

N-ALKANES IN THE DISSOLVED AND PARTICULATE WATER PHASES OF SHATT AL-ARAB ESTUARY AND NORTH-WEST ARABIAN GULF

H.T. AL-SAAD , S.M. SHAMSHOOM & J.K. ABAYCHI*

Marine Science Centre - University of Basrah, Basrah, Iraq

***Biology departement, College of Science, Baghdad Univ, Iraq**

ABSTRACT

N-alkanes have been analysed by high resolution capillary gas chromatography in the dissolved and particulate phases of water samples collected over a period of 13 months from Jun 1993 to July 1994 in different environments of Shatt Al-Arab estuary and North-West region of the Arabian Gulf.

Several differences have regularly been observed between the dissolved and particulate fractions. Furthermore, an apparent source-related decoupling between both phases has been found in the estuary.

N-alkanes distribution in dissolved and particulate were characterized by two patterns. The first in the range of C13 to C23 with high C17 and slight predominance of even carbon n-alkanes which associated with biological phenomena, and the second in the range of >C23 with predominance of odd carbon n-alkanes of aquatic terrestrial plants input. Pristane and Phytane were the most isoprenoids found in most samples suggesting biogenic origin, while squalane and Unresolved Complex Mixture (UCM) could have biogenic and anthropogenic origins.

The result indicated that there was a distinct seasonal variation of n-alkanes in the dissolved and particulate phases of the water of Shatt Al-Arab estuary and North-West region of the Arabian Gulf being lowest in all stations during summer and highest in winter.

INTRODUCTION

Hydrocarbons, i.e. chemical compounds composed mainly of the elements carbon and hydrogen, are the principal components of fossil fuels. Crude oil and oil products are the major sources of hydrocarbons but they are not the only source. Other sources exist which contribute to the hydrocarbons load of the marine environment. These derive from incomplete combustion processes and recent biosynthesis.

Due to specificity of biosynthetic pathways, the number of the individual hydrocarbons synthesized by organisms is very much smaller than that found in crude oil or in oil products.

Among aliphatic hydrocarbons synthesized by organisms, those containing an odd number of carbon atoms predominately. Olefins occur frequently and at relatively high concentrations, whereas aromatic hydrocarbons are scarce.

The main producers of biogenic hydrocarbons are phytoplankton (Blumer et al., 1971), benthic algae (Youngblood and Blumer, 1973), zooplankton (Avogon and Blumer, 1968), bacteria (Han and Calvin, 1969) and from terrestrial origin which is mainly associated with higher plants metabolism (Simoneit, 1993).

Based on estimates of primary production and the proportion of hydrocarbons to other cell constituents, the global input of biogenic hydrocarbons may far exceed that of petrogenic hydrocarbons. However, not only are the molecular compositions of the two sources different but also the input kinetics. Biogenic hydrocarbons are generated slowly and over vast areas; their input thus matches the degradative capacity of hydrocarbons-utilizing micro-organisms (GESAMP, 1993).

Estuaries are of special scientific interest to environmentalists world wide. They constitute areas of transport and deposition of continental inputs into the coastal environments. The dynamics of the fine-grained particles and particle-associations in the zones of mixing waters with different characteristics are complex.

Once contaminants are introduced into the sea they are subject to complex physical and chemical changes which depend on the physical and chemical status of the contaminants. Each contaminant will be partitioned between the water as "dissolved" and "particulate" phases.

The knowledge of dissolved and particulate organic matter in Shatt Al-Arab estuary and the North-West Arabian Gulf is rather limited. Accordingly, the present study aims at providing a better understanding of the environmental components of this estuary and its relation to that of the North Western part of the Arabian Gulf. In this respect, assessment of the chemical nature, occurrence and possible origin of petroleum hydrocarbons in the area, was investigated through determination of seasonal variations in n-alkanes dissolved in water and those in particulate matter indicating the main ecological factors acting upon weathering of oil in the estuary.

MATERIALS AND METHODS

Seven sampling sites have been selected from Shatt Al-Arab estuary and North West Arabian Gulf for the study of N-alkanes in dissolved and particulate. The sampling programme was carried for the period of Jun 1993-July 1994. Water sampling (50L) were obtain approximately the 1m of the water column in well washed glass bottle from each of the seven stations (Fig.1).

The water samples were suction filtered as soon as possible (within 5h through preignited 450°C) using preweighed 0.45µm pore size whatman GF/F Glass Fiber Filter. Material passing through the filter were considered as "dissolved", with the retained as "particulate". Dissolved hydrocarbons were extracted by solvent extraction following the procedure of UNESCO (1976). In this, 100ml of nanograde carbon tetrachloride (CCl_4) was used in two successive 50ml extractions and the extracts were combined. To the combined extracts anhydrous sodium sulphate was added to break any emulsion and to remove excess water. The CCl_4 extract were reduce in volume to less than 5ml using a rotary evaporator. The reduce extract was carefully pipetted into a precleaned 10ml volumetric flask, making sure any residual particles of sodium sulphate were excluded and evaporated to dryness by a stream of pure nitrogen. The flask was then rinsed with fresh hexane and the rinsing used to make the sample volume to exactly 5ml. N-alkanes dissolved in water were isolated by column chromatography (Type LC column with frit, stopcock and inlet joint 400mmX22mm, supplied from supelco SA.) 20g of 5% deactivated florasil was added to the glass column. The extract was then applied to the head of a column and eluted with 50ml of hexane to isolated the N-alkanes.

Before extracting suspended particulate matter, the particulate fraction on GF/F filters were freeze-dried in a Edward K4 freeze-dryer Modulyo. The extraction procedure was based upon that of Gutox and Saliot(1980). The glass fiber filters were placed in a pre-extracted cellulose thimbel and soxhlet extracted with 150ml methanol:benzene (1:1) mixture for 24h. At the end of this period, the extract was transferred to a storage flask and the sample was further extracted with a fresh solvent. The combined extracts were reduced in volume to ca 10ml in a rotary vacuum evaporator. It was then saponified for 2h with a solution of 4N KOH in 1:1 methanol:benzene. After extracting the unsaponified matter with hexane, the extract was dried over anhydrous Na_2SO_4 , concentrated by a stream of N_2 . The concentrated extract was cleaned up by column chromatography on 5% deactivated florasil. the n-alkanes was eluted with 50ml of hexane reduced to a suitable volume by a stream of pure N_2 prior to analysis by capillary gas chromatography. For this study a Perkin Elmer Sigma 300 capillary gas chromatograph equipped with Flame Ionization Detector (FID) and splitless mode injection port was used.

Quantification of peaks and identification of n-alkanes in chromatograms was achieved

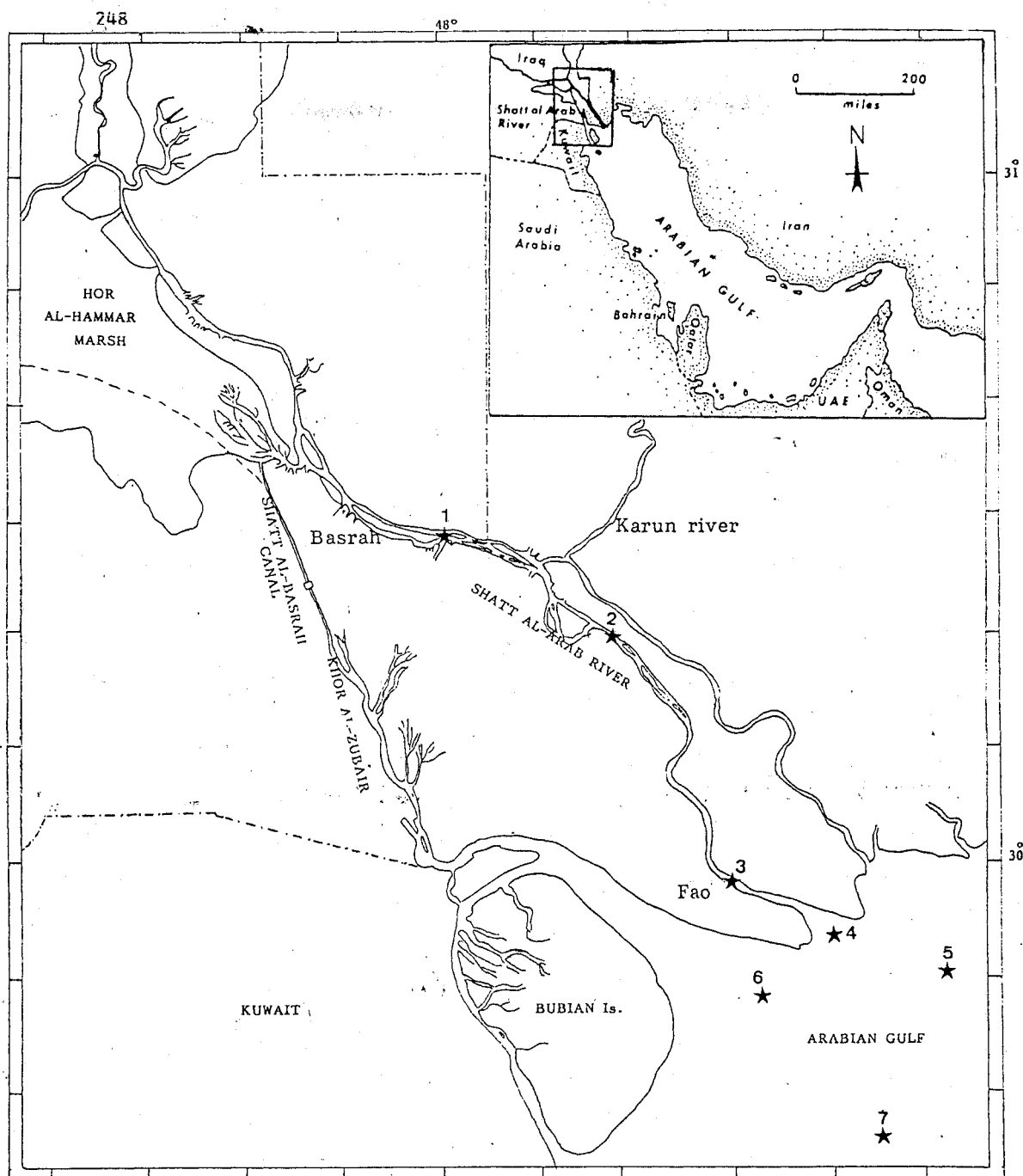


Fig.1-Map of Shatt Al-Arab estuary and North-West Arabian Gulf showing the position of stations

by Perkin-Elmer computing integrator model LC-100. The fused silica capillary column used was a Wall Coated Open Tubular (WCOT) 50mX0.25mm.i.d. SE-30 (methylsilicone)(Perkin-Elmer). Helium was used as a carrier gas with a linear velocity 1.5ml/min. Operating temperatures for detector and injector were 350 and 320°C respectively. The column was operated under temperature programmed conditions from 60°C for 4min to 280°C for 30min with a rate of 4°C/min. The Unresolved complex Mixture (UCM), which also called the unresolved envelop was measured by planimetry.

