



Seasonal and regional variations of hydrocarbon concentrations and origin of n-alkanes in sediments of Iraq Southern marshes

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Abstract

For the period Jan.(2006)toFeb(2007) during(14)months,sediment samples were collected from different sites of Iraq southern marsh land;Al-Bargah,Al-Hammar and Al-Gebayesh station. Analysis were done for the determination of total hydrocarbon concentrations using the spectrofluometric method by comparing samples with a standard solution of Iraq crude oil.Total Petroleum Hydrocarbon Concentrations(TPH) indicated that there were regional and seasonal variations.(TPH) ranged from (0.458) $\mu\text{g/g}$ dry weight in Autumn season at Al-Hammar station to (1.250) $\mu\text{g/g}$ dry weight at Al-Gebayesh station during winter(2006).Gas chromatography also used to identify the concentration and origin of n-alkanes in sediment samples,total n-alkanes ranged between(6.53) $\mu\text{g/g}$ dry weight at Al-Hammar station during summer season to (31.46) $\mu\text{g/g}$ dry weight at Al-Gebayesh station during winter (2006).Studying Pristan ,Phytan and Carbon Preference Index (CPI) indicated the biogenic source of hydrocarbone compounds.

1- Introduction

The importance of Iraqi southern marsh lands came from its effect on the environment,its highly storage of fishes and water plants and also its ability to reduce the harmful concentrations of chemical pollutants as pesticides and

hydrocarbons in sediments of Iraq Southern marshes.

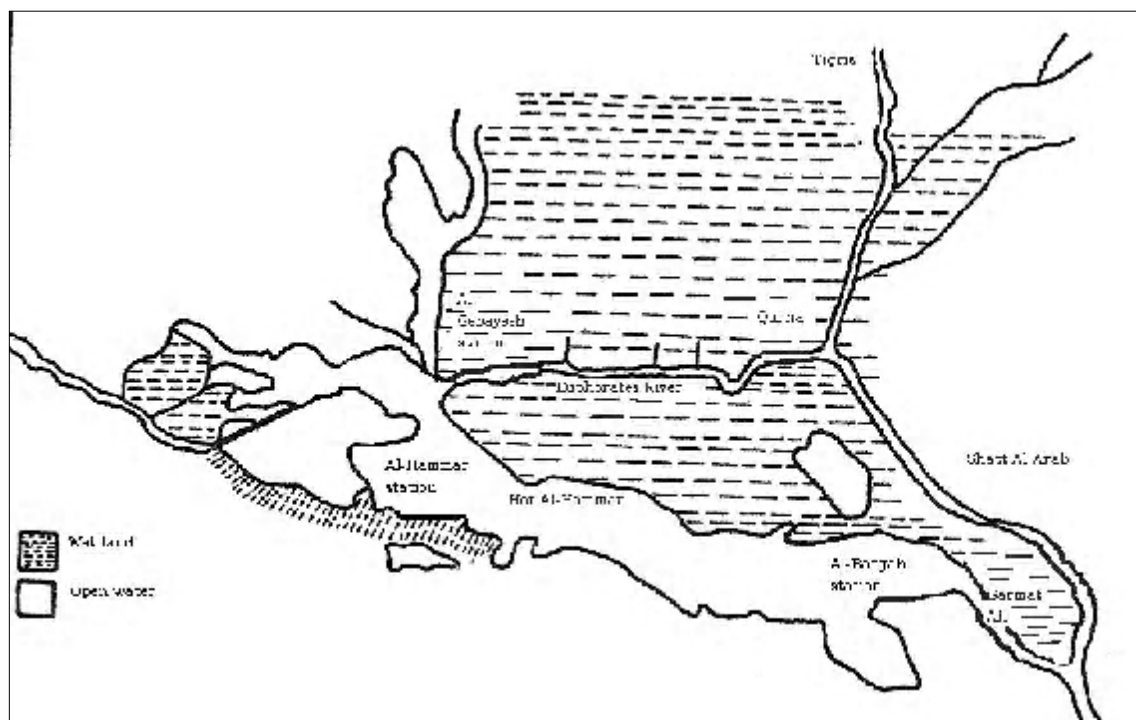
Increasing of population and fishing activities caused the increasing concentrations of petroleum hydrocarbons. The source of hydrocarbons in the marshlands could be biogenic by the

natural seepage and the production of certain plants and microorganisms or anthropogenic sources as in transportation accidents of crude oil (Al-Saad and Al-Timari, 1993). Hydrocarbons in the water body could be accumulated on the surface sediments in (0-20cm) layer. Petroleum hydrocarbon concentrations in the sediments of Iraqi southern marshes were studied by (Al-Saad and Al-Timari, 1989; 1993) and also they have studied the Polycyclic Aromatic Hydrocarbons in the sediments of Iraqi marsh lands in (1994). The aim of this study is to investigate the distribution and variation of total petroleum hydrocarbons in the sediments of Iraqi southern marshes and also the detection of origin and concentrations of n-alkanes in the sediments.

2-Analysis and Methods:

Sediment samples were collected from three sites along Iraq southern marshes (1)Al-Bargah(2)Al-Gebayesh and

(3)Al-Hammar as shown in figure(1). These sediments were collected by means of Vanveen grab sampler then stored in polyethylene bags. Extraction of samples began by using freeze drying method and then powdered by using mechanical mortar. The powder then sieved with stainless steel sieve (62 μ m). We used the method of Goutex and Saliot (1980) for extraction hydrocarbons from the sediments. Total Petroleum Hydrocarbons were analyzed by Spectrofluorometer of the type (Shimadzu, RF540) with recorder (DR-3) at emission wave length (360nm) after excitation at 310nm. Basrah crude oil was used as arbitrary standard. Gas chromatography of the type (Sigma300 Perkin-Elmer) with the capillary column and recorder (LC-100) was used to identify the origin of n-alkanes by the detection of the ratios of CPI (Carbon Preference Index), Pristane, Phytane, and Pristane: Phytane ratio.



3- Results:

Concentrations of Total Petroleum Hydrocarbons in the sediments of the studying stations are presented in table (1). The results had been taken for five seasons and three replicates for each sample. Total Petroleum Hydrocarbons (TPH) concentration ranged from $(0.458)\mu\text{g/g}$ dry weight recorded at (Al-Hammar) station during Autumn(2006) to $(1.250)\mu\text{g/g}$ dry weight recorded at (Al-Gebayesh) station during Winter(2006).

Types and Total concentrations of n-alkanes during seasons (2006), Pristane, Phytane and CPI ratio are presented in tables (2,3) total n-alkane concentration ranged between $(6.53)\mu\text{g/g}$ dry weight at (Al-Hammar) station during summer(2006) to $(31.46)\mu\text{g/g}$ dry weight recorded at (Al-Gebayesh) station during Winter(2006). The ratio of CPI which is $\sum\text{odd}/\sum\text{even}$ and Pristane:Phytane ratio were more than(1) which indicated the biogenic source of hydrocarbons.

Table (1) Total and average of seasonal concentrations of Petroleum Hydrocarbons in the sediment samples of the study stations ($\mu\text{g/g}$)dry weight

Season	Range of Concentration	Station	Average	Average of Seasonal concentration
Winter 2006	0.950-0.980	Bargah	0.965	1.021
	0.985-1.250	Gebayesh	1.0128	
	0.962-0.981	Hammar	0.971	
Spring 2006	0.781-0.801	Bargah	0.791	0.808
	0.815-0.835	Gebayesh	0.823	
	0.800-0.821	Hammar	0.810	
Autmn 2006	0.644-0.671	Bargah	0.657	0.637
	0.693-0.721	Gebayesh	0.705	
	0.458-0.693	Hammar	0.550	
Summer 2006	0.731-0.752	Bargah	0.741	0.779
	0.815-0.831	Gebayesh	0.822	
	0.754-0.790	Hammar	0.775	
Winter 2007	0.915-0.930	Bargah	0.922	0.977
	0.961-1.201	Gebayesh	1.047	
	0.951-0.972	Hammar	0.961	

Table(2) Types and total concentrations of n-alkanes in the sediments of study stations during winter(2006)($\mu\text{g/g}$) dry weight.

n-alkane	Station		
	Al-Bargah	Al-Gebayesh	Al-Hammar
C13	N.d	0.98	0.34
C14	0.94	1.12	0.51
C15	1.12	1.25	0.54
C16	0.73	1.31	1.76
C17	1.71	3.11	2.13
C18	0.43	3.01	1.11
C19	0.24	3.05	1.23
C20	0.18	2.11	0.97
C21	0.76	2.35	0.73
C22	0.62	1.98	0.18
C23	0.98	1.73	0.11
C24	0.54	1.22	0.31
C25	0.32	1.31	1.27
C26	0.21	0.98	0.91
C27	0.19	1.02	0.94
C28	0.13	0.73	0.72
C29	1.23	2.75	1.18
C30	0.98	1.12	0.92
C31	0.13	0.22	0.16
C32	0.06	0.11	0.13
Total concentration	10.50	31.46	16.15
CPI	1.17	1.29	1.14
Pristane	1.52	2.17	1.79
Phytane	0.76	2.09	1.08
Pristane:Phytane	2	1.03	1.65
C17:Pristane	1.12	1.43	1.18
C18:Phytane	0.56	1.44	1.02

Table(3) Types and total concentrations of n-alkanes in the sediments of study stations during Summer(2006)($\mu\text{g/g}$) dry weight.

n-alkane	Station		
	Al-Bargah	Al-Gebayesh	Al-Hammar
C13	N.d	0.11	N.d
C14	0.13	0.25	N.d
C15	0.21	0.31	0.19
C16	0.16	0.46	0.11
C17	1.13	1.27	0.93
C18	1.06	1.11	0.88
C19	0.96	1.05	0.59
C20	0.51	0.98	0.36
C21	0.46	0.76	0.31
C22	0.22	0.18	0.19
C23	0.16	0.25	0.13
C24	0.11	0.15	0.09
C25	0.65	0.88	0.86
C26	0.13	0.23	0.11
C27	0.32	0.51	0.23
C28	0.51	0.71	0.46
C29	0.94	1.05	0.76
C30	0.23	0.91	0.13
C31	0.16	0.43	0.11
C32	0.11	0.15	0.69
Total concentration	8.07	12.18	6.53
CPI	1.54	1.37	1.69
Pristane	0.98	1.13	0.81
Phytane	0.91	1.08	0.78
Pristane:Phytane	1.07	1.04	1.03
C17:Pristane	1.15	1.12	1.14
C18:Phytane	1.16	1.02	1.12

4-Discussions

The surface layer of sediments which used for studying the seasonal and regional variations of hydrocarbon concentrations and types of n-alkanes was (0-5)Cm thickness because 56% of hydrocarbons in water are adsorbed on sediments (Knap and Williams,1982;Al-Saad,1996)

From table(1) we can notice that the total petroleum hydrocarbon concentrations ranged between (0.458) $\mu\text{g/g}$ dry weight recorded at Al-Hammar station in Autumn (2006) to(1.250) $\mu\text{g/g}$ dry weight recorded at Al-Gebayesh station during winter (2006). Al-Saad (1983) found that total petroleum hydrocarbons ranged between (2.60-20.50) $\mu\text{g/g}$ dryweight and Al-Saad (1996) recorded concentrations between (2.46-38.33) $\mu\text{g/g}$ dryweight during summer to winter season in the sediments of Shatt Al-Arab.Lower concentrations of total petroleum hydrocarbons in the sediments of Iraqi marshes belongs to the absence of oil tanker traffic and deballasting water. Goldberg (1976) concluded that concentrations between (1-4) $\mu\text{g/g}$ dryweight in sediments indicate un polluted area.We can also notice seasonal variation in the concentrations of total hydrocarbons in sediments because the weather temperature affect the water temperature and that lead to affect the

sedimentation levels of organic matters (Hussain *et al*,1991).

Biodegradation also affect the sedimentation levels because bacterial activity depends upon the available oxygen and nutrients (GESAMP,1993).The organic matter found in the sediments of Iraqi marshes carried by the Euphorates and then accumulated on the sediments of the marshes (Al-Saad and Al-Timari,1994).

The types and origin of n-alkanes are shown in tables (2,3).N-alkanes enter the aquatic environment by various ways like the geochemical factors,anthropogenic source,biosynthesis of aquatic organisms and biodegradation of algae,diatoms and aquatic plants (Al-Saad,1996).

Al-Saad and Al-Timari(1993) found that n-alkanes accumulated in the upper layer of sediments (0-20)cm,and Diatoms are the most abundant phytoplanktons in Al-Hammar marsh and it was responsible for the even number of n-alkanes (Al-Zubaidi,1985).We can notice the abundance of Odd number of n-alkanes (C23-C37) this result is close to the results of (Al-Saad and Al-Timari,1993),the reason is related to the abundance of the waxy layer found in the leaves of aquatic plants and grasses. Low molecular carbons (C13-C19) that related to the bacterial activity (Salot,1981).

The presence of phytane originated from the analysis of phytyl compound in the Chlorophyll of higher plants and also Pristane originated from Diatoms and green algae (Simonet,1993).The ratio of Pristane: Phytane indicates the origin of n-alkanes of the sample if the ratio is more than(1) that means the biogenic source of sample or if it is less than (1) that means the anthropogenic source of sample, and it is the same for CPI(Carbon Preference Index)(Al-Saad 1983,1996) .

The anthropogenic sources come from the input of weather inputs,wastes of factories and natural sipage which carried by the rivers to the Marshes (Law,1981). Seasonal variation of n-alkane concentrations was found in marsh sediments concentrations were more in Winter and Spring than in Autumn and Summer seasons.The reason was related to the variance of air temperature that affect water temperature(Hussain *et al*,1991).High temperatures lead to the evaporation of low molecular weight hydrocarbons and also increase the microbial Biodegradation of organic matters (Al-Saad, 1983 ; 1996; Hussain *etal*, 1991).

5-References

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التباين الفصلي الموقعي لتراكيز المركبات الهيدروكاربونية وأصل الألكانات الأعتيادية لعينات من رواسب أهوار العراق الجنوبية.

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الخلاصة

في الدراسة الحالية وللفترة من يناير (2006) الى فبراير (2007)، تم جمع عينات الرواسب لثلاث محطات على طول أهوار العراق الجنوبية وهي محطات البركة، الجبايش والعمار .
تم قياس التراكيز الكلية للمركبات الهيدروكاربونية باستخدام طريقة التفلور بمقارنة التراكيز الكلية مع محلول قياسي من نפט خام البصرة بواسطة جهاز Spectrofluorophotometer. دلت قياسات التراكيز الكلية على وجود تباين فصلي وموقعي في عينات الدراسة اذ تراوحت بين (0.458) مايكغم/غم وزن جاف خلال فصل الصيف لمحطة العمار الى (1.250) مايكغم/غم وزن جاف في محطة الجباهش خلال شتاء (2006) .
تم استخدام تقنية الكروموتغرافيا الغازية Gas chromatography لقياس التراكيز الكلية للمركبات الأليفاتية الكلية وأصل ونوعية هذه المركبات. في عينات الرواسب تراوحت تراكيز المركبات الأليفاتية الكلية بين (6.53) مايكغم/غم وزن جاف في محطة العمار خلال فصل الصيف الى (31.46) مايكغم/غم وزن جاف في محطة الجبايش خلال فصل شتاء (2006). وقد دلت دراسة بعض المؤشرات كدليل تفضيل الكربون (CPI) ونسبة البرستان:الفايتان ونسب C17:البرستان و C18: الفايتان على الأصل الحياتي لهذه المركبات في عينات الدراسة.