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MARSH BULLETIN 15(1) April (2020) 12–18

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N-alkanes in sediment of Al-Hammar marsh, Southern Iraq.

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Abstract

During 2018, a study has been carried out to determine the distribution of aliphatic hydrocarbons in the sediment of five locations in Al-Hammar marsh which are (Lusan Harer, Almusahab, Almultaka, Alnakara and Alburka) respectively. Analyses were done for the determination of N-alkanes concentrations by using gas chromatography. The total n-alkane concentration ranged between (6.176) µg/g dry weight at (Alburka) to (8.835) µg/g dry weight recorded at (Almusahab). The main sources of N-alkanes were anthropogenic according to CPI, while the sources according to pristine/phytane were pyrogenic value at all sites.

Keywords: N-alkanes, marshes, sediment, Basrah

Introduction

The marsh region located in southern of Iraq which formed by peak flood of the two rivers Tigris and Euphrates, and it has maximum about length of 218 Km and a width about of 170 Km, they are estimated about (3500Km^2) which is covered by water (Al-Mousawi,1988; Al- Saad *et al.*,1996).

Iraqi southern marshes form a large triangular region bounded by three major southern cities: Nasiriyah to the west, Amarah to the northeast, and Basrah to the south. Their vast area covers 20,000 square kilometers of open water, and includes both permanent and seasonal marshes. Three major areas are the Al-Hammar, the Central, and the Al-Hawizeh Marshes form the core of the marsh land of southern Iraq. It is centered on the meeting of the great Tigris and Euphrates River. Such specific wetlands of the southern part of Iraq play a vital role in the maintenance of biodiversity in the Middle East, primarily because of their large size, the richness of their aquatic vegetation and their isolation from other comparable systems (Bedair *et al*., 2006).

The importance of the marsh comes from its impressed on the environment, as a regarded highly storage of flood plains, freshwater lake, and fishes and also it represents one of natural ecosystem to degrease the contamination of chemical pollutant such as pesticides and hydrocarbons (Talal *et al*., 2010).

The environmental pollution recently has become one of the problems that effected on human life and living organisms, this problem grown up as result of industrial development and increasing in population (Alshmery,2013; Abdoul-Aziz *et. al.*, 2019).

Sediment and suspended particles given good information about dynamic of compound such as chemical pollutant in aquatic environment (Altimari *et al*.,1997).

Petroleum pollution has long been of great concern since there are components in petroleum which have mutagenic and carcinogenic impacts on organisms. The global increasing demand for fuel besides accidental oil spills are two major contributors to the release of petroleum into the environment (Singh *et al*., 2012).

Petroleum hydrocarbons enter the aquatic environment by many ways like leakage tanks or pipelines, decomposition in addition the accident spill and land disposal of petroleum wastes, therefore; sediment pollutant by hydrocarbons in numbers areas of oil producing countries is an important problem. (Barakat *et.al*.,2001; Kelome *et.al.*,2012 and Al –Saad *et al*. ,2015).

