

Seasonal variations of particulate fatty acids in waters of Shatt Al-Arab River and northwest Arabian Gulf

H.T. Al-Saad¹, A.A. Hantoush¹, M.A. Al-Hello¹ and M.K. Zukhair²

¹Marine Science Center, ²Science College, Basrah University, Iraq

Abstract - The particulate fraction of the fatty acids was investigated in water samples collected from different stations along the Shatt Al-Arab River and North-West Arabian Gulf during the period June 1993 to July 1994. Samples were analyzed by gas chromatography. Several qualitative and quantitative differences were observed. In general, palmitoleic acid (16:1), palmitic acid (16:0), heptadecanoic acid (17:0), stearic acid (18:0), oleic acid (18:1) and linoleic acid (18:2) were found to be the most abundant fatty acids in the region. Total particulate fatty acids showed large variations, from 1.45 µg/gm at station 7 (Arabian Gulf) during summer 1993 to 18.91 µg/gm at station 2 (Shatt Al-Arab River at Al-Fao town) during winter 1993. The main sources of odd and even number of fatty acids were phytoplankton and microbial activities, while aquatic plants were missing in most sites.

Introduction

The lipids are a large and diverse group of naturally occurring organic compounds that are related by their solubility in non-polar organic solvents (e.g. ether, chloroform, acetone and benzene) and generally insoluble in water references. The common feature of these lipids is that they are all esters of moderate to long chain fatty acids. Fatty acids can be derived from plankton, benthic organisms, sea grasses and marsh plants (Rodier and Khalil, 1982).

Particulate matter fatty acids are indicators of biological phytoplankton species composition and environmental parameters influencing the biochemical composition of phytoplankton are effective factors in controlling the change in particulate fatty acids (Mayzaud *et al.*, 1989). A comparison of the dissolved and particulate fractions indicates the existence of dynamic inter-relationships and various turnover processes between these components. The inability of glass-fiber filters to retain all small particles means that there is some inclusion of lipids from living bacteria and small phytoplankton in "dissolved" lipid extracts (Parrish, 1988). Ehrhardt *et al.* (1980) reported the presence of fatty acid methyl esters as occurring naturally in seawater, and the drainage water may be expected to contain lipids of natural rather than biogenic sources.

Furthermore, little is known on the fatty acids composition of particulate matter in Iraq. Al-Timari and Al-Saad (1990); Al-Saad and Al-Timari (1993) and Hantoush, *et al.* (2001) reported on the concentrations of fatty acids in the sediments and some fish species from the southern marshes, Shatt Al-Arab River and North West of Arabian Gulf. However,

several papers have described the fatty acid composition of particulate fraction for water samples in other aquatic sites of the world (Goutx and Saliot, 1980 ; Kattner *et al.* 1983 ; Gomez-Belinchon *et al.*, 1988 ; Parrish, 1988 ; Parrish *et al.*, 1992 ; Drieux *et al.*, 1998 ; Mannino and Harvey, 1999 ; Hama, 1999 ; Saliot *et al.*, 2002 and Mills *et al.*, 2003).

The origin of the dissolved and particulate fatty acids in sea water was not evident from a comparison of their individual distribution patterns with those found in phytoplankton, zooplankton or in higher trophic forms. The aim of this study is to clarify chemical characteristics of particulate fatty acids and their concentrations in Shatt Al-Arab estuary and North West Arabian Gulf.

Materials and Methods

Water samples were taken during the period June 1993 to July 1994 from seven stations in Shatt Al-Arab River and north-west Arabian Gulf (Figure 1), for the study of fatty acids in particulate fraction.

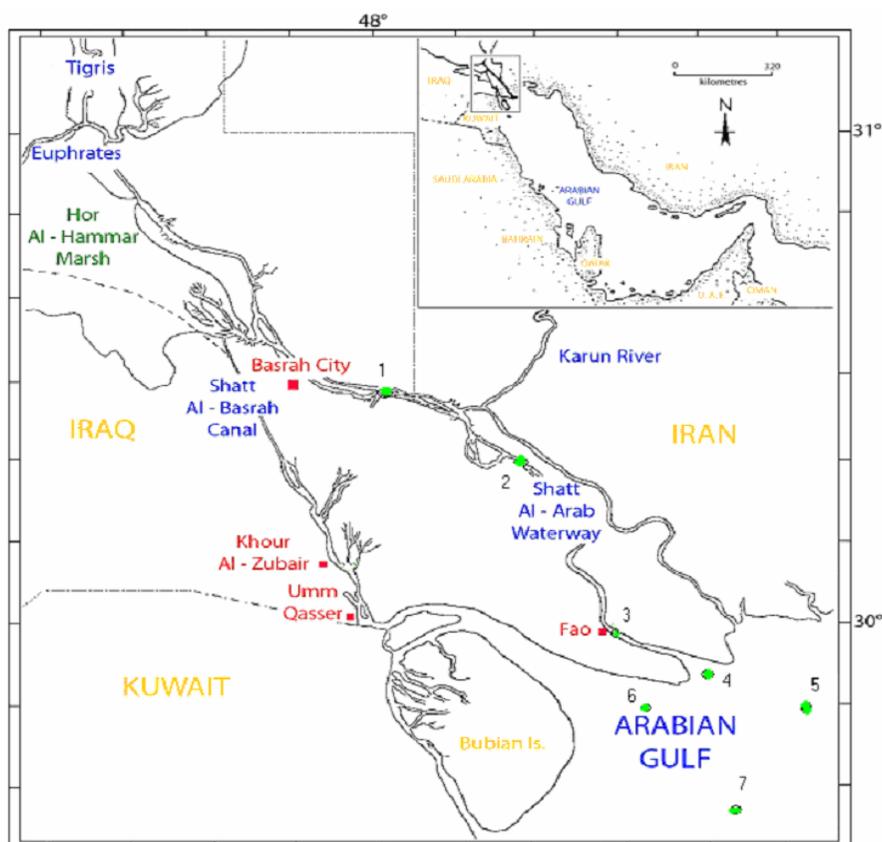


Figure 1. Map of the Shatt Arab River and NW Arabian Gulf showing the sampling stations.

Each sample (5 L) was filtered through a glass-fiber filter (Whatman GF/F) to separate the dissolved and particulate phases. The particulate fatty acids on the filter were extracted with 100 ml chloroform for 16 hours period, and the lipid fraction was rotary evaporated to dryness by a stream of pure nitrogen (Kattner and Brockmann, 1978). It was then saponified for two hours with a solution of 4N KOH in methanol: benzene (1:1). After extraction, the free fatty acids were released by 6N HCl extracted with petroleum ether. The petroleum ether was evaporated in a stream of purified, dry nitrogen. Three milliliters of 14% $\text{BF}_3\text{-CH}_3\text{OH}$ reagent were added to the residue in the test tube and the mixture was boiled for 2 min., converting the free fatty acids to their respective methyl esters (Metcalf and Schmitz, 1961). The analyses of fatty acids were done by Perkin Elmer Sigma 300 capillary gas chromatography equipped with Flame Ionization Detector (FID) and splitless model injection. The fused silica capillary column was a wall Coated Open Tubular (WCOT) 50m X 0.25mm.i.d. Helium was used as a carrier gas (1.5 ml / min.). Operating temperatures for detector and injector were 350 °C and 320 °C respectively. The column was operated under temperature programmed conditions from 50 °C for 4 min. to 280 °C for 30 min. with a rate of 4 °C / min.

Results and Discussion

Fatty acids analyses have been used to monitor changes in aquatic environment, and to characterize ground water communities. Also, analysis of its profiles developed from fatty acids methyl esters or phospholipids fatty acids has been applied to characterize biological communities in a broad range of terrestrial and aquatic systems (Banowetz *et al.*, 2006).

The particulate fraction of fatty acids concentrations varied from one site to another during different seasons (Tables 1, 2, 3, 4 and 5). The fatty acids were dominated by even carbon numbers ranging from the carbon chain length of C_{16} – C_{20} , including unsaturated and branched acids. The mean values of particulate fatty acids showed large variations, 0.014 $\mu\text{g/gm}$ of C_{13} to 0.417 $\mu\text{g/gm}$ of C_{16} (figure 2), 0.047 $\mu\text{g/gm}$ of C_{24} to 0.506 $\mu\text{g/gm}$ of C_{18} (figure 3), 0.049 $\mu\text{g/gm}$ of C_{13} to 0.820 $\mu\text{g/gm}$ of C_{18} (figure 4), 0.027 $\mu\text{g/gm}$ of C_{24} to 0.429 $\mu\text{g/gm}$ of C_{17} (figure 5) and 0.031 $\mu\text{g/gm}$ of C_{23} to 0.413 $\mu\text{g/gm}$ of C_{16} (figure 6). The proportion of fatty acids in the particulate matter is lowest during the exponential growth phase of phytoplankton. The fatty acids patterns changed as soon as the sample contained a large amount of particulate lipids, which shows correlations to the dissolved surface-active substances. Fatty acids along with triglycerides, are involved in many biogeochemically significant processes occurring within the sea. Fatty acids have long been considered as a useful tracers of the source of organic matter and indicators of the biological activity of water and sediments (Rodier and Khalil, 1982). They have a potential role as precursors to several types of dissolved organic matter, including aldehydes and humic substances. Fatty acids formed about 3 % of the dissolved organic matter (DOM) in seawater (Kieber *et al.*, 1997). They are probably related to plankton and the remineralization of detritus (Kattner *et al.*, 1983).

Table (1). Concentration of particulate fatty acids ($\mu\text{g}/\text{gm}$) in water of Shatt Al-Arab River and north-west Arabian Gulf during summer 1993.

Carbon number	Station						
	1	2	3	4	5	6	7
C₁₃	0.01	0.03	0.03	0.03	ND	ND	ND
iso C₁₄	0.06	0.06	0.09	0.10	ND	ND	ND
C₁₄	0.07	0.18	0.10	0.16	0.08	0.03	0.01
iso C₁₅	0.06	0.21	0.13	0.18	0.09	0.02	0.03
ante C₁₅	0.05	0.23	0.21	0.16	0.07	0.05	0.02
C₁₅	0.09	0.28	0.24	0.28	0.09	0.08	0.07
iso C₁₆	0.16	0.42	0.32	0.30	0.12	0.06	0.07
C_{16:1}	0.32	0.73	0.62	0.28	0.10	0.09	0.09
C₁₆	0.41	0.98	0.83	0.32	0.16	0.12	0.10
iso C₁₇	0.15	0.06	0.13	0.12	0.09	0.06	0.07
ante C₁₇	0.08	0.09	0.16	0.16	0.08	0.08	0.06
C₁₇	0.24	0.38	0.34	0.21	0.06	0.13	0.04
C_{18:2}	0.16	0.88	0.45	0.20	0.16	0.24	0.12
C_{18:1}	0.18	0.74	0.36	0.23	0.18	0.16	0.14
C₁₈	0.19	0.28	0.21	0.29	0.20	0.23	0.12
C₁₉	0.17	0.17	0.14	0.16	0.09	0.10	0.07
C_{20:1}	0.17	0.16	0.12	0.12	0.17	0.13	0.10
C₂₀	0.15	0.13	0.10	0.13	0.14	0.12	0.09
C₂₁	0.09	0.10	0.09	0.09	0.07	0.10	0.08
C₂₂	0.08	0.12	0.09	0.10	0.11	0.09	0.08
C₂₃	0.03	0.08	0.06	0.06	0.04	0.07	0.05
C₂₄	0.02	0.05	0.04	0.04	0.02	0.02	0.04

ND: Not Detected.

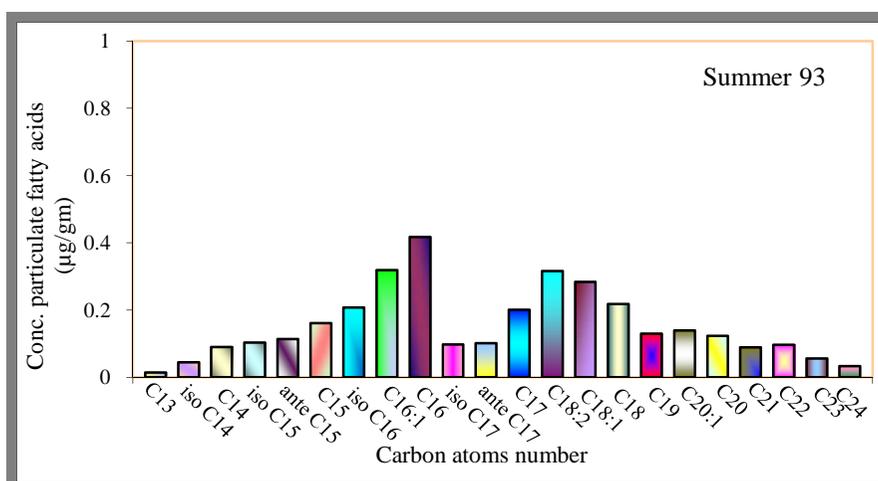
Figure (2). Mean concentration of particulate fatty acids ($\mu\text{g}/\text{gm}$) of the seven stations, during summer 1993.

Table (2). Concentration of particulate fatty acids ($\mu\text{g}/\text{gm}$) in water of Shatt Al-Arab River and north-west Arabian Gulf during autumn 1993.

Carbon number	Station						
	1	2	3	4	5	6	7
C₁₃	0.07	0.13	0.06	0.08	0.03	0.03	ND
iso C₁₄	0.13	0.44	0.22	0.18	0.09	0.05	0.03
C₁₄	0.31	0.68	0.45	0.36	0.19	0.08	0.07
iso C₁₅	0.18	0.53	0.53	0.28	0.11	0.09	0.03
Ante C₁₅	0.17	0.45	0.26	0.21	0.14	0.07	0.03
C₁₅	0.13	0.42	0.30	0.27	0.10	0.13	0.08
iso C₁₆	0.20	0.57	0.49	0.35	0.18	0.16	0.11
C_{16:1}	0.27	0.67	0.65	0.38	0.22	0.19	0.13
C₁₆	0.36	0.85	0.73	0.43	0.31	0.21	0.27
iso C₁₇	0.26	0.74	0.55	0.21	0.21	0.11	0.05
Ante C₁₇	0.17	0.45	0.42	0.28	0.11	0.16	0.16
C₁₇	0.13	0.38	0.49	0.36	0.26	0.11	0.24
C_{18:2}	0.26	0.56	0.53	0.48	0.24	0.13	0.18
C_{18:1}	0.35	0.76	0.60	0.52	0.38	0.18	0.16
C₁₈	0.49	0.88	0.74	0.61	0.31	0.26	0.25
C₁₉	0.27	0.51	0.34	0.31	0.10	0.18	0.11
C_{20:1}	0.31	0.35	0.30	0.23	0.09	0.16	0.08
C₂₀	0.23	0.32	0.26	0.28	0.10	0.08	0.07
C₂₁	0.14	0.26	0.17	0.16	0.03	0.09	0.05
C₂₂	0.11	0.17	0.28	0.19	0.03	0.11	0.04
C₂₃	0.07	0.14	0.17	0.08	ND	0.04	ND
C₂₄	0.06	0.09	0.07	0.06	ND	0.05	ND

ND: Not Detected.

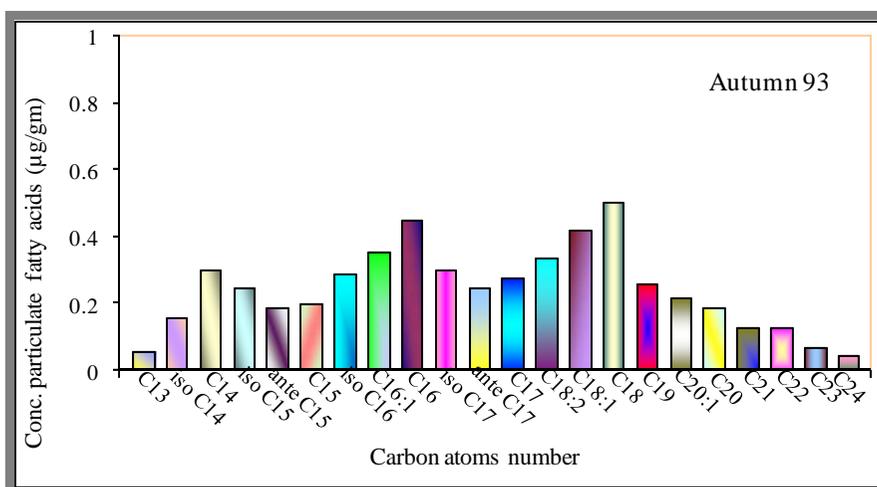


Figure (3). Mean concentration of particulate fatty acids ($\mu\text{g}/\text{gm}$) of the seven stations, during autumn 1993.

Table (3). Concentration of particulate fatty acids ($\mu\text{g}/\text{gm}$) in water of Shatt Al-Arab River and North-West Arabian Gulf during winter 1993.

Carbon number	Station						
	1	2	3	4	5	6	7
C₁₃	ND	0.22	ND	0.10	0.02	ND	ND
iso C₁₄	0.09	0.27	0.18	0.29	0.09	ND	ND
C₁₄	0.18	0.60	0.26	0.15	0.12	0.07	0.06
iso C₁₅	0.21	0.72	0.35	0.23	0.16	0.06	ND
ante C₁₅	0.36	1.33	0.48	0.22	0.15	0.09	0.13
C₁₅	0.54	1.04	0.59	0.33	0.19	0.13	0.16
iso C₁₆	0.27	0.58	0.54	0.41	0.20	0.16	0.12
C_{16:1}	0.21	0.63	0.43	0.46	0.22	0.18	0.19
C₁₆	0.63	1.29	1.49	0.65	0.28	0.26	0.28
iso C₁₇	0.30	0.99	0.36	0.22	0.17	0.16	0.11
ante C₁₇	0.37	0.77	0.46	0.32	0.29	0.19	0.13
C₁₇	0.48	1.43	1.68	0.50	0.31	0.20	0.23
C_{18:2}	0.31	0.99	0.39	0.70	0.22	0.26	0.20
C_{18:1}	0.46	1.15	0.72	0.78	0.32	0.28	0.24
C₁₈	0.69	1.73	1.33	0.99	0.42	0.28	0.30
C₁₉	0.42	1.48	0.28	0.83	0.36	0.20	0.26
C_{20:1}	0.36	1.03	0.26	0.68	0.32	0.18	0.12
C₂₀	0.30	0.95	0.18	0.48	0.28	0.14	0.10
C₂₁	0.21	0.63	0.16	0.30	0.21	0.10	0.08
C₂₂	0.18	0.51	0.06	0.16	0.17	0.07	0.06
C₂₃	0.09	0.38	0.03	0.10	0.09	0.06	0.05
C₂₄	0.09	0.19	0.02	0.07	0.09	0.05	0.03

ND: Not Detected.

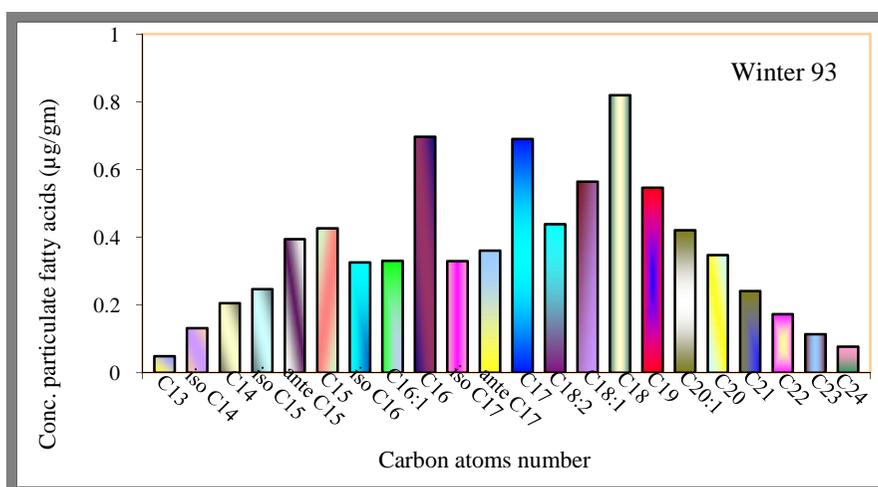
Figure (4). Mean concentration of particulate fatty acids ($\mu\text{g}/\text{gm}$) of the seven stations, during winter 1993.

Table (4). Concentration of particulate fatty acids ($\mu\text{g}/\text{gm}$) in water of Shatt Al-Arab River and north-west Arabian Gulf during spring 1994.

Carbon number	Station						
	1	2	3	4	5	6	7
C ₁₃	0.04	0.05	0.03	0.06	0.03	0.02	0.02
iso C ₁₄	0.08	0.10	0.04	0.04	0.02	0.03	0.04
C ₁₄	0.22	0.16	0.07	0.08	0.09	0.03	0.07
iso C ₁₅	0.20	0.19	0.07	0.10	0.10	0.03	0.05
ante C ₁₅	0.21	0.30	0.21	0.20	0.15	0.06	0.08
C ₁₅	0.26	0.25	0.31	0.18	0.09	0.09	0.18
iso C ₁₆	0.21	0.36	0.28	0.22	0.11	0.03	0.14
C _{16:1}	0.24	0.46	0.33	0.30	0.15	0.09	0.10
C ₁₆	0.26	0.65	0.52	0.36	0.18	0.13	0.14
iso C ₁₇	0.29	0.62	0.43	0.34	0.17	0.14	0.10
ante C ₁₇	0.42	0.67	0.55	0.40	0.20	0.18	0.09
C ₁₇	0.49	0.78	0.64	0.44	0.22	0.23	0.20
C _{18:2}	0.40	0.68	0.38	0.52	0.26	0.12	0.14
C _{18:1}	0.21	0.55	0.72	0.50	0.30	0.18	0.10
C ₁₈	0.10	0.70	0.48	0.46	0.28	0.24	0.09
C ₁₉	0.05	0.45	0.43	0.42	0.21	0.17	0.09
C _{20:1}	0.12	0.36	0.33	0.24	0.17	0.15	0.04
C ₂₀	0.03	0.28	0.17	0.18	0.09	0.07	0.06
C ₂₁	0.02	0.22	0.07	0.06	0.06	0.11	0.04
C ₂₂	0.02	0.18	0.07	0.12	0.03	0.10	0.07
C ₂₃	0.01	0.09	0.05	0.04	0.02	0.02	0.03
C ₂₄	0.01	0.05	0.03	0.04	0.02	0.01	0.03

ND: Not Detected.

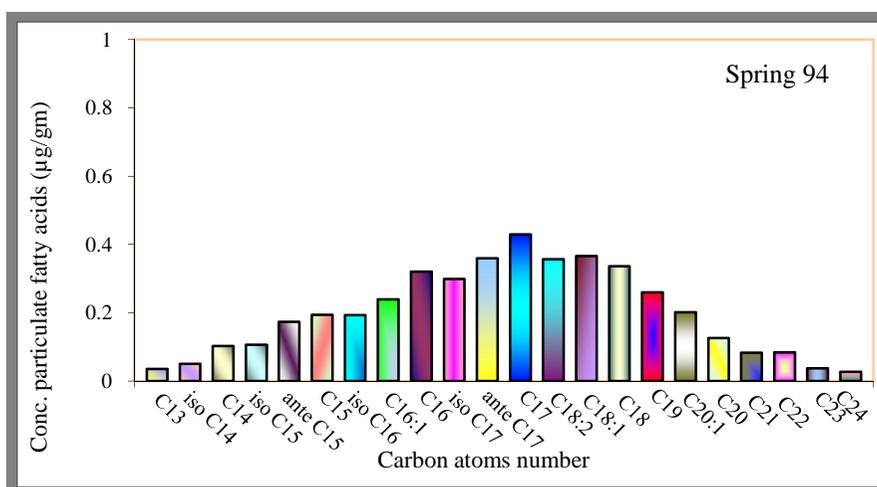
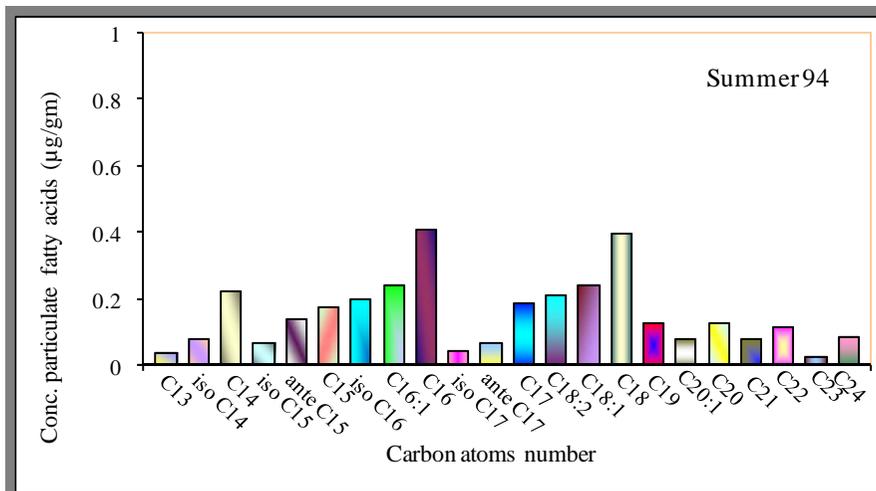


Figure (5). Mean concentration of particulate fatty acids ($\mu\text{g}/\text{gm}$) of the seven stations, during spring 1994.

Table (5). Concentration of particulate fatty acids ($\mu\text{g}/\text{gm}$) in water of Shatt Al-Arab River and north-west Arabian Gulf during summer 1994.

Carbon number	Station						
	1	2	3	4	5	6	7
C₁₃	ND	0.23	ND	0.04	ND	ND	ND
iso C₁₄	ND	0.31	0.06	0.08	0.08	0.02	0.02
C₁₄	0.14	0.46	0.34	0.24	0.18	0.08	0.16
iso C₁₅	ND	0.11	0.16	0.10	0.09	0.03	0.02
ante C₁₅	0.23	0.31	0.13	0.09	0.12	0.06	0.04
C₁₅	0.20	0.42	0.21	0.12	0.16	0.08	0.08
iso C₁₆	0.24	0.21	0.32	0.20	0.16	0.16	0.14
C_{16:1}	0.22	0.29	0.36	0.22	0.18	0.20	0.23
C₁₆	0.41	0.76	0.38	0.38	0.32	0.36	0.28
iso C₁₇	ND	0.11	0.10	0.10	ND	ND	ND
ante C₁₇	ND	0.12	0.16	0.12	0.09	ND	ND
C₁₇	0.16	0.47	0.20	0.18	0.11	0.12	0.10
C_{18:2}	0.18	0.33	0.34	0.22	0.11	0.20	0.13
C_{18:1}	0.18	0.51	0.25	0.24	0.14	0.23	0.16
C₁₈	0.28	0.86	0.48	0.46	0.26	0.28	0.20
C₁₉	0.13	0.35	0.10	0.09	0.06	0.13	0.06
C_{20:1}	0.06	0.13	0.32	0.06	ND	ND	ND
C₂₀	0.05	0.12	0.18	0.26	0.16	0.10	0.03
C₂₁	0.07	0.18	0.13	0.04	0.09	0.06	0.02
C₂₂	0.09	0.22	0.28	0.14	0.06	0.03	0.02
C₂₃	0.06	0.16	ND	ND	ND	ND	ND
C₂₄	0.33	0.28	ND	ND	ND	ND	ND

ND: Not Detected.

Figure (6). Mean concentration of particulate fatty acids ($\mu\text{g}/\text{gm}$) of the seven stations, during summer 1994.

The relationship between the fatty acid composition of particulate lipids and photosynthetically produced lipids indicated that polyunsaturated fatty acids (PUFA) observed in particulate lipid were mainly associated with phytoplankton (Hama, 1999). The occurrence and distribution of fatty acids in the phytoplankton and in the particulate and dissolved organic matter of the aquatic environment were investigated as means of delineating the pathways and transformations of organic carbon from its origin in the phytoplankton through higher trophic levels into the sediments. The seasonal changes in fatty acids are usually related to the combined influence of environmental factors such as light, nutrient deficiency, temperature ...etc. (Mayzaud *et al.*, 1989). The common feature of the different types of experiments described in the literature seems to be focusing on the occurrence of myristic, palmitic and palmitoleic acid as main components in diatoms as well as eicosapentaenoic acid (20:5) and a low proportion of fatty acids with 18 carbon atoms (Kattner *et al.*, 1983).

Total fatty acids were calculated as the sum of all individual fatty acids. The concentration of total fatty acids in particulate fraction ranged from 1.45 $\mu\text{g/gm}$ at station 7 during summer 1993 to 18.91 $\mu\text{g/gm}$ at station 2 during winter 1993. Regional average of total fatty acids concentrations ranged from 3.35 $\mu\text{g/gm}$ in summer 1993 to 7.93 $\mu\text{g/gm}$ in winter 1993, while seasonal average total fatty acids was ranged from 2.01 $\mu\text{g/gm}$ at station 7 to 10.14 $\mu\text{g/gm}$ at station 2 (Table 6).

Table (6). Concentration of total fatty acids (TFA) ($\mu\text{g/gm}$) in particulate fraction of Shatt Al-Arab River and north-west Arabian Gulf.

Seasons	Stations							Regional Average
	1	2	3	4	5	6	7	
Summer 1993	2.94	6.36	4.86	3.72	2.12	1.98	1.45	3.347
Autumn 1993	4.67	10.35	8.61	6.31	3.23	2.67	2.14	5.426
Winter 1993	6.75	18.91	10.25	8.97	4.68	3.12	2.85	7.933
Spring 1994	3.89	8.15	6.21	5.30	2.95	2.23	1.90	4.376
Summer 1994	3.03	6.94	4.50	3.38	2.37	2.14	1.69	3.436
Seasonal Average	4.256	10.142	6.886	5.536	3.070	2.428	2.006	

From the results a significant proportion of the total fatty acids may be affected by both spring-bloom and summer biological production, therefore possible reasons for these seasonal variations are processes brought about by temperature variations including evaporation, bacterial degradation, adsorption as well as chemical oxidation. The salt content and lower temperature of most gulf waters would significantly reduce the solubility of lipid compounds (Parrish, 1988).

Conclusion

The variations in particulate fatty acid concentrations are irregular, with alternating minima and maxima. We believed that the concentration of total fatty acids of the particulate matter increased sharply during phytoplankton blooms and decomposition of their cells. Also, the odd and even numbers of fatty acids were produced by phytoplankton, bacteria and fungi.

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التغيرات الفصلية في محتوى الأحماض الدهنية الدقائقية في نهر شط العرب وشمال غرب الخليج العربي

حامد طالب السعد¹، عباس عادل حنتوش¹، محسن عبد الرسول الحلوا¹
و مها خلف زغير²
¹مركز علوم البحار، ²كلية العلوم جامعة البصرة، البصرة - العراق

المستخلص جمعت عينات من مياه سبعة مواقع بيئية مختلفة على امتداد شط العرب وشمال غرب الخليج العربي لدراسة الأحماض الدهنية الدقائقية خلال الفترة بين شهر حزيران 1993 وشهر تموز 1994. حلت عينات الأحماض الدهنية الدقائقية باستخدام جهاز كروماتوغرافيا الغاز. شوهد ظهور غير منتظم في كمية بعض الأحماض الدهنية ونوعيتها، فقد سادت وبشكل ملحوظ الأحماض الدهنية: البالميتوليك والبالمتيك والهيبتاديكانويك والستياريك والأوليك واللينوليك. أبدت تراكيز الأحماض الدهنية الكلية اختلافاً معنوياً في معدلاتها، إذ تراوحت من 1.45 مايكروغرام/ غرام في الموقع (7) (الخليج العربي) خلال صيف 1993 إلى 18.91 مايكروغرام/ غرام في الموقع (2) (شط العرب عند مدينة الفاو) خلال شتاء 1993. تعد العوالق النباتية والأحياء المجهرية (البكتريا والفطريات) المصدر الرئيسي للأحماض الدهنية مع قلة تواجد النباتات المائية في معظم مواقع الدراسة.