


Figure (5) normal alkanes in Alnakara

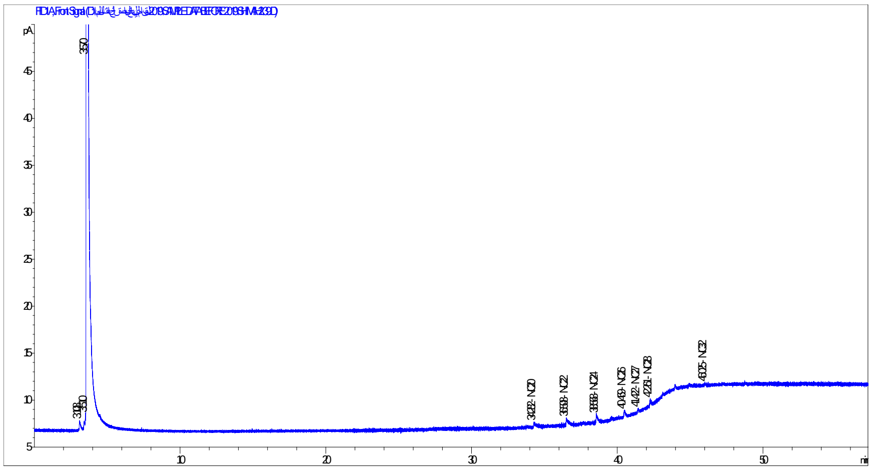


Figure (6) normal alkanes in Alburka

Table (2) shows a comparison between the concentrations of the n-alkanes of the current study with previous studies which showed that the results of the current study were lower than the previous ones that may be because of the dilution caused by the rainfall during the sampling period.

Table (2) comparison between the concentrations (μg/l) of the n-alkanes of the current study with previous studies

Region	Total alkanes μg	References
Al- Hammar marsh	0.14 – 6.20	(Al-Saad and Al-Timari, 1993)
Al-Huiza marsh	1.14 – 34.46	(AlKhatib, 2008)
Al- Hammar marsh	2.41 – 3.13(dissolved part)	(Talal, 2008)
Al – Chibaysh marsh	0.32 – 2.98	(Al-Atbee, 2018)
Al – Hammar marsh	0.001 – 0.039	Present study

Conclusions and recommendations

The study showed a decrease in the concentrations of total alkanes in Al-Hammar marshes water. The few concentrations present are from anthropogenic sources. Dominance of some specific even numbered compounds over the odd ones . Therefore, we recommend periodic monitoring of hydrocarbon compounds in general and alkanes in particular in marsh waters to monitor pollution levels in the area.

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