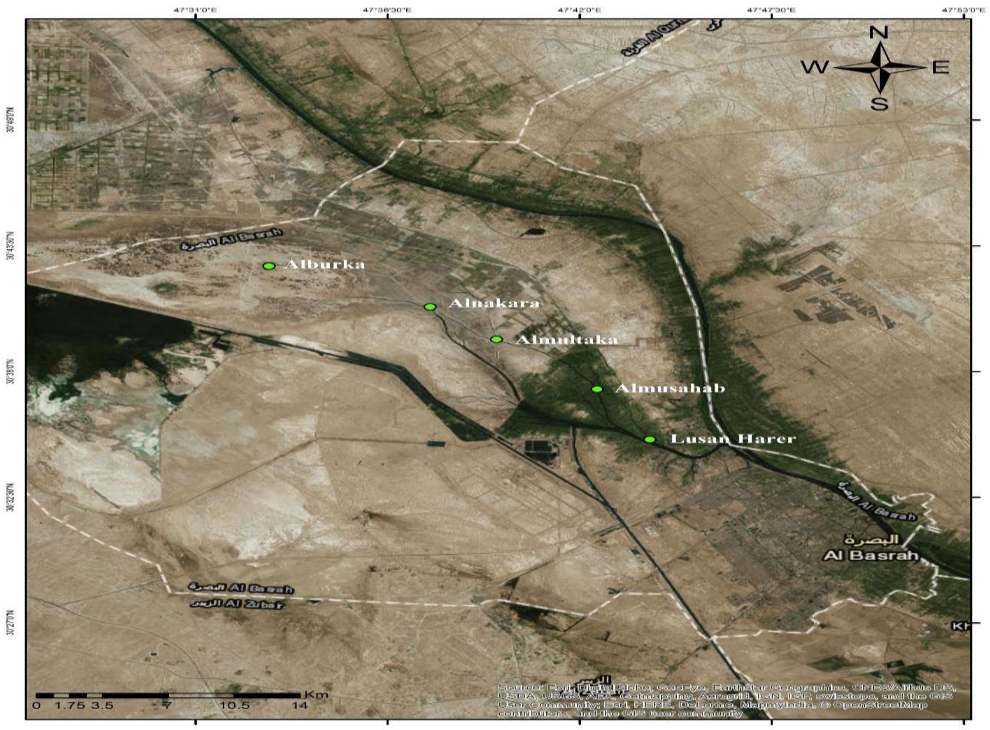
N-Alkane is a kind of hydrocarbons which included two types of carbons chain odd and even numbers of carbon atom and can be 64 carbons with substitutes or branch alkyl, according to Carbon Preference Index(CIP), the ratio in concentration of odd number carbon which has been sources biogenic to even numbers usually comes from petrogenic. (Al-Hejuje *et al*.,2015).

The aim of this study is to determine the distribution and origin sources of n-alkanes in sediment at different sites along Al-Hammar marsh southern of Iraq.

Materials and methods

During the winter season in 2018, sediment samples were collected by using van veen grab sampler during 2018, from five locations in Al-Hammar marsh as flowed (Lusan Harer, Almusahab, Almultaka, Alnakara and Alburka), as shown in figure (1). The samples were preserved by using aluminum foil, and placed in an ice box until reaching the laboratory .

The sediment samples were dried by using freeze dryer then grind finely in an agate electrical mortar and sieved through a 63 µm mesh sieve, stored until analysis. Twenty-five grams of sieved sediments were placed in cellulose thimble and extracted by using soxhlet intermittent extraction (Goutx and Saliot, 1980) with mixed solvents (120 ml) methanol: benzene (1:1 v/v) for 48 hrs. The combined extracts were saponification for 2 hours by adding (15ml) 4M MeOH(KOH) at the same temperature and cooled to room temperature.



(Fig. 1) The study area.

The unsaponification matter was extracted with (50 ml) n-hexane using separator funnel. The upper unsaponification matter with hexane (hydrocarbons) was passed through open – chromatographic column which contents the glass wool at the bottom, then layer from 5% deactivated silica gel, as well as the layer from alumina, and finally layer from anhydrous sodium sulfate to collect fraction of aliphatic hydrocarbons.

Standard aliphatic compounds (C7-C33) were used to inject in gas chromatography to detect quantities and qualities of aliphatic compounds in sediments samples. Helium was used as carrier gas in liquid Gas Chromatography with linear velocity of 1 ml./min. and flam ionization detector(FID). The operating temperatures for injector and detector were 280°C and 300°C, respectively. Column (model Agilent 19091J-101HP-5 5% phenyl Methyl Siloxan with dimensions (50 m.*200µm*0.33µm) was used for aliphatic separation. The column temperature was held for 60 min at 35°C as initial temperature for 13 min. then 5°C/min to 280°C.

Table (1) Concentrations of n-alkanes (µg/g) dry weigh in sediment samples of locations during 2018.

Carbon Number	Lusan Harer	Almusahab	Almultaka	Alnakara	Alburka
C10	0.014	0.016	0.014	0.012	0.010
C11	0.013	0.014	0.012	0.610	0.084
C12	0.120	0.142	0.120	0.119	0.110
C13	0.023	0.032	0.210	0.020	0.020
C14	0.162	0.174	0.143	0.132	0.123
C15	0.021	0.031	0.020	0.020	0.018
C16	0.062	0.072	0.054	0.042	0.032
C17	0.127	0.130	0.116	0.101	0.100
C18	0.192	0.201	0.162	0.154	0.145
C19	0.316	0.365	0.215	0.210	0.203
C20	0.392	0.410	0.312	0.309	0.298
C21	0.625	0.730	0.514	0.412	0.136
C22	1.123	1.235	1.152	1.143	1.354
C23	1.254	1.342	1.143	1.132	1.126
C24	1.024	1.080	1.011	1.000	0.934
C25	0.724	0.825	0.643	0.534	0.426
C26	0.526	0.686	0.428	0.310	0.306
C27	0.218	0.314	0.216	0.203	0.201
C28	0.162	0.184	0.140	0.121	0.119
C29	0.143	0.154	0.133	0.130	0.128
C30	0.120	0.193	0.110	0.108	0.102
C31	0.110	0.210	0.092	0.076	0.063
C32	0.094	0.120	0.084	0.074	0.065
C33	0.085	0.093	0.064	0.053	0.042
C34	0.043	0.054	0.033	0.032	0.021
C35	0.026	0.028	0.021	0.010	0.010
Sum	**7.719**	**8.835**	**7.162**	**7.067**	**6.176**
S. D.	**± 1.1**	**± 1.1**	**± 1.1**	**± 1.1**	**± 1.1**
Odd	3.685	4.268	3.399	3.511	2.557
Even	4.034	4.567	3.763	3.556	3.619
Pristine	0.110	0.134	0.117	0.131	0.100
Phytane	0.182	0.268	0.154	0.142	0.254

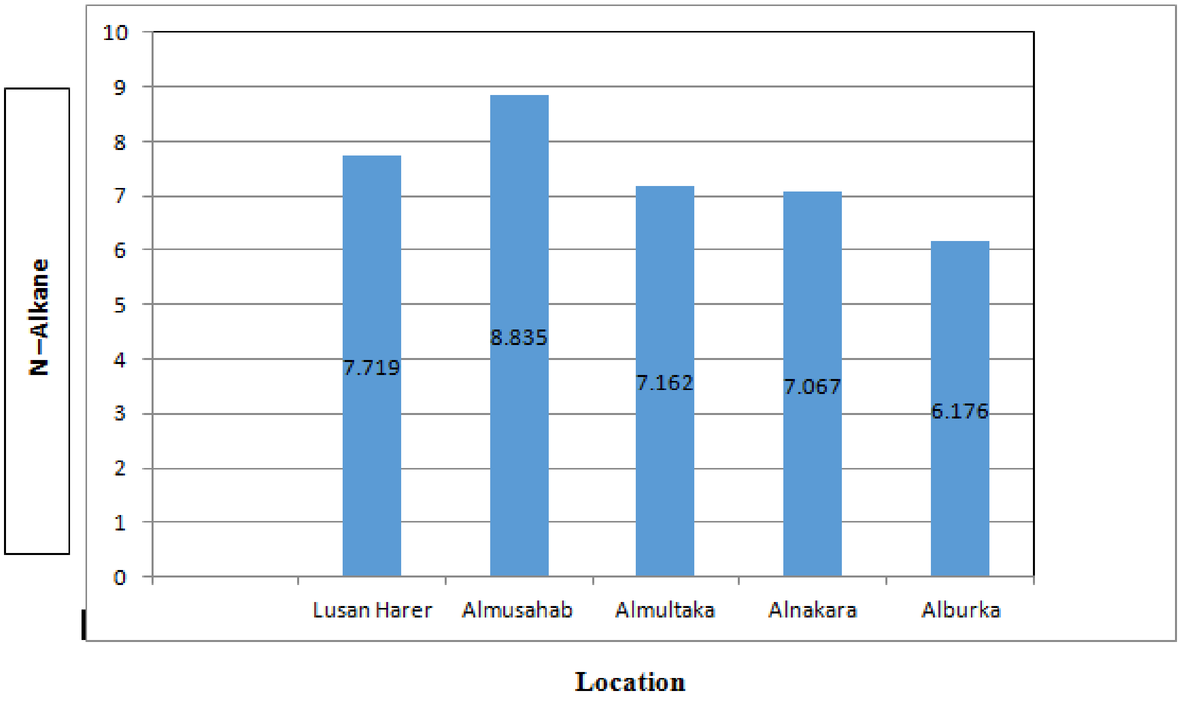


Fig (2) mean concentrations of n-alkane (µg/g) at locations.

Result and dissection

Types and total concentrations of n-alkanes presented in table (1) and Fig (2). We can notice that the total n-alkane concentration ranged between (6.176) µg/g dry weight at (Alburka) to (8.835) µg/g dry weight at (Almusahab).

Biodegradation affected in the sedimentation levels because bacterial activity depends upon the available oxygen and nutrients (GESAMP,1993). The organic materials found in the sediments of Iraqi marshes carried by the Euphrates and then accumulated on the sediments of the marshes (Al-Saad and Al-Timari,1994).
The anthropogenic sources come from the input of weather, wastes of factories and natural seepage which carried by the Tigris and Euphrates to the Marshes (Talal *et al.*, 2010).
Al-Khatib (1998) pointed that C17, C18 and C19 were originated from algae and bacteria, whereas Tala (2008) pointed that the high values of odd carbon number chains of C17 in sediments was a result of the presence sulfuric reducer bacteria (*Desulfovibrio desulforicans*) in the sediments, while the C19 indicating the algal origin. Al-Khatib (2008) pointed that the high values of C25, C27, and C29 in sediments indicating decomposition of the higher plant tissues Al-Hejuje (2014).
Abundance of short chain even carbon numbers n-alkanes C18 and C20 indicate a petroleum source and a values of CPI and the ratio of pri /phy which are less than one or close to one supported this conclusion (Al-Saad and Al-Timari ,1993; Stout *et al.*, 2002; Wang and Fingas, 2005; Al-Khatib ,2008; Talal *et al.*, 2010; Fagbote and Olanipekun ,2013). While the n-alkanes from C24 to C35 table (1). Long chain odd carbon numberes C27, C29, C31 and C33 are derived from wax of vascular higher plant leaves (Meyer ,2003), whereas the main source of long chain even carbon numbers C20 - C30 in sediments are produced by bacterial activity (Simoneit ,1993; Al-Timari ,2001; Al-Khatib ,2008). Same conclusion has been reached by Rushdi *et al.*, (2006) in sediments of Iraqi southern marshes, Al-Saad and Al-Timari (1993), Talal (2008) in sediments of Hor Al-Hammar, Al-Khatib (2008) in Hor Al- Howaiza and Al- Taie (2013) in sediments of Hor Al-Azim and Abdoul-Aziz (2019)

Table (2) N-Alkanes pollution indices values in sediment samples at the studied locations.

Location	CPI	Pristine /phytane	C17/C18	C17/pristine	C18/phytane
Lusan Harer	0.913	0.604	0.661	1.154	1.054
Almusahab	0.934	0.500	0.646	0.970	0.750
Almultaka	0.903	0.759	0.716	0.991	1.051
Alnakara	0.987	0.922	0.655	0.770	1.084
Alburka	0.706	0.393	0.689	1.000	0.570

The ratio of CPI and Pristine/Phytane ratio were less than (1) which indicated the anthropogenic source of hydrocarbons, while pristine/phytane ratio were less than 1 referred to a pyrogenic origin, the value of C17/ pri indicated the presence of weathering of oil and hydrocarbons at (Almusahab, Almultaka and Alnakara) while it indicates the presence of oil compounds at Lusan Harer and Alburka. C18 / phy less than 1 at Almusahab and Alburka that indicates the presence of weathering of oil and hydrocarbons, while the high value of this ratio at (Lusan Harer, Almultaka and Alnakara) indicates the presence of oil compounds.

Table (3): Comparison between the levels of n-alkanes (µg/g dry weight) in soil for the present study with the other previously studies.

Studied Areas	n-alkane(µg/g)	References
Shatt Al-Arab River &NW Arabian Gulf	6.97-55.67	Al-Saad (1995)
Shatt Al-Arab River &NW Arabian Gulf	3.470 – 8.952	Al-Khatib (1998)
Al-Howaiza Marsh	3.43 – 42.38	Al-Khatib (2008)
Al-Hammar Marsh	6.53 - 31.46	Talal (2008)
AL-Azim marsh	5.33-35.41	Al – taie (2013)
Shatt Al-Arab River	4.76 – 10.09	Al-Hejuje (2014)
Shatt Al-Arab River	0.244-8.243	Al–Mahana (2015)
West Qurna-2 Oil field	4.999-43.324	Karem *et al*(2016)
Al-Hammar Marsh	**6.176-8.835**	**The present work**

If we compared our data of N-alkanes with previous studies on the area during the last two decades (Table 3), we found that it is located within the ranges of the previous studies, as a conclusion, these sediments have some n-alkanes, and the main sources of these alkanes come from different sources such as bacteria, phytoplankton, algae and higher plants.

REFERENCES

Abdoul-Aziz, H.F.; Al-Hejuje, M and Al-Saad, H.T. (2019). Aliphatic (n-alkanes) hydrocarbon compounds in core sediments at AL-Chibayish marsh in Thi-Qar province, southern Iraq, Marsh Bulletin (in press).

Al-Hejuje, M.M. (2014). Application of water quality and pollution indices to evaluate the water and sediments status in the middle part of Shatt Al-Arab River. Ph.D. Thesis, Biology Department, College of Science, University of Basrah, 239 pp.

Al-Khatib, F.M.H. (1998). Distribution of hydrocarbons compound and their sources in sediment cores from Shatt Al-Arab Estuary and N.W. Arabian Gulf. M.Sc. thesis, Basrah Univ., 95 pp.

Al-Khatib, F.M.H. (2008). Determination the concentration, origin and distribution of hydrocarbons compounds in water, sediments and some biota of Hor Al-Howaiza, south of Iraq and their sources. Ph.D., thesis, College of Science, University of Basrah, 228 pp.

Al-Shmery, A.Y.H. (2013). Estimation of some heavy metals in clams, sediments and water from Shatt Al-Arab and treatment by porcellanite rocks. M. Sc. Thesis, Chemistry Department, College of Education for Pure Science, University of Basrah, 100 pp.

Al-Mahana, D.S. (2015). Distribution and sources of Total Hydrocarbons, N-Alkane and Poly Cyclic Aromatic compounds in sediments cores of Shatt Al-Arab coast, Khor Al-Zubair and Um-Qaser. M.Sc thesis, College of Science, University of Basrah, 124 pp.

Al-Saad, H.T. (1995). Distribution ad source of hydrocarbons in Shatt Al-Arab Estuary and North West Arabian Gulf. Ph.D. Thesis, Basrah Univ., 186 pp.

Al-Saad, H.T. and Al-Timari, A.A.K. (1994). Biogenic and anthro-pogenic n-alkanes in sediment marshes of Iraq. Mar. Mesopotam. 9: 277-288.

Al-Saad, H.T.; Farid, W.A.; Ateek, A.A.; Sultan A.W.; Ghani, A.A. and Mahdi, S. (2015). N-Alkanes in surficial soils of Basrah city, Southern Iraq. International Journal of Marine Science, 5(52): 1-8.

Al-Saad, H.T.; Shamsaoom, S.M. and Abaychi, J.K. (1996). n-alkanes in aquatic plant of Hor Al-Hammar marsh, Iraq. Mar. Mesopot. 11(2): 281-288.

Al-Timari, A.A.K. (2001). Review: Levels of oil pollution during the last to decades in the Southern of Iraq and Arabian Gulf.Mar. Mesopot.16(2):289- 309.

Al-Timari, A.A.K.; Al-Saad, H.T. and Darmoian, S.A. (1997). Distribution and Sources of n-alkanes in sediment cores from Al-Hammar marsh Southern Iraq. Mar. Mesopot. 12(2): 315-330.

Bedair, H.M.; Al-Saad, H.T. and Salman, N.A. (2006). Iraq's Southern marshes something special to be conserved; A case study. Marsh Bull. 2(1): 99-126.

Fagbote, O.E. and Olanipekun, E.O. (2013). Characterization and sources of Aliphatic Hydrocarbons of river Oluwa at Agbabu Bitumen Deposit area, western Nigeria. Journal of scientific research and reports .2(1):228-243.

GESAMP, (1993). IMO/FAO/UNESCO/WHO/IAEA/UN/UNE Joint Group of Experts on the Scientific Aspect of Marine Pollution. (GESAMP) Impact off all and related chemicals and wastes on the marine environment. Report and studies No. 50, Imo, London. 180 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.

Law (1981) Hydrocarbon con cen tration in water and sediment from U.K marine water determined by fluorescence spectroscopy. Mar. pollut. Bull. 12:153-157.

Meyers, P.A. (2003). Applications of organic geochemistry to paleol-imnological reconstraction. asummery of examples from the Laurentian great lakes .Org. Geochemical .34:261-289.

Rushdi, A.I.; Douabul, A.A.Z.; Mohammed, S.S. and Simoneit, B.R.T. (2006). Composition and sources of extractable organic matter in Mesopotamian marshland surface sediments of Iraq. 1: Aliphatic lipids. Environ. Geol., 50: 857- 866.

Simoneit, B.R. (1993). Aqeous high temptrture and high pressure organic geochem of hydrothermal vent systems. Geochemicaet cosmoshemica Acta. 57 :2231-2243.

Stout, S.A.; Uhler, A. D.; McCarthy, K.J. and Emsbo-Mattingly, S. (2002). Chemical fingerprinting of hydrocarbons. In: Murphy BL, Morrison R (Eds.), Introduction to Environmental Forensics. Academic Press, Boston.137-260.

Tal, S. (2008). Global warming. The World of Thought Magazine, 37(2): 66-67.

Talal, A.A.; Al-Adhub, A.Y. and Al-Saad, H.T. (2010). Seasonal and reagional variatitions of hydrocarbon concentrations and origin of n-alkanes in sediments of Iraq Southern marshes. Marsh Bulletin 5(2):197-206.

Wang, Z. and Fingas, M. (2005). Oil and petroleum product finger-printing analysis by gas chromatographic techniques. In: Nollet L, (ED.), Chromatographic Analysis of the Environment, third ed. CRC Press, New York. 1027-1101.

ألالكانات في رواسب هور الحمار- جنوب العراق

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المستخلص

تناولت الدراسة الحالية قياس وتوزيع المركبات الأليفاتية (الألكانات) في رو اسب هور الحمار ولخمسة مناطق هي (لسان حرير والمسحب والملتقى والنكاره والبركة) خلال فصل الشتاء من عام 2018, حيث تم قياس تركيز الألكانات الاعتيادية باستخدام جهاز كروماتوغرافيا الغاز (GC), ووجد أن تركيز الالكانات قد تراوح من (6.17 مايكروغرام للغرام الواحد) في البركة إلى (8.835 مايكرو غرام للغرام الواحد) كوزن جاف في منطقة المسحب، وبينت الدراسة أن المصدر الرئيسي لهذه الالكانات غير طبيعي نسبة إلى قياس معامل التفضيل الكاربوني (CPI)، كما لوحظ أن بعض التراكيز تعود إلى مصادر طبيعية نسبة إلى البرستين والفايتين (pri/phy).

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كلمات مفتاحية: الكانات اعتيادية، أهوار، رواسب، البصرة