

Distribution and sources of dissolved fatty acids in water of Shatt Al-Arab estuary and Northwest Arabian Gulf

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ABSTRACT One meter water column of the Shatt Al-Arab estuary and Northwest Arabian Gulf was sampled at seven stations during a 14 months period (June 1993 - July 1994). Dissolved fatty acids samples were analyzed to examine water quality. After filtration, the fatty acids composition of the chloroform-soluble was analyzed in the dissolved fraction by gas chromatography. Stearic acid had the highest proportion of saturated acids in several samples of dissolved fatty acids followed by heptadecanoic acid and palmitic acid. Palmitoleic acid, oleic acid and linoleic acid were the most abundant unsaturated acids. The other saturated and unsaturated acids had medium to low concentrations. There were significant differences in total fatty acids concentrations of the seven sites. Regional average total fatty acids ranged from 1.95 $\mu\text{g/l}$ in Summer 1993 to 6.46 $\mu\text{g/l}$ in Winter 1993, while seasonal average total fatty acids ranged from 1.78 $\mu\text{g/l}$ at station 7 to 6.69 $\mu\text{g/l}$ at station 2.

INTRODUCTION

The measurement of pollutants in combination with biogenic lipids would be useful in the study of the distributions of pollutants, since all lipids can potentially act as solvents, transporters or sinks for pollutants (Parrish, 1988). There is great structural variety among the lipids, they 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 & benzene) and general insolubility in water. The common feature of these lipids is that they are all esters of moderate to long chain fatty acids. In the aquatic environments, fatty acids are supplied by two major sources, i.e. natural processes (living organisms and their detritus) and human activities (domestic, industrial and agricultural wastes) (Matsumoto, 1981). Fatty acid 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). Fatty acids can be derived from planktons, benthic organisms, sea grasses and marsh plants (Rodier and Khalil, 1982).

However, little is known on the features of fatty acids in Iraqi waters, but there are many works reporting fatty acids in many aquatic environments (Gomez-Belinchon *et al.*, 1988; Kattner and Brockmann, 1990; Parrish *et al.*, 1992; Osterroht, 1993; Derieux *et al.*, 1998; Mannino and Harvey, 1999 and Saliot *et al.*, 2002). The main purpose of the present study was to examine differences in the distribution of dissolved fatty acids and their concentrations along the Shatt Al-Arab estuary and the North West Arabian Gulf.

MATERIALS AND METHODS

Water samples were taken during the period of June 1993-July 1994 from seven stations along the Shatt Al - Arab estuary and the North West Arabian Gulf (Fig. 1) for the study of fatty acids in dissolved fraction. The sample (5 L) was filtered through a glass-fiber filter (Whatman GF/F) to separate the dissolved and particulate phases. The filtrate was extracted three times with 100 ml of chloroform. Also, the lipid extracts was roto-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 extracting, the free fatty acids were released by 6N HCl extracted with petroleum ether. The acids extracts were then methylated by a solution of 14 % $\text{BF}_3\text{-CH}_3\text{OH}$ reagent (Metcalf and Schmitz, 1961). In the present study, a Perkin Elmer Sigma 300 capillary gas chromatography equipped with Flame Ionization Detector (FID) and splitless model injection was used. The fused silica capillary column was a wall Coated Open Tubular (WCOT) 50 m X 0.25 mm.i.d. Helium 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.

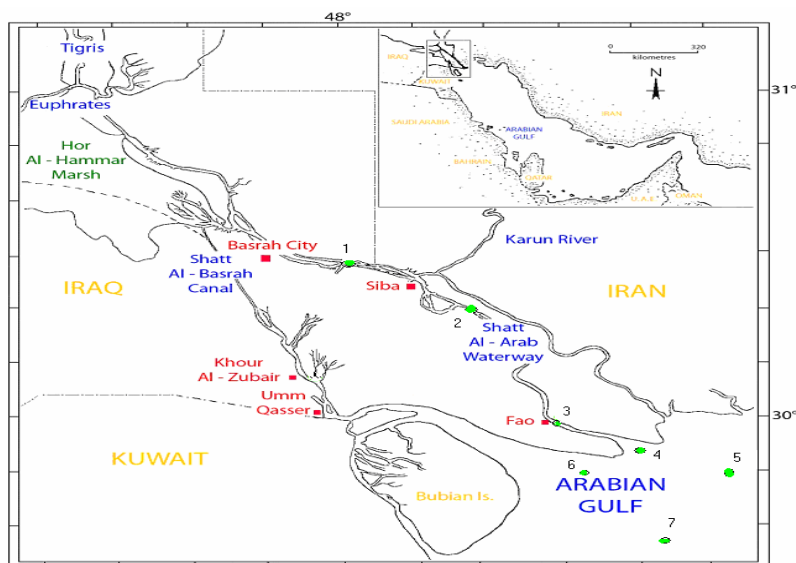


Fig. 1: Map of the Shatt Arab estuary and North West Arabian Gulf showing the sampling stations.

RESULTS AND DISCUSSION

Dissolved fatty acids often showed a distribution with a maximum of palmitic acid, palmitoleic acid, heptadecanoic acid, stearic acid, oleic acid and linoleic acid. Their levels were higher in winter than in summer as shown in Tables 1 - 5 and Figures 2 - 6, also their concentrations in the dissolved fraction varied from one station to others, which might be due to varied abundance phytoplankton and higher aquatic plants. Quantitatively, palmitic acid has been found to be one of

Table 1: Concentration of dissolved fatty acids ($\mu\text{g/l}$) in water of Shatt Al-Arab estuary and North - West Arabian Gulf during summer 1993.

Carbon Number	Station						
	1	2	3	4	5	6	7
C ₁₃	0.01	0.03	0.07	ND	ND	ND	0.01
iso C ₁₄	0.02	0.07	0.06	ND	0.02	ND	0.01
C ₁₄	0.02	0.06	0.05	0.07	0.02	0.02	0.02
iso C ₁₅	0.12	0.10	0.07	0.09	0.01	0.01	0.02
ante C ₁₅	0.12	0.12	0.09	0.10	0.03	0.06	0.03
C ₁₅	0.13	0.09	0.06	0.13	0.06	0.09	0.08
iso C ₁₆	0.06	0.17	0.12	0.10	0.07	0.06	0.05
C _{16:1}	0.07	0.13	0.67	0.27	0.10	0.09	0.07
C ₁₆	0.21	0.49	0.09	0.17	0.10	0.16	0.08
iso C ₁₇	0.07	0.09	0.06	0.05	0.09	0.13	0.04
ante C ₁₇	0.19	0.12	0.09	0.08	0.06	0.10	0.03
C ₁₇	0.14	0.20	0.12	0.06	0.07	0.19	0.05
C _{18:2}	0.12	0.42	0.34	0.33	0.16	0.10	0.08
C _{18:1}	0.10	0.35	0.28	0.26	0.14	0.09	0.07
C ₁₈	0.08	0.29	0.20	0.12	0.12	0.06	0.08
C ₁₉	0.07	0.18	0.17	0.10	0.09	0.05	0.04
C _{20:1}	0.04	0.16	0.15	0.08	0.08	0.02	0.03
C ₂₀	0.06	0.17	0.13	0.06	0.05	0.02	0.03
C ₂₁	0.03	0.13	0.06	0.05	0.03	0.01	0.02
C ₂₂	0.02	0.12	0.05	0.03	0.01	0.01	0.01

ND: Not Detected

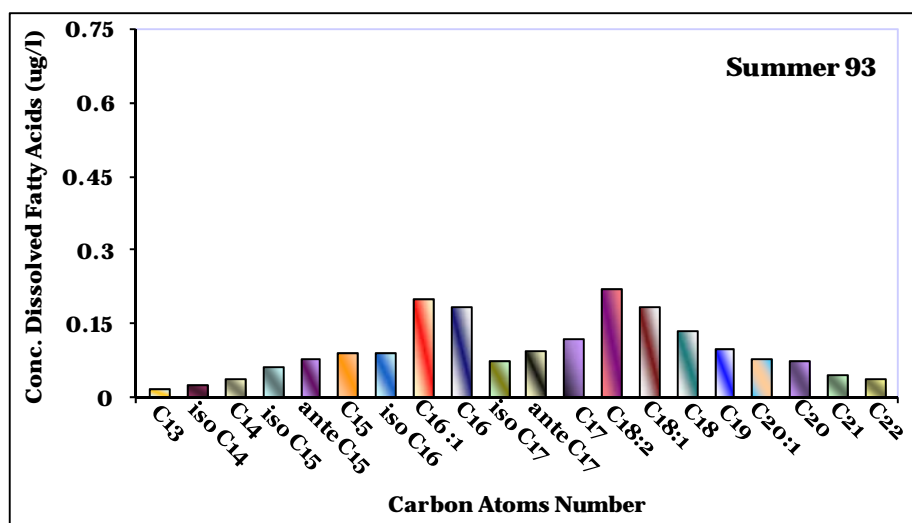


Fig. 2: Mean concentration of dissolved fatty acids ($\mu\text{g/l}$) in the study area during summer 1993.

Table 2: Concentration of dissolved fatty acids ($\mu\text{g/l}$) in water of Shatt Al-Arab estuary and North - West Arabian Gulf during autumn 1993.

Carbon Number	Station						
	1	2	3	4	5	6	7
C ₁₃	0.05	0.11	0.04	0.09	0.02	ND	ND
iso C ₁₄	0.09	0.14	0.14	0.22	0.08	0.02	0.03
C ₁₄	0.33	0.24	0.49	0.38	0.26	0.16	0.12
iso C ₁₅	0.17	0.30	0.13	0.13	0.09	0.09	0.05
ante C ₁₅	0.10	0.20	0.18	0.16	0.13	0.13	0.07
C ₁₅	0.13	0.35	0.26	0.26	0.28	0.16	0.09
iso C ₁₆	0.28	0.49	0.36	0.22	0.26	0.18	0.09
C _{16:1}	0.36	0.40	0.54	0.36	0.24	0.22	0.13
C ₁₆	0.52	0.46	0.63	0.48	0.21	0.32	0.19
iso C ₁₇	0.16	0.54	0.22	0.18	0.21	0.21	0.07
ante C ₁₇	0.22	0.40	0.26	0.22	0.28	0.26	0.08
C ₁₇	0.36	0.41	0.30	0.36	0.27	0.28	0.06
C _{18:2}	0.82	0.44	0.13	0.38	0.16	0.36	0.38
C _{18:1}	0.64	0.59	1.17	0.45	0.28	0.32	0.26
C ₁₈	0.48	0.73	1.08	0.56	0.35	0.41	0.18
C ₁₉	0.24	0.70	0.19	0.22	0.29	0.20	0.09
C _{20:1}	0.16	0.40	0.18	0.18	0.23	0.13	0.06
C ₂₀	0.09	0.36	0.14	0.16	0.17	0.12	0.05
C ₂₁	0.06	0.33	0.22	0.10	0.06	0.10	0.05
C ₂₂	0.09	0.39	0.08	0.19	0.13	0.22	0.03

ND: Not Detected

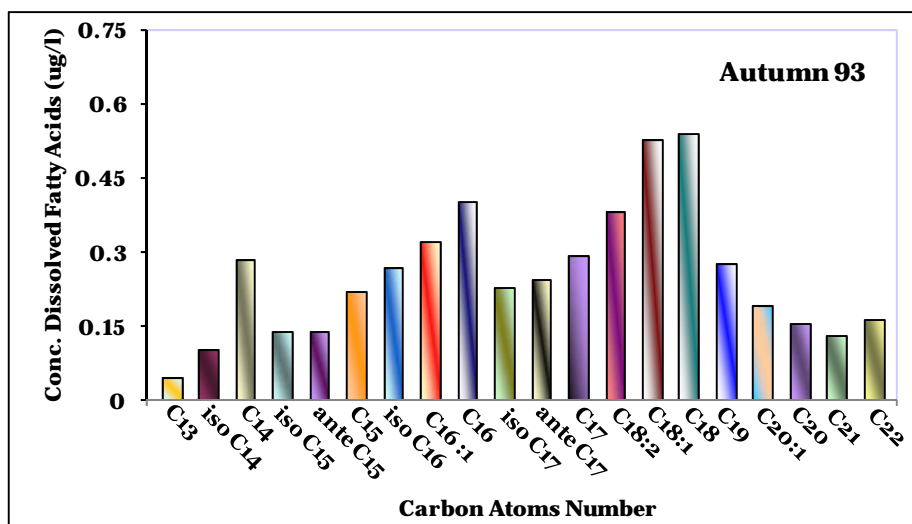


Fig. 3: Mean concentration of dissolved fatty acids ($\mu\text{g/l}$) in the study area during autumn 1993.

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

Carbon Number	Station						
	1	2	3	4	5	6	7
C ₁₃	0.03	0.12	ND	ND	0.03	ND	0.03
iso C ₁₄	0.09	0.12	ND	0.05	0.10	ND	0.08
C ₁₄	0.06	0.32	0.14	0.05	0.15	0.06	0.11
iso C ₁₅	0.18	0.18	0.18	0.09	0.10	ND	0.07
ante C ₁₅	0.24	0.20	0.19	0.09	0.14	ND	0.09
C ₁₅	0.27	0.40	0.36	0.16	0.22	0.09	0.13
iso C ₁₆	0.36	0.44	0.53	0.34	0.34	ND	0.16
C _{16:1}	0.86	0.72	0.64	0.42	0.30	0.22	0.28
C ₁₆	0.39	0.98	0.82	0.60	0.45	0.74	0.36
iso C ₁₇	ND	1.22	0.64	ND	ND	ND	0.28
ante C ₁₇	ND	1.36	0.80	0.40	ND	ND	0.27
C ₁₇	0.84	0.84	0.48	0.45	0.56	0.54	0.23
C _{18:2}	1.14	1.28	0.84	0.60	ND	0.58	0.26
C _{18:1}	0.78	1.36	0.52	1.36	ND	0.49	0.33
C ₁₈	0.63	1.44	0.42	0.71	0.98	0.37	0.20
C ₁₉	0.30	0.76	0.39	0.28	0.78	0.30	0.11
C _{20:1}	0.24	0.42	0.24	0.16	ND	0.20	0.08
C ₂₀	0.18	0.28	0.17	0.12	0.30	0.30	0.07
C ₂₁	0.15	0.18	0.06	0.02	0.20	0.21	0.02
C ₂₂	0.09	0.12	0.04	0.03	0.17	0.18	0.01

ND: Not Detected

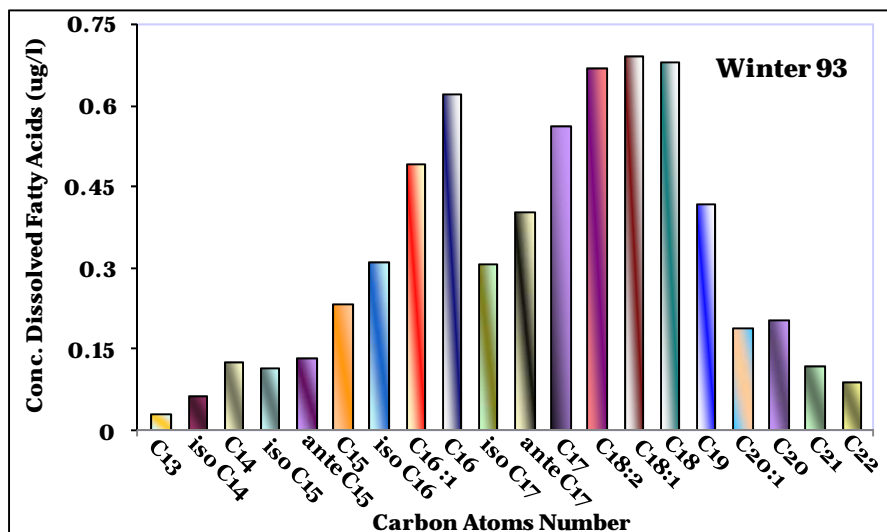


Fig. 4: Mean concentration of dissolved fatty acids ($\mu\text{g}/\text{l}$) in the study area during winter 1993.

Table 4: Concentration of dissolved fatty acids ($\mu\text{g/l}$) in water of Shatt Al-Arab estuary and North - West Arabian Gulf during spring 1994.

Carbon Number	Station						
	1	2	3	4	5	6	7
C ₁₃	0.04	0.03	0.02	0.02	0.01	0.01	0.01
iso C ₁₄	0.20	0.08	0.06	0.08	0.04	0.02	0.02
C ₁₄	0.12	0.11	0.09	0.04	0.03	0.04	0.03
iso C ₁₅	0.08	0.10	0.10	0.06	0.08	0.07	0.02
ante C ₁₅	0.06	0.11	0.09	0.17	0.07	0.17	0.02
C ₁₅	ND	0.28	0.12	ND	0.18	0.12	0.16
iso C ₁₆	ND	0.13	0.06	0.17	0.16	0.10	0.07
C _{16:1}	ND	0.36	0.30	0.16	0.18	0.12	0.17
C ₁₆	0.46	0.54	0.43	0.18	0.22	0.18	0.19
iso C ₁₇	0.18	0.29	0.18	0.13	0.19	0.14	0.11
ante C ₁₇	0.16	0.60	0.22	0.22	0.13	0.16	0.12
C ₁₇	0.34	0.62	0.13	0.26	0.17	0.20	0.14
C _{18:2}	0.12	0.72	0.10	0.46	0.12	0.16	0.16
C _{18:1}	0.08	0.78	0.45	0.25	0.30	0.14	0.14
C ₁₈	0.28	0.38	0.38	0.22	0.28	0.25	0.20
C ₁₉	0.14	0.26	0.16	0.18	0.11	0.13	0.13
C _{20:1}	ND	0.18	ND	ND	0.09	0.09	0.06
C ₂₀	0.26	0.17	0.13	0.17	0.06	0.06	0.05
C ₂₁	0.18	0.11	0.10	0.12	0.03	0.05	0.03
C ₂₂	0.12	0.06	0.07	0.06	0.02	0.02	0.02

ND: Not Detected