RESULTS AND DISCUSSIONS

The composition of *n*-alkanes extracted from dissolved phase in water during the five seasons is presented in Table 1. The seasonal variations of total *n*-alkanes in these samples are shown in Table 2a and Fig.2a. The total concentrations of dissolved *n*-alkanes in water varied from 0.94 µg/l at station 7 to 4.97 µg/l at station 2 in summer, and from 2.86 µg/l at station 7 to 16.60 µg/l at station 2 in winter. In general the concentrations of *n*-alkanes were much higher in winter than in summer. The average of *n*-alkanes in dissolved phase were always higher (10.68 µg/l) at station 2 and lower (1.89 µg/l) at station 7 (Table 2b and Fig.2b). Quantitative result of the analysis of *n*-alkanes in the dissolved phase of water presented in Table 3.

The range of carbon chain length of dissolved *n*-alkanes were C13-C32. A number of other hydrocarbons were present in the aliphatic fraction, including pristane, range (0.04-0.97 µg/l) phytane, range (0.02-0.92 µg/l), and squalane, range(0.01-1.38 µg/l) Table 3.

Values of dissolved *n*-alkanes odd/even, Carbon Preference Index (CPI) from C13 to C32 were calculated separately from each sampling section (Table 3), they varied from 0.90 to 2.73.

Representative gas chromatograms of dissolved *n*-alkanes from station 3 are shown in Fig.3.

The *n*-alkanes distribution were characterized by two patterns, the first in the range of C14 to C23 with high C17 and a slight predominance of even carbon *n*-alkanes, and the second in the range >C23 with predominance of odd carbon *n*-alkanes (Fig.3). On the other hand, the anthropogenic contribution of hydrocarbons was indicated by the presences of Unresolved Complex Mixture (UCM) in all the samples range from 0.02 to 5.63 µg/l.

The composition of particulate phase *n*-alkanes extracted from the water of shatt Al-Arab estuary and North-West Arabian Gulf during summer 1993, autumn, winter, spring and summer 1994 is presented in Table 4. The seasonal variations of the concentrations of the total particulate phase *n*-alkanes are shown in Table 5a and Fig.4a. The total *n*-alkanes concentration was calculated by summing C13 to C32

Table- 1-
Concentrations of Dissolved n-Alkanes (µg/L) in water of Shatt Al-Arab river
and North-West Arabian Gulf

Station	Carbon number																					
	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32		
Summer 1993																						
1	0.01	0.02	0.04	0.06	0.20	0.08	0.18	0.06	0.14	0.06	0.19	0.04	0.16	0.06	0.20	0.04	0.19	0.05	0.03	0.02		
2	0.02	0.16	0.19	0.18	0.25	0.27	0.23	0.18	0.28	0.31	0.36	0.29	0.39	0.28	0.42	0.30	0.25	0.26	0.19	0.16		
3	0.02	0.05	0.08	0.09	0.08	0.12	0.10	0.17	0.21	0.17	0.28	0.19	0.28	0.19	0.26	0.19	0.17	0.09	0.07	0.06		
4	0.01	0.02	0.02	0.13	0.19	0.18	0.17	0.16	0.17	0.16	0.14	0.15	0.14	0.15	0.14	0.13	0.10	0.09	0.06	0.06		
5	0.02	0.01	0.04	0.03	0.06	0.09	0.09	0.08	0.07	0.19	0.10	0.09	0.19	0.13	0.13	0.05	0.04	0.03	—	—		
6	—	—	0.02	0.01	0.17	0.16	0.08	0.08	0.09	0.07	0.09	0.04	0.06	0.07	0.06	0.04	0.04	0.03	—	—		
7	0.01	0.01	0.06	0.06	0.09	0.03	0.09	0.08	0.07	0.06	0.09	0.04	0.06	0.05	0.06	0.03	0.03	0.02	—	—		
Autumn 1993																						
1	—	—	0.04	0.19	0.25	0.33	0.27	0.31	0.40	0.31	0.28	0.18	0.12	0.12	0.27	0.28	0.25	0.13	0.10	0.04		
2	0.03	0.08	0.11	0.18	0.32	0.38	0.29	0.43	0.53	0.82	1.43	1.97	0.68	0.57	1.21	1.14	0.98	0.76	0.28	0.18		
3	0.05	0.10	0.17	0.30	0.55	0.35	0.53	0.45	0.66	0.57	1.02	0.52	0.40	0.42	1.07	0.17	0.15	0.17	0.15	0.12		
4	0.04	0.04	0.09	0.18	0.37	0.25	0.46	0.55	0.65	0.48	0.62	0.41	0.46	0.36	0.60	0.53	0.39	0.20	0.09	0.03		
5	—	—	0.04	0.08	0.29	0.26	0.23	0.24	0.26	0.16	0.23	0.20	0.28	0.26	0.34	0.25	0.14	0.11	0.07	0.04		
6	—	—	—	0.06	0.22	0.28	0.30	0.24	0.30	0.25	0.26	0.21	0.27	0.22	0.25	0.16	0.21	0.09	0.08	—		
7	—	—	0.02	0.03	0.18	0.22	0.17	0.20	0.18	0.16	0.17	0.10	0.12	0.09	0.16	0.19	0.11	0.08	0.06	0.02		
Winter 1993																						
1	0.03	0.04	0.09	0.13	0.26	0.24	0.28	0.27	0.13	0.12	0.25	0.21	0.34	0.30	0.45	0.31	0.39	0.23	0.09	0.09		
2	0.12	0.29	0.43	0.39	1.02	1.05	0.95	1.25	0.99	0.86	0.95	0.79	0.85	1.22	1.28	0.92	1.58	0.66	0.58	0.42		
3	0.02	0.02	0.03	0.03	0.60	0.67	0.96	0.99	0.91	0.83	0.78	0.51	0.50	0.52	0.63	0.95	0.55	0.37	0.20	0.12		
4	0.03	0.02	0.02	0.14	0.41	0.39	0.52	0.61	0.63	0.46	0.58	0.61	0.55	0.39	0.68	0.65	0.58	0.46	0.36	0.25		
5	0.03	0.01	0.03	0.08	0.12	0.18	0.20	0.38	0.22	0.25	0.24	0.28	0.30	0.30	0.33	0.29	0.27	0.20	0.18	0.10		
6	—	—	0.04	0.04	0.74	0.20	0.24	0.18	0.13	0.10	0.12	0.14	0.18	0.23	0.64	0.24	0.20	0.12	0.11	0.08		
7	—	0.02	0.01	0.13	0.24	0.26	0.20	0.16	0.21	0.18	0.15	0.19	0.22	0.27	0.26	0.21	0.10	0.03	0.02	—		
Spring 1994																						
1	—	—	0.03	0.03	0.07	0.08	0.12	0.13	0.16	0.18	0.22	0.26	0.24	0.20	0.25	0.12	0.10	0.06	0.05	0.03		
2	0.12	0.18	0.24	0.26	0.44	0.46	0.52	0.50	0.56	0.50	0.54	0.58	0.64	0.72	0.86	0.50	0.42	0.31	0.24	0.18		
3	—	—	0.05	0.05	0.25	0.21	0.09	0.29	0.24	0.19	0.21	0.31	0.24	0.26	0.29	0.24	0.21	0.14	0.07	0.02		
4	0.02	0.03	0.08	0.09	0.16	0.18	0.22	0.23	0.26	0.18	0.28	0.19	0.24	0.20	0.23	0.20	0.13	0.10	0.06	0.03		
5	—	0.05	0.03	0.17	0.05	0.08	0.15	0.22	0.17	0.15	0.19	0.13	0.22	0.15	0.10	0.07	0.05	0.03	0.01	—		
6	0.02	0.04	0.05	0.18	0.13	0.16	0.14	0.15	0.18	0.13	0.11	0.10	0.12	0.10	0.18	0.06	0.07	0.03	0.03	0.01		
7	—	—	0.04	0.08	0.20	0.13	0.16	0.21	0.12	0.10	0.15	0.09	0.06	0.04	0.05	0.03	0.02	0.02	—	—		
Summer 1994																						
1	—	—	0.01	0.03	0.08	0.11	0.10	0.11	0.13	0.12	0.16	0.11	0.19	0.16	0.11	0.11	0.06	0.03	0.02	0.02		
2	—	—	0.09	0.19	0.39	0.57	0.39	0.43	0.30	0.28	0.40	0.36	0.19	0.29	0.43	0.20	0.26	0.18	0.15	0.09		
3	—	—	—	0.13	0.22	0.19	0.13	0.17	0.23	0.21	0.36	0.13	0.19	0.17	0.27	0.21	0.23	0.13	0.06	—		
4	0.03	0.06	0.08	0.06	0.24	0.11	0.28	0.16	0.19	0.16	0.09	0.14	0.16	0.13	0.18	0.09	0.10	0.06	0.05	0.03		
5	—	—	—	0.03	0.10	0.12	0.13	0.16	0.13	0.11	0.16	0.10	0.16	0.09	0.11	0.09	0.06	0.05	0.03	—		
6	—	—	0.02	0.03	0.11	0.12	0.06	0.10	0.10	0.12	0.13	0.11	0.08	0.06	0.08	0.04	0.06	0.05	0.03	0.02		
7	—	—	0.01	0.03	0.08	0.06	0.07	0.05	0.08	0.07	0.09	0.06	0.05	0.04	0.08	0.04	0.03	0.02	0.02	0.01		

— = Not detected.

Table-2 -

a) Seasonal values of total n-alkanes in Dissolved water of Shatt Al-Arab estuary and North-West Arabian Gulf, June 1993-July 1994.

Station number	Concentrations in ($\mu\text{g/l}$)				
	Summer (1993)	Autumn (1993)	Winter (1993)	Spring (1994)	Summer (1994)
1	1.83	3.87	4.25	2.33	1.66
2	4.97	12.37	16.60	8.78	5.19
3	2.87	8.32	10.19	3.36	3.03
4	2.37	6.80	8.34	3.11	2.40
5	1.44	3.42	3.99	2.02	1.63
6	1.11	3.40	3.73	1.99	1.32
7	0.94	2.26	2.86	1.50	0.89

b) Regional average values of total n-alkanes in Dissolved water of Shatt Al-Arab estuary and North-West Arabian Gulf, June 1993-July 1994

Station number	Average concentrations ($\mu\text{g/l}$)
1	3.06
2	10.68
3	6.18
4	5.15
5	2.71
6	2.55
7	1.89

=====

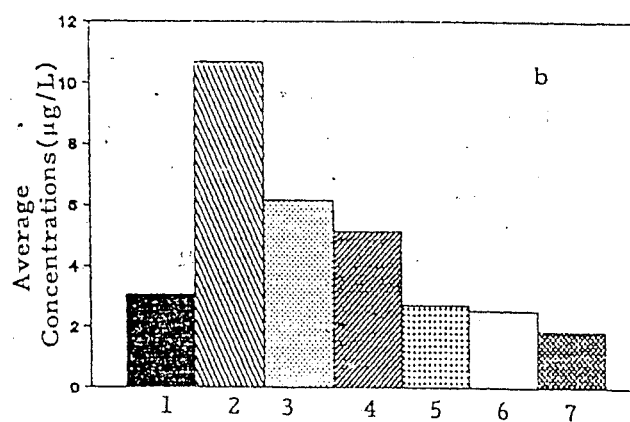
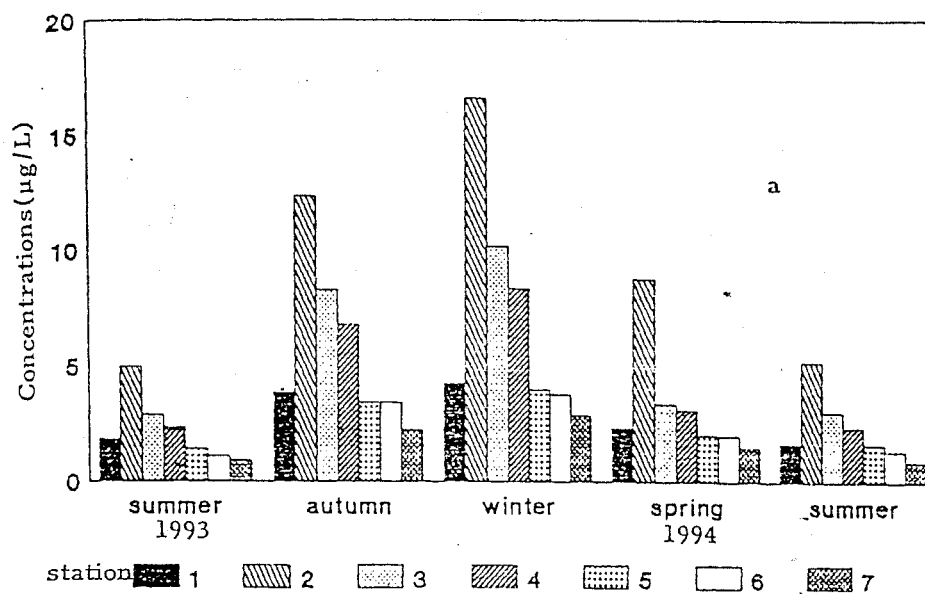


Fig. 2- a)seasonal,b)regional variations of total n-alkanes in dissolved phase of Shatt Al-Arab river and North-West Arabian Gulf

Table- 3 -

Odd and even carbon number with Pristane, Phytane, Squalane, Unresolved Complex Mixture (UCM) and total N-Alkanes in Dissolved water of Shatt Al-Arab estuary and North-West Arabian Gulf, June 1993-July 1994.

STATION	ODD	EVEN	CPI	PRI	PHY	PRI PHY	C17 PRI	C18 PHY	SQU	UCM	TOTAL N-ALKANES (µg/L)
Summer 1993											
1	1.34	0.49	2.73	0.19	0.10	1.90	1.05	0.80	—	0.06	1.83
2	2.58	2.39	1.07	0.17	0.20	0.85	1.47	1.35	0.13	0.21	4.97
3	1.55	1.32	1.17	0.09	0.08	1.12	0.88	1.50	0.01	0.08	2.87
4	1.14	1.23	0.92	0.12	0.09	1.33	1.58	2.00	0.02	0.12	2.37
5	0.74	0.70	1.05	0.05	0.04	1.25	1.20	2.25	—	0.03	1.44
6	0.61	0.50	1.72	0.12	0.13	0.92	1.41	1.23	—	0.02	1.11
7	0.56	0.38	1.47	0.06	0.05	1.20	1.50	0.60	—	0.03	0.94
Autumn 1993											
1	1.98	1.89	1.04	0.20	0.41	0.48	0.80	1.24	—	1.31	3.87
2	5.86	6.51	0.90	0.29	0.37	0.78	0.90	0.97	0.32	5.63	12.37
3	4.95	3.37	1.46	0.46	0.32	1.43	0.83	0.91	0.21	3.28	8.32
4	3.77	3.03	1.24	0.30	0.28	1.07	0.81	1.12	0.11	2.67	6.80
5	1.88	1.54	1.22	0.20	0.24	0.83	0.68	0.92	—	1.42	3.42
6	1.89	1.51	1.25	0.19	0.29	0.65	0.86	1.03	—	1.38	3.40
7	1.17	1.09	1.07	0.16	0.20	0.80	0.88	0.90	—	1.03	2.26
Winter 1993											
1	2.31	1.94	1.19	0.20	0.23	0.86	1.30	1.04	0.18	2.31	4.25
2	8.75	7.84	1.11	0.97	0.92	1.05	1.05	1.14	1.38	4.69	16.60
3	5.18	5.01	1.03	0.42	0.53	0.79	1.42	1.26	0.62	2.48	10.19
4	4.36	3.98	1.09	0.11	0.21	0.52	3.72	1.85	0.42	1.38	8.34
5	1.92	2.07	0.92	0.09	0.12	0.75	1.33	1.50	0.36	0.28	3.99
6	2.40	1.33	1.80	0.32	0.53	0.60	2.31	0.37	0.09	0.19	3.73
7	1.41	1.45	0.97	0.16	0.20	0.80	1.50	1.30	0.18	1.26	2.86
Spring 1994											
1	1.24	1.09	1.13	0.07	0.06	1.16	1.00	1.33	—	1.02	2.33
2	4.58	4.20	1.09	0.32	0.42	0.76	1.37	1.09	0.62	3.12	8.78
3	1.65	1.71	0.96	0.18	0.16	1.12	1.38	1.31	0.18	1.20	3.36
4	1.68	1.43	1.17	0.14	0.15	0.93	1.14	1.20	—	1.98	3.11
5	0.97	1.05	0.92	0.04	0.02	2.00	1.25	4.00	—	1.07	2.02
6	1.03	0.96	1.07	0.10	0.08	1.25	1.30	2.00	—	0.02	1.99
7	0.80	0.70	1.14	0.18	0.11	1.63	1.11	1.18	—	0.73	1.50
Summer 1994											
1	0.86	0.80	1.07	—	—	—	—	—	—	0.06	1.66
2	2.59	2.60	0.99	0.21	0.13	1.61	1.85	4.38	0.09	2.08	5.19
3	1.69	1.34	1.26	—	—	—	—	—	—	—	3.03
4	1.40	1.00	1.40	0.18	0.08	2.25	1.33	1.37	0.06	1.31	2.40
5	0.88	0.75	1.17	0.08	0.10	0.80	1.25	1.20	—	0.12	1.63
6	0.67	0.65	1.03	0.09	0.18	0.50	1.22	0.66	—	0.38	1.32
7	0.51	0.38	1.34	0.06	0.10	0.60	1.33	0.60	—	0.25	0.89

CPI = Carbon Preference Index.

— = Not detected.

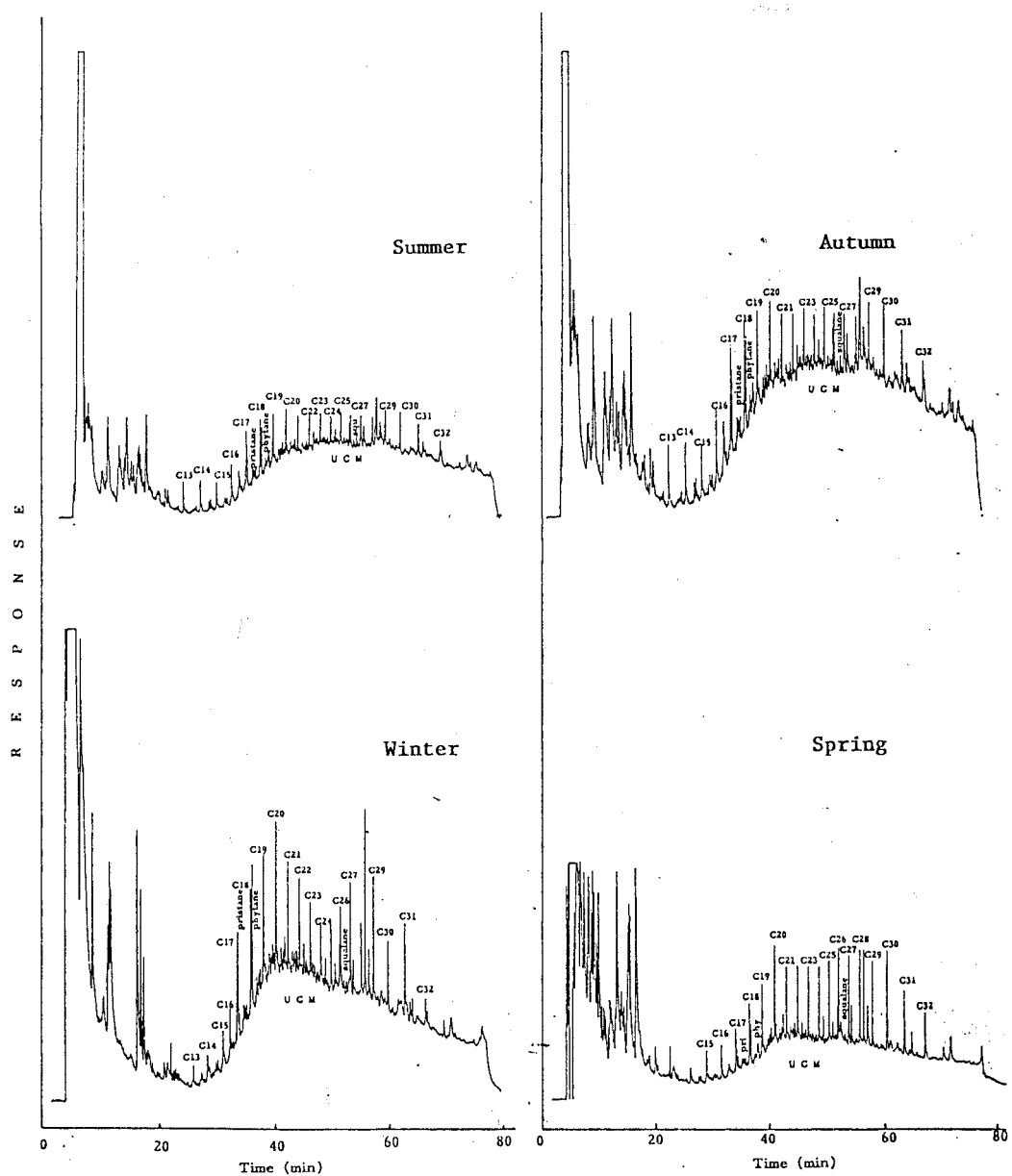


Fig.3- Representative capillary gas chromatograms (GC/FID) of n-alkanes in dissolved phase from station 3 during the four seasons

Table-4-
Concentrations of Particulate n-Alkanes (µg/g) in water of Shatt Al-Arab river
and North-West Arabian Gulf

Station	Carbon number																		31	32
	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30		
Summer 1993																				
1	0.01	0.01	0.09	0.08	0.14	0.20	0.21	0.16	0.18	0.17	0.16	0.15	0.23	0.12	0.22	0.11	0.08	0.05	0.02	0.02
2	—	—	0.02	0.02	0.37	0.42	0.28	0.43	0.52	0.36	0.28	0.16	0.53	0.24	0.79	0.20	0.22	0.20	0.17	0.10
3	0.01	0.01	0.02	0.02	0.14	0.21	0.19	0.15	0.31	0.23	0.15	0.12	0.32	0.18	0.45	0.20	0.16	0.14	0.13	0.05
4	0.01	0.01	0.02	0.04	0.21	0.23	0.27	0.20	0.24	0.18	0.28	0.21	0.19	0.21	0.18	0.17	0.17	0.14	—	—
5	0.01	0.01	0.01	0.09	0.12	0.16	0.16	0.16	0.19	0.14	0.17	0.20	0.23	0.14	0.17	0.14	0.09	0.03	—	—
6	—	—	0.02	0.02	0.17	0.03	0.10	0.14	0.15	0.14	0.16	0.18	0.16	0.14	0.16	0.13	0.12	0.10	0.02	0.02
7	—	—	0.01	0.01	0.10	0.09	0.08	0.09	0.09	0.17	0.18	0.15	0.19	0.17	0.20	0.10	0.09	0.06	—	—
Autumn 1993																				
1	0.03	0.03	0.10	0.08	0.22	0.24	0.34	0.30	0.38	0.29	0.32	0.26	0.35	0.28	0.39	0.20	0.27	0.15	0.10	0.08
2	0.10	0.25	0.31	0.42	0.60	0.67	0.70	0.67	0.59	0.56	0.91	0.70	0.84	0.73	0.56	0.63	0.25	0.35	0.24	0.21
3	0.04	0.12	0.21	0.25	0.42	0.59	0.48	0.42	0.38	0.29	0.48	0.42	0.46	0.50	0.63	0.54	0.50	0.38	0.33	0.21
4	0.10	0.12	0.14	0.13	0.38	0.50	0.46	0.32	0.36	0.29	0.34	0.32	0.46	0.38	0.45	0.41	0.46	0.29	0.23	0.15
5	—	0.08	0.06	0.11	0.28	0.26	0.22	0.23	0.26	0.24	0.21	0.24	0.28	0.26	0.31	0.26	0.18	0.16	0.10	—
6	—	—	0.03	0.03	0.18	0.22	0.29	0.25	0.23	0.21	0.26	0.18	0.27	0.16	0.18	0.13	0.16	0.08	0.09	0.06
7	—	—	0.04	0.06	0.12	0.10	0.19	0.18	0.13	0.16	0.14	0.10	0.12	0.17	0.20	0.11	0.16	0.11	0.06	0.05
Winter 1993																				
1	0.01	0.01	0.02	0.31	0.62	0.59	0.52	0.51	0.53	0.40	0.44	0.49	0.25	0.32	0.43	0.37	0.27	0.10	0.05	0.01
2	—	—	0.06	0.12	0.83	1.92	1.20	1.10	1.09	1.85	0.73	0.68	0.43	0.58	0.77	0.48	0.32	0.10	0.09	0.09
3	—	0.09	0.15	0.27	0.72	0.90	1.17	0.84	0.72	0.68	0.49	0.21	0.27	0.36	0.57	0.37	0.27	0.21	0.09	—
4	—	—	0.07	0.17	0.58	0.35	0.92	0.82	1.22	0.98	0.95	0.40	0.37	0.25	0.18	0.14	0.11	0.06	—	—
5	—	0.03	0.07	0.06	0.42	0.51	0.73	0.38	0.26	0.35	0.40	0.47	0.50	0.27	0.12	0.10	0.09	0.06	0.05	—
6	—	0.01	0.03	0.14	0.31	0.36	0.39	0.42	0.46	0.38	0.39	0.25	0.39	0.33	0.36	0.16	0.13	0.07	0.06	—
7	—	0.03	0.06	0.09	0.19	0.21	0.26	0.22	0.28	0.25	0.21	0.26	0.28	0.19	0.26	0.16	0.10	0.07	0.03	—
Spring 1994																				
1	0.03	0.05	0.09	0.12	0.18	0.20	0.23	0.26	0.28	0.20	0.30	0.21	0.29	0.23	0.26	0.23	0.16	0.13	0.10	0.06
2	—	—	0.08	0.16	0.54	0.70	0.65	0.75	0.62	0.58	0.55	0.49	0.40	0.32	0.35	0.38	0.27	0.24	0.16	0.08
3	—	—	0.16	0.23	0.38	0.25	0.49	0.40	0.38	0.30	0.36	0.35	0.18	0.15	0.30	0.26	0.20	0.19	0.16	0.13
4	0.03	0.05	0.06	0.09	0.21	0.18	0.26	0.24	0.32	0.21	0.32	0.38	0.42	0.46	0.39	0.26	0.23	0.09	0.06	0.03
5	—	—	0.03	0.06	0.26	0.18	0.24	0.28	0.23	0.21	0.20	0.18	0.15	0.11	0.14	0.13	0.10	0.09	0.06	0.03
6	—	—	0.03	0.05	0.18	0.12	0.20	0.29	0.25	0.23	0.26	0.22	0.18	0.16	0.12	0.10	0.09	0.06	—	—
7	—	—	0.10	0.18	0.20	0.16	0.14	0.16	0.10	0.22	0.18	0.16	0.10	0.06	0.09	0.02	0.03	0.02	—	—
Summer 1994																				
1	—	—	—	—	0.15	0.12	0.20	0.29	0.39	0.23	0.15	0.10	0.12	0.15	0.22	0.10	0.05	0.03	—	—
2	—	—	0.15	0.20	0.44	0.59	0.63	0.70	0.48	0.51	0.30	0.23	0.21	0.10	0.18	0.10	0.08	0.05	—	—
3	—	—	0.09	0.18	0.38	0.31	0.28	0.32	0.47	0.26	0.28	0.22	0.09	0.14	0.12	0.06	0.03	0.01	—	—
4	—	—	0.05	0.07	0.12	0.26	0.21	0.28	0.30	0.22	0.21	0.10	0.13	0.16	0.20	0.15	0.28	0.10	0.03	0.02
5	—	—	—	—	0.09	0.15	0.20	0.28	0.42	0.26	0.16	0.15	0.11	0.12	0.08	0.05	0.03	0.03	—	—
6	—	—	—	—	0.06	0.14	0.20	0.28	0.40	0.18	0.14	0.10	0.17	0.08	0.09	0.06	0.03	0.02	—	—
7	—	—	—	—	0.08	0.12	0.18	0.21	0.23	0.20	0.18	0.12	0.09	0.06	0.05	0.06	0.03	0.02	—	—

— = Not detected

Table- 5ⁱⁱ

a) Seasonal values of total n-alkanes in particulate water of Shatt Al-Arab estuary and North-West Arabian Gulf, June 1993-July 1994

Station number	Concentrations in (µg/g)				
	Summer (1993)	Autumn (1993)	Winter (1993)	Spring (1994)	Summer (1994)
1	2.41	4.41	6.25	3.61	2.30
2	5.31	10.29	12.44	7.32	4.95
3	3.19	7.65	8.38	5.27	3.24
4	2.96	6.29	7.57	4.29	2.89
5	2.22	3.74	4.87	2.68	2.13
6	2.03	3.01	4.64	2.54	1.95
7	1.78	2.18	3.15	1.92	1.68

b) Regional average values of total n-alkanes in particulate water of Shatt Al-Arab estuary and North-West Arabian Gulf, June 1993-July 1994

Station number	Average concentrations (µg/g)
1	4.17
2	8.84
3	6.12
4	5.27
5	3.37
6	3.05
7	2.23

compounds. A range of 1.73 $\mu\text{g/g}$ at station 7 to 5.31 $\mu\text{g/g}$ at station 2 in summer and a range of 3.15 $\mu\text{g/g}$ at station 7 to 12.44 $\mu\text{g/g}$ at station 2 during winter (Table 5b and Fig. 4b). Higher concentrations of n-alkanes were observed in winter than summer. The quantitative result of the analysis of particulate n-alkanes are presented in Table 6. The distribution patterns of these n-alkanes showed some variations between the sampling sites. The concentrations of pristane, phytane and squalane are presented in Table 6, and they ranged between 0.03–0.98, 0.09–1.13, and 0.02–0.63 $\mu\text{g/g}$ respectively. Pristane and phytane were the most isoprenoid in the samples suggesting biological origin. The odd to even carbon number ratio of n-alkanes was calculated over the same range C13–C32. This gave values ranged from 0.79 to 1.49, which reflect different sources of n-alkanes in the particulate phase. Typical gas chromatograms of station 3 are illustrated in Fig. 5. Normal alkanes showed a regular distribution pattern of the odd and even carbon numbers for compounds between C13 to C32 with additional characteristics associated with biological phenomena; abundance of C17 and C19 of algal origin and C25, C27 and C29 of terrestrial plants inputs was evident. The presence of UCM range (0.06–4.38 $\mu\text{g/g}$) may reflect the anthropogenic (urban and petroleum related) inputs.

The analysis of dissolved and particulate matter in Shatt Al-Arab estuary and North West region of the Arabian Gulf has shown the presence of a wealth of hydrocarbon markers providing information on the sources of organic matter. The basin of Shatt Al-Arab estuary has been reported to receive annually considerable amount of hydrocarbons (Al-Saad and Al-Timari, 1993). Al-Saad (1995), and Bedair and Al-Saad (1992) indicated that both biogenic and anthropogenic inputs are transported in the form of dissolved and particulate adsorbed matter within the water column of this economically important water body.

The concentration of total n-alkanes obtained in dissolved phase ranged from 0.89 to 16.60 $\mu\text{g/l}$ and for particulate phase from 1.68 to 12.44 $\mu\text{g/g}$. A summary of pertinent concentrations of dissolved and particulate n-alkanes from a number of different geographical areas are compared with those obtained in the present investigation (Table 7 and 8) respectively. This data indicated that the area contains lower levels of n-alkanes than other areas of the world.

Kennicutt and Jeffery (1981) observed that the aliphatic fractions of dissolved and particulate materials in the Gulf of Mexico were dominated by n-alkanes in the range C16 to C32. Dissolved aliphatic hydrocarbons often showed a bimodal distribution with a maximum of C19 or C20 which was likely to have a source of phytoplankton and a second maximum at C32 which was likely to have a source of terrestrial plants. N-alkanes have been found to account for 20% of total hydrocarbons in seawater (Goutx and Saliot, 1980).

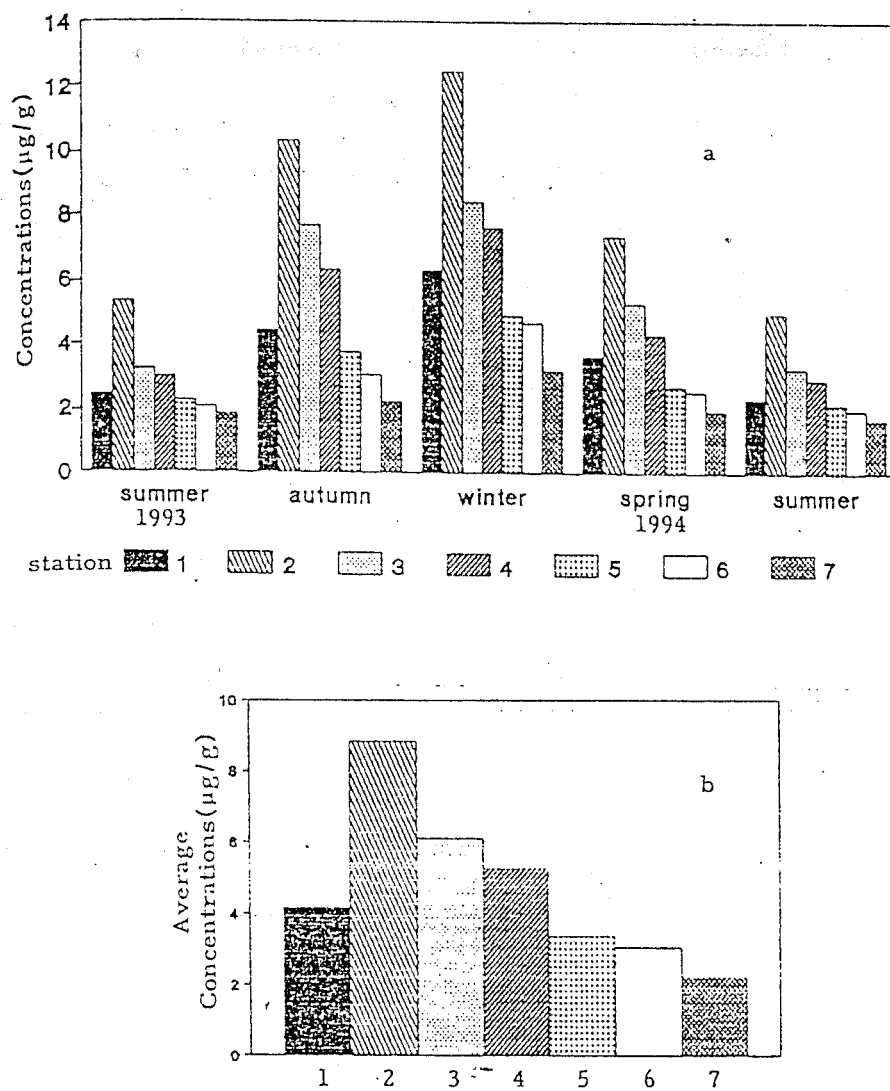


Fig. 4 - a)seasonal,b)regional, variations of total n-alkanes in particulate phase of Shatt Al-Arab river and North-West Arabian Gulf

Table - 6 -

Odd and even carbon number with Pristane, Phytane, Squalane, Unresolved Complex mixture (UCM) and total
N-Alkanes in Particulate water of Shatt Al-Arab estuary and North-West Arabian Gulf, June 1993-July 1994.

STATION	ODD	EVEN	CPI	PRI	PHY	PRI PHY	C17 PRI	C18 PHY	SQU	UCM	TOTAL N-ALKANES (µg/g)
Summer 1993											
1	1.34	1.07	1.25	0.09	0.20	4.50	1.55	1.00	0.02	0.13	2.41
2	3.18	2.13	1.49	0.33	0.40	0.82	1.12	1.05	0.63	1.82	5.31
3	1.88	1.31	1.43	0.09	0.11	0.81	1.55	1.90	0.02	0.42	3.19
4	1.57	1.39	1.12	0.21	0.23	0.91	1.00	1.00	0.02	0.32	2.96
5	1.15	1.07	1.07	0.10	0.11	0.90	1.20	1.45	—	0.23	2.22
6	1.10	0.90	1.22	0.13	0.09	1.44	1.30	0.33	—	0.09	2.00
7	0.94	0.84	1.11	0.14	0.18	0.77	0.71	0.50	—	0.06	1.78
Autumn 1993											
1	2.50	1.91	1.30	0.20	0.21	0.95	0.90	0.87	0.23	2.36	4.41
2	5.10	5.19	0.98	0.52	0.56	0.92	0.86	0.83	0.54	4.38	10.29
3	3.93	3.72	1.05	0.39	0.56	0.69	0.92	0.94	0.31	3.22	7.65
4	3.38	2.91	1.16	0.26	0.42	0.61	0.68	0.84	0.21	2.89	6.29
5	1.90	1.84	1.03	0.19	0.20	0.95	0.67	0.76	—	1.83	3.74
6	1.69	1.32	1.28	0.17	0.20	0.85	0.94	0.90	—	2.33	3.01
7	1.16	1.02	1.13	0.08	0.09	0.88	0.66	0.90	—	0.89	2.18
Winter 1993											
1	3.14	3.11	1.00	0.52	0.50	1.04	1.19	1.18	0.20	2.36	6.25
2	5.52	6.92	0.79	0.72	1.02	0.70	1.15	1.88	0.31	4.21	12.44
3	4.45	3.73	1.13	0.98	1.13	0.86	0.73	0.79	0.03	2.48	8.38
4	4.40	3.17	1.38	0.42	0.47	0.89	1.38	0.74	—	1.52	7.57
5	2.64	2.23	1.18	0.48	0.63	0.79	0.87	0.80	0.18	2.71	4.87
6	2.52	2.12	1.18	0.26	0.43	0.60	1.19	0.83	0.29	3.46	4.64
7	1.67	1.48	1.12	0.09	0.13	0.69	2.11	1.61	0.09	1.56	3.15
Spring 1994											
1	1.92	1.69	1.13	0.16	0.17	0.94	1.12	1.17	0.11	2.31	3.61
2	3.62	3.70	0.97	0.44	0.68	0.64	1.22	1.02	0.22	4.23	7.32
3	2.81	2.46	1.14	0.30	0.28	1.07	1.26	0.89	0.18	2.20	5.27
4	2.30	1.99	1.15	0.20	0.16	1.25	1.05	1.12	0.23	2.46	4.29
5	1.41	1.27	1.11	0.24	0.20	1.20	1.08	0.90	—	1.62	2.68
6	1.31	1.23	1.06	0.14	0.13	1.07	1.28	0.92	—	1.41	2.54
7	0.94	0.98	0.95	0.12	0.09	1.33	1.66	1.77	—	0.93	1.92
Summer 1994											
1	1.28	1.02	1.25	0.23	0.13	1.76	0.65	0.92	—	0.15	2.30
2	2.47	2.48	0.99	0.36	0.45	0.80	1.22	1.31	0.08	2.36	4.95
3	1.74	1.50	1.16	0.16	0.52	0.30	2.37	0.59	—	1.24	3.24
4	1.53	1.36	1.12	0.10	0.22	0.45	1.20	1.18	0.03	1.73	2.89
5	1.09	1.04	1.04	0.03	0.18	0.16	3.00	0.83	—	1.06	2.13
6	1.09	0.86	1.26	—	0.20	—	—	0.70	—	1.03	1.95
7	0.89	0.79	1.12	—	0.16	—	—	0.75	—	0.97	1.68

CPI = Carbon Preference Index.

— = Not detected.

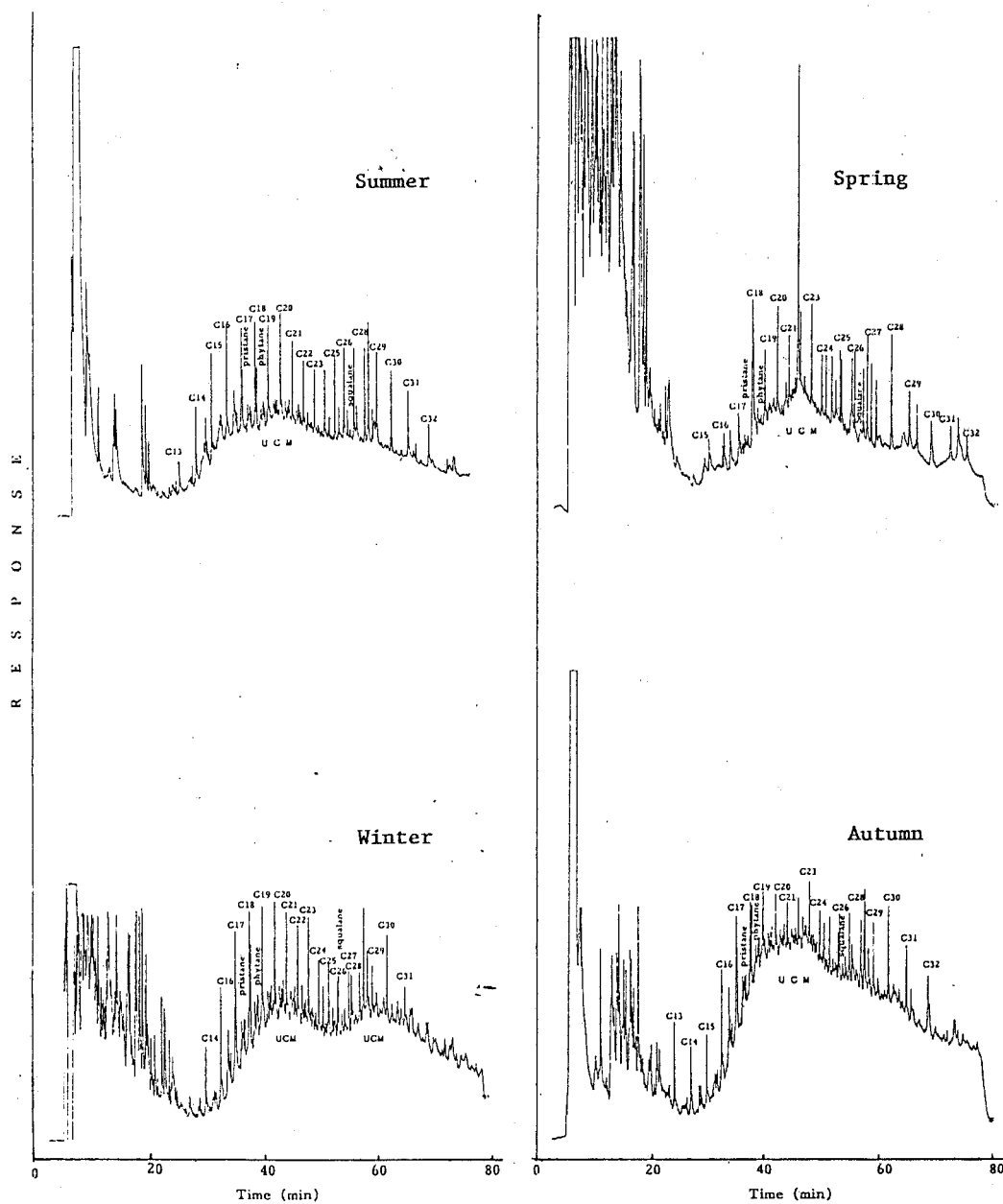


Fig.5- Representative capillary gas chromatograms (GC/FID) of n-alkanes in particulate phase from station 3 during four seasons

Table -7-
Comparison of values of Dissolved n-alkanes in Shatt Al-Arab River and
North-West Arabian Gulf with other values of the world

Location	Concentration ($\mu\text{g/l}$)	References
Tropical region of Atlantic	5.7	Marty & Sailot (1976)
North-Sea	2.4-7.2	Hardy et al., (1977)
North-Atlantic (U.S.A)	14-60	Boehm (1980)
Villefranche bay (France)	0.13-44.60	Goutx & Sailot (1980)
Mediterranean Sea	0.0-20.6	Ho et al., (1984)
Erbo Delta (Espain)	5.3-35	Gomez Belinchon et al., (1988)
South Georgia (U.S.A)	2.06-10.14	Cripps (1989)
Bermoda	0.40-1.31	Ehrhardt & Burns (1990)
Antratic	4.4-11.1	Cripps (1992)
Shatt Al-Arab Estuary	3.20-8.40	Bedair & Al-Saad (1992)
Mediterranean	49-51	Ehrhardt & Petrick (1993)
Shatt Al-Arab & NW Arabian Gulf	1.89-10.68	Present study

Table-8-
Comparison of values of Particulate n-alkanes in Shatt Al-Arab River
and North-West Arabian Gulf with other values of the world

Location	Concentration ($\mu\text{g/g}$)	References
Willenfranche bay (France)	0.02-12.0*	Goutx & Sailot (1980)
North-West Atlantic	0.99*	Boehm (1980)
Erbo Delta (Espain)	16.0-290.0	Gomez Belinchon et al., (1988)
South Georgia	1040	Cripps (1989)
Terranova Bay (Antratica)	13.0-103.0	Desideri et al., (1991)
Shatt Al-Arab Estuary	1.48-5.80	Bedair & Al-Saad (1992)
Shatt Al-Arab & NW Arabian Gulf	2.23-8.84	Present study

* = concentrations in (ng/l)

Boehm (1980) and Goutx and Saliot (1980) examined seasonal variations in dissolved and particulate hydrocarbons. They found that particulate hydrocarbons concentrations were related to biological productivity, while, dissolved hydrocarbons seemed to be more of an indicator of pollution.

The n-alkanes distribution of dissolved and particulate in the study area are characterized by two patterns. The first in the range of C13 to C23 with high C17 and a slight predominance of even carbon n-alkanes, and the second is in the range >C23 with predominance of odd carbon n-alkanes (Figs. 3 and 5). This mode has also been observed previously in water and sediment of the same area (Grimalt et al., 1985; Bedair and Al-Saad, 1992 and Al-Saad and Al-Timari, 1993).

N-alkanes with odd carbon numbers lower than C21 such as C15, C17 and C19 are commonly found in algae (Goutx and Saliot, 1980 and Youngblood et al., 1971), C20 to C28 model n-alkanes without carbon number preference, maximizing around C23, may be produced by bacterial activity (Grimalt et al., 1985 and Grimalt and Albaiges, 1990) and C25 to C32 odd carbon number n-alkanes are indicative of higher plants (Simoneit, 1991). This may be considered as evidence for the aquatic biogenic origin of n-alkanes in Shatt Al-Arab estuary and North-West Arabian Gulf. Many aquatic plants are abundant in Shatt Al-Arab estuary and are likely to be the main source of n-alkane in the estuary (Bedair and Al-Saad, 1992 and Al-Saad, 1994).

The contribution of other sources of n-alkanes in our samples may be due to higher land-based vegetation, reflected by the predominance of n-alkanes with an odd number of carbon atoms. This predominance is observed for the first time in the present samples, and encountered in a more pronounced manner in the water probably under the effect of aeoline contributions, and terrestrial inputs derived from plant material (Al-Saad and Al-Timari, 1993).

The relatively high C17 may indicate that photo-synthesis organism are the main source of n-alkanes in this estuary.

Other evidence on the aquatic biogenic origin of n-alkanes may be derived from diatoms populations which contain a range of n-alkanes from C15 to C31. Diatoms have been found to be the most dominant group of phytoplankton in Shatt Al-Arab estuary (Al-Saboonchi and Al-Saad, 1988) and North-West Arabian Gulf (Al-Handal, 1988). Therefore it may be concluded that diatoms are the most likely source of n-alkanes with even to odd carbon predominance encountered in Shatt Al-Arab estuary and North-West Arabian Gulf. Therefore, the distribution of such alkanes can be utilized as a potential marker for defining diatoms as contributors to marine sediments.

The isoprenoids hydrocarbons in the dissolved and particulate phase result mainly from aquatic organisms either directly, in the case of pristane, from zooplankton and from decomposition of algae (Blumer and Snyder, 1963), and phytane originating from several types of bacteria and from deposition of algae (Simoneit, 1991),

or these isoprenoids came indirectly from aquatic biomolecules such as chlorophyll (Didyk et al., 1978). Chlorophyll from land-plant sources providing the high molecular weight n-alkanes could serve as a source of some isoprenoids hydrocarbons. Pristane and phytane were the most common isoprenoids obtained in the present study.

Weathered petroleum product could also include pristane and phytane as natural by-product. The ratio of these isoprenoids with C17 to pristane and C18 to phytane for dissolved and particulate phases are listed in Table 3 and 6 respectively. These ratios involve both biogenic and anthropogenic compounds, and confirm the strong biodegradation of hydrocarbons occurring in the area (Cripps, 1989).

Squalane was also present in some samples, which is presumably derived from artificial sources, except for fossil fuel product, rather than from natural sources. Although squalane has widely been used everyday's life, it has scarcely been found in living organism (Cripps, 1990).

Al-Saad (1990) and Al-Saad and Al-Timari (1993) concluded that presence of squalane in Shatt Al-Arab estuary and North-West Arabian Gulf may originated from living organisms or from anthropogenic sources.

All chromatograms of the sampled analysed showed a measurable unresolved envelope (hump). The material in this envelope is often referred to as the Unresolved Complex Mixture (UCM). Concentration of UCM for dissolved and particulate samples are listed in Table 3 and 6 respectively and shown in Figs. 3 and 5. In general the presence of UCM is normally associated with petroleum contamination (Gough and Rowland, 1990). However, there are possible sources of UCM other than human activities like those synthesized by some anaerobic nonphotosynthetic bacteria (Han and Calvin, 1969) and green algae which are widely distributed in natural environment (Brook et al., 1977). At the same time microbial oxidation of hydrocarbons in either the sediment or water will reduce the n-alkanes contents relative of UCM. UCM detected in the present study could be related to the production, use and transportation of petroleum products around the port area of Abadan (Grimalt et al., 1985). Thus, the natural biogenic materials must be distinguished from the anthropogenic components in order to reconcile possible source.

Carbon Preference Index (CPI) a measure of carbon number predominance of homologous compound series is useful to make an estimation of plant wax contribution versus fuel contamination.

Reflecting biochemical specificity, the n-alkanes of plant wax show a pronounced odd carbon number predominance or $CPI > 1$, while fossil fuel hydrocarbons have $CPI = 1$ (Simoneit, 1993). In the present samples n-alkanes ranged from C13 to C32, while a definite odd carbon number predominance above C23. Almost all samples, strongly suggest the predominance of vascular plant wax input. This is in agreement with (Bedair and Al-Saad, 1992; Al-Saad and Al-Timari, 1993 and Grimalt and

Albaiges, 1990). Therefore, CPI more than one indicates more complex biogenic sources, while with station 2, the pattern is easily obscured by petroleum contamination which tend to reduce CPI to unity. The odd and even carbon number n-alkanes are present in equal amount in petroleum products such as kerosine, diesel soots, engine oil and used crankcase oil (Mazurek et al., 1991). These artificial hydrocarbons sources contain a large proportion of UCM (Gough and Rowland, 1990).

In station 2, even-carbon numbered n-alkanes were present as the major constituents. This may again be explained by the contribution of hydrocarbons of artificial sources. Moreover, atmospheric fallout, oil washing from road, disposal of crankcase oil and industrial lubricants and accidental or intentional discharge of fuel oil are possible sources of artificial hydrocarbons to urban river water (Bedair and Al-Saad, 1992 and Gough and Rowland, 1990).

One reason for the low concentrations of dissolved alkanes may be their poor water solubility as compared with aromatic fractions (Wan et al., 1990).

Dissolved alkanes may be removed by microbial decomposition too (Leahy and Colwell, 1990). Low n-pentadecane/pristane and n-octadecane/phytane ratio often invoked demonstrate microbial hydrocarbon degradation, since normal hydrocarbons are biodegraded more rapidly than those with a branched carbon chain (Ratledge, 1978). However microbial degradation play a limited role in removing saturated hydrocarbons from nutrient-depleted water, which is not the case in the study area.

Since microbial decomposition could be a slow process, other effective "sink" must exist to keep hydrocarbon concentrations at the observed low levels (Ehrhardt and Petrick, 1993). In this respect Burns et al., (1985) showed that large fractions of hydrocarbons input is transported from the surface seafloor by rapidly sinking zooplankton fecal pellets, and that a considerable fraction of this hydrocarbon is biodegraded before the incorporation of the remainder to the sediments.

Another potential mechanism of removal is "photo-oxidation". N-alkanes lacking absorption band at sea surface solar UV frequencies (Ehrhardt and Petrick, 1993). However Ehrhardt and Weber (1991) showed that the Anthraquinone-sensitized photo-decomposition of n-alkanes is relatively effective. Of many photo-sensitizers likely to be present, Anthraquinone and Fluorenone were demonstrated by their characteristic mass spectra to occur in North-West Arabian Gulf water (Ehrhardt and Burns, 1993). This strongly suggest that photo-oxidation not only change the composition of oil residues dissolved in surface water by structure-dependent preferential depletion, but also like to play an important role in removing dissolved

hydrocarbons from oligotrophic water bodies (Ehrhardt and Burns, 1993). Small particles suspended in water are either biogenic (living or dead) or originating from the breaking apart of environmental degraded, floating lump of oil. They may also be composed of mineral phases. Biogenic particles, i.e. plankton, zooplankton and organic detritus, contain biosynthesized hydrocarbons, as has been shown by Blumer et al., (1971). As the lipophilicity of biogenic particles is higher than that of water, and lithogenic particles scavenge dissolved lipophilic material from water and, upon sinking, mediate its vertical transport. In the particulate phase, a value of Cpl greater than unity indicates a recent biogenic contribution. The adsorption of petrogenic aliphatic hydrocarbons from solution and/or the possible presence of microscopic solid oil residue did not eliminate the biogenic signature in the particulate material. This finding is an evidence of decoupling of dissolved and particulate hydrocarbons and co-occurs with the result published by several authors (Boehm, 1980; Goutx and Saliot, 1980; Albaiges et al., 1984; Gomez-Belinchorn et al., 1988 and Ehrhardt and Petrick, 1993). There are major quantitative differences between dissolved and particulate n-alkanes during cold and warm periods.

Levels of n-alkanes (biogenic and anthropogenic) are from two or four times as higher in winter for both dissolved and particulate than in summer (Tables 1 and 5 and Figs. 2 and 4). Possible reasons for these seasonal variations are processes brought about by temperature variations, including evaporation, bacterial degradation, adsorption as well as chemical oxidation.

N-alkanes in the environment are biodegraded primarily by the bacteria under the effect of temperature. At low temperature the viscosity of oil increases, the volatilization of toxic short chain alkanes is reduced, and their water solubility increases (Leahy and Colwell, 1990). Rates of degradation are generally observed to decrease with decreasing temperature. The rate of microbial degradation of hydrocarbons is dependent, amongst other variable, upon the availability of nutrients and hydrocarbon degraders have to compete for these with other planktonic organisms. There is, thus, reason to believe that microbial decomposition of n-alkanes should be a relatively slow process under conditions of nutrient limitation. Such conditions are often encountered during cold winter, making degradation a slow process. On the other hand the intense sunlight may enhance the importance of a different mode of decomposition i.e. photo-oxidation (Ehrhardt and Burns, 1990).

Physical, chemical and biological removal mechanism will also reduce the concentration of photo-oxidation products of n-alkanes product under the local conditions, however, their combined rates must be slower than the corresponding rates of n-alkanes degradation. In a situation where the joint effect of removal mechanisms is even less effective, concentrations of photo-oxidation product may

therefore reach considerable values relative to n-alkanes precursors, as has been observed in Arabian Gulf water by Ehrhardt and DouAbul (1989). This reduces the concentrations of n-alkanes during summer due to their rapid photolysis, there is a clear seasonal variations in the average values of suspended matter being at maximum in winter. Therefore, higher concentrations of n-alkanes observed in the water during winter could be caused in part by the decreased sedimentation of sorbed n-alkanes. The same conclusion was reached by Douabul and Al-Saad (1985).

Accordingly the effects of temperature variations including bacterial degradation, photochemical oxidation as well as adsorption are postulated to produce pronounced seasonal variations of n-alkanes in Shatt Al-Arab estuary and North-West Arabian Gulf.

As a conclusion :

- ## N-alkanes distribution in dissolved and particulate were characterized by two patterns. The first in the range of C13 to C23 with high C17 and slight predominance of even carbon n-alkanes which associated with biological phenomena, and the second in the range of >C23 with predominance of odd carbon n-alkanes of aquatic terrestrial plants inputs.
- ## Pristane and phytane were the most isoprenoids found in most samples suggesting biological origin, while squalane and UCM could have biogenic or anthropogenic origins.
- ## Diatoms were likely source of n-alkanes with even to odd carbon predominance encountered in Shatt Al-Arab estuary and North-West Arabian Gulf, and therefore the distribution of such alkanes could be utilized as a potential marker for defining diatoms as contributors to aquatic sediment.
- ## An evidence of decoupling of dissolved and particulate hydrocarbons was found in Shatt Al-Arab estuary.
- ## There is a seasonal variations of n-alkanes in dissolved and particulate phases of the water of Shatt Al-Arab estuary and North-West region of the Arabian Gulf.

REFERENCES

- Albaiges, J., Grimalt, J., Bayona, M., Risèbrough, R., Delappe, B. and Walker, H.W. (1984) Dissolved, particulate and sedimentary hydrocarbons in a deltic environment. *Org. Geochem* 6:237-248.
- Al-Handal, A.K. (1988) Plankton Diatoms of North-West Arabian Gulf. *Mar. Mesopotamica* 3:43-101.
- Al-Saad, H.T. (1990) Distribution and sources of aliphatic hydrocarbons in fish from the Arabian Gulf. *Mar. Pollut. Bull.* 21:155-157.
- Al-Saad, H.T. (1994) Distribution of petroleum hydrocarbons in aquatic plant of Hor Al-Hammar marsh, Iraq. *Mar. Mesopotamica* 9:313-321.
- Al-Saad, H.T. (1995) Distribution and Sources of hydrocarbons in Shatt Al-Arab estuary and North-West Arabian Gulf. Ph.D thesis. Basrah Univ. P.186.
- Al-Saad, H.T. and Al-Timari, A.K. (1993) Seasonal variations of dissolved normal alkanes in the water marshes of Iraq. *Mar. Pollut. Bull.* 26:559-564.
- Al-Saboonchi, A.M. and Al-Saad, H.T. (1988) Check list of the algae from Shatt Al-Arab river, Iraq. *J. Univ. Kuwait (Sci.)* 15:79-97.
- Avigan, J. and Blumer, M. (1968) On the origin of pristane in marine organisms. *J. Lipids. Res.* 9:350-352.
- Bedair, H.M. and Al-Saad, H.T. (1992) Dissolved and particulate adsorped hydrocarbons in the water of Shatt Al-Arab river, Iraq. *Water. Air Soil pollut.* 61:397-408.
- Blumer, M., Guillard, R.R.L. and Chase, L. (1971) Hydrocarbons of marine phytoplankton. *Mar. Biol.* 8:183-189.
- Blumer, M. and Snyder, W.D. (1963) Isoprenoid hydrocarbons in recent sediment. Presence of pristane and probal absence of phytane. *Science* 150:1588-1589.
- Boehm, P.D. (1980) Evidence for the decoupling of dissolved, particulate and surface microlayer hydrocarbons in northwestern Atlantic continental shelf waters. *Mar. Chem.* 9:255-281.
- Brooks, P.W., Eglinton, G., Gaskell, S.J., McHugh, D.J., Maxwell, J.P. and Phillips, R.P. (1977) Lipids in recent sediments. Part II. Branch and cyclic alkanes and alkonic acids of some temperature lacustrine and sub-tropical lagoonal/tidal flat sediment. *Chem. Geol.* 20:189-204.
- Burns, K.A., Villeneuve, J.P. and Fowler, S.W. (1985) Fluxes and residence time of hydrocarbons in the coastel Mediterranean: How important are the biota. *Estu. Coast. Shelf. Sci.* 20:313-330.
- Cripps, G.C. (1989) Problems in the identification of anthropogenic hydrocarbons against natural background levels in the Antractic. *Antractic Sci.* 1:307-312.
- Cripps, G.C. (1990) Hydrocarbons in the seawater and pelagic organisms of the southern ocean. *Polar Biol.* 10:393-402.
- Cripps, G.C. (1992) Baseline levels of hydrocarbons in seawater of southern ocean. Natural variability and regional patterns. *Mar. Pollut. Bull.* 24:109-114.
- Desideri, P., Lepri, L. and Chechini, L. (1991) Organic compounds in seawater and pack ice in terranova bay (Antractica). *Annali. Chim.* 81:395-416.
- Didyk, B.M., Simoneit, B.R.T., Brassel, S.C. and Eglinton, G.C. (1978) Organic geochemical indicator of paleoenvironmental conditions of sedimentation. *Nature* 272:216-222.

- DouAbul, A.A.Z. and Al-Saad, H.T. (1985) Seasonal variation of oil residues in water of Shatt Al-Arab river, Iraq. *Water, Air Soil Pollut.* 24:237-246.
- Ehrhardt, M. and Burns, K. (1993) hydrocarbons and related photo-oxidation products in Saudia Arabian gulf coastel waters and hydrocarbons in underlying sediment and bioindicators bivalves. *Mar. Pollut. Bull.* 27: 187-199.
- Ehrhardt, M.G. and Burns, K.A. (1990) Petroleum-derived organic compounds concentrated from inshore waters of Bermuda. *J. Exp. Mar. Biol. Ecol.* 128: 35-47.
- Ehrhardt, M. and DouAbul, A.A.Z. (1989) Dissolved petroleum residues and Alkylbenzene photo-oxidation products in the upper Arabian Gulf. *Mar. Chem.* 26:363-370.
- Ehrhardt, M. and Petrick, G. (1993) On the composition of dissolved and particulate association fossile fule residues in Mediterranean surface water. *Mar. Chem.* 42:57-70.
- Ehrhardt, M. and Weber, R.R. (1991) Formation of low molecular weight carbonyl compounds by sensitized photochemical decomposition of aliphatic hydrocarbons in seawater. *Fresenius J. Anal. Chem.* 339:772-776.
- GESAMP. (1993) Joint Group of Experts on the Scientific Aspect of Marine Pollution impact of oil and related chemical and wastes on the marine environment. Report and studies No.50, IMO, London. pp180.
- Gomez-Belinchon, J.I., Lopp, R., Grimalt, J.O. and Albaiges, J. (1988) The decoupling of hydrocarbons and fatty acids in the dissolved and particulate water phases of a deltic environment. *Mar. Chem.* 25:325-348.
- Gough, M.A. and Rowland, S.J. (1990) Characterization of unresolved complex mixture of hydrocarbons in petroleum. *Nature* 334:648-650.
- Goutx, M. and saliot, A. (1980) Relationship between dissolved and particulate fatty acids and hydrocarbons, chlorophyll a, and zooplankton biomass in villefranche bay, Mediterranean sea. *Mar. Chem.* 8:299-318.
- Grimalt, J.O. and Albaiges, J. (1990) Characterization of depositional environments of the Erbo Delta (Western Mediteeeanean) by the study of sedimentary lipid markers. *Mar. Geology.* 95:207-224.
- Grimalt, J., Albaiges, J., Al-Saad, H.T. and DouAbul, A.A.Z. (1985) n-alkanes distribution in surface sediments from the Arabian Gulf. *Naturwissenschaften* 72:35-37.
- Han, J. and Calvin, M. (1969) Hydrocarbons distribution of algae and bacteria and microbiological activity in sediment. *Proc. Natl. Acad. Sci. U.S.A.* 64:436-443.
- Hardy, R., Mackie, P.R., Whittle, J.K., McIntyre, A.D. and Blackman, R.A.A. (1977) Occurrence of hydrocarbons in the surface film, sub-surface water and sediment in the waters around the united Kingdom. *Rapp. P-V Reun Cons Inst Explor Mer.* 171:61-65.
- Ho, R., Marty, J.C., Saliot, A. (1984) Hydrocarbons in the western mediterranean. In: *Chemistry and analysis of hydrocarbons in the environment.* (Edt. Albaiges, J., Frei, J.W.) Gordon and Breach, London. pp 232-251.
- Kennicutt, II, M.C. and Jeffrey, L.M. (1981) Chemical and GC-MS characterization of marine dissolved lipid. *Mar. Chem.* 10:367-387.
- Leahy, J.G. and Colwell, R.R. (1990) Microbial degradation of hydrocarbons in the environment. *Microbiological Reviews.* 54:305-315.
- Marty, J.C. and Saliot, A. (1976) Hydrocarbons (n-alkanes) in surface microlayer of seawater. *Deep Sea. Res.* 23:863-873.

-
- Mazurek, M., Cass, G.R. and Simoneit, B.R.T. (1991) Biological input to visibility-reducing aerosol particles in remote arid southwestern United States. *Envir. Sci. Technol.* 25:684-694.
- Ratledge, C. (1978) Degradation of aliphatic hydrocarbons. In: *Developments in biodegradation of hydrocarbons-1* (Edt. Watkinson, R.J.) Applied Sci. Publ. London. PP 1-46.
- Simoneit, B.R.T. (1991) Organic geochemistry of deep sea-drilling project cores from legs 63-66-A- synthesis of source, preservation and maturation of organic matter in Quaternary and Neogene sediments from active continental margin. In: *The Gulf and peninsular province of California*, (Edt. Davphin, J.p. and Simoneit, B.R.T.) *Ammier. Assoc. petroleum. Geol. Memoir* 47 (1991). Tulsa, OK, USA.
- Simoneit, B.R.T. (1993) Aqueous high temperature and high pressure organic geochemistry of hydrothermal vent systems. *Geochemica et Cosmochemica Acta.* 57:3231-3243.
- UNESCO (1976) Guide to operational procedures for IGOSS pilot project on marine pollution (petroleum) monitoring, Intergovernmental Oceanographic Commission, Manual and Guide No.7, pp:1-10.
- Wan, Y.S., Bobra, M., Bobra, A.M., Maijanen, A., Suntio, L. and Mackay, D. (1990) The water solubility of crude oils and petroleum products. *Oil Chem. Pollut.* 7:54-87.
- Youngblood, W.W. and Blumer, M. (1973) Alkanes and alkenes in marine benthic algae. *Mar. Biol.* 21:163-172.
- Youngblood, W.W., Blumer, M., Guillard, R.L. and Fiore, F. (1971) Saturated and unsaturated hydrocarbons in marine benthic algae. *Mar. Biol.* 8:190-201.

الالكانات الاعتيادية في الجزء الذائب والعالق لمصب شط العرب وشمال غرب الخليج العربي

حامد طالب-السعد ، صباح متي شمشوم و جمال * كامل العبايجي
مركز علوم البحار - جامعة البصرة - البصرة - العراق
* قسم علوم الحياة - كلية العلوم - جامعة بغداد

المستخلص

تم تحليل الالكانات الاعتيادية باستخدام تقنية الغال الكروموتوغرافي المزود بالعمود الشعري في الجزء الذائب والعلق لمياه مصب شط العرب وشمال غرب الخليج العربي خلال ١٣ شهر من حزيران ١٩٩٣ الى تموز ١٩٩٤ .

لوحظ تغيرات في هذه المركبات بالجزء الذائب والعلق وان هناك حالة من التقارن التزاوجي بين الجزئين في منطقة المصب .

توزيع مركبات الالكانات في الجزء الذائب والعلق كان على هيئة نموذجين الاول في مدى كاربون ١٣ الى كاربون ٢٣ مع زيادة في ذرة كاربون ١٧ وسيادة طفيفة لذرات الكاربون المزدوجة الذي يكون مرتبط بالمصادر الطبيعية ، والثاني في مدى اكبر من كاربون ٢٣ مع سيادة لذرات الكاربون المفردة التي مصدرها من النباتات الارضية . لوحظ وجود مركبات البرستين والفائتين في معظم العينات والتي كان مصدرها طبيعي بينما وجود السكوالين والمواد غير الذائبة دليلا على المصادر الطبيعية والبشرية لهذه المركبات .

بينت الدراسة بان هنالك تغير فصلي واضح لمركبات الالكانات في الجزء الذائب والعلق لمياه شط العرب وشمال غرب الخليج العربي كون اقل التراكيز لوحظت في فصل الصيف واعلاها في فصل الشتاء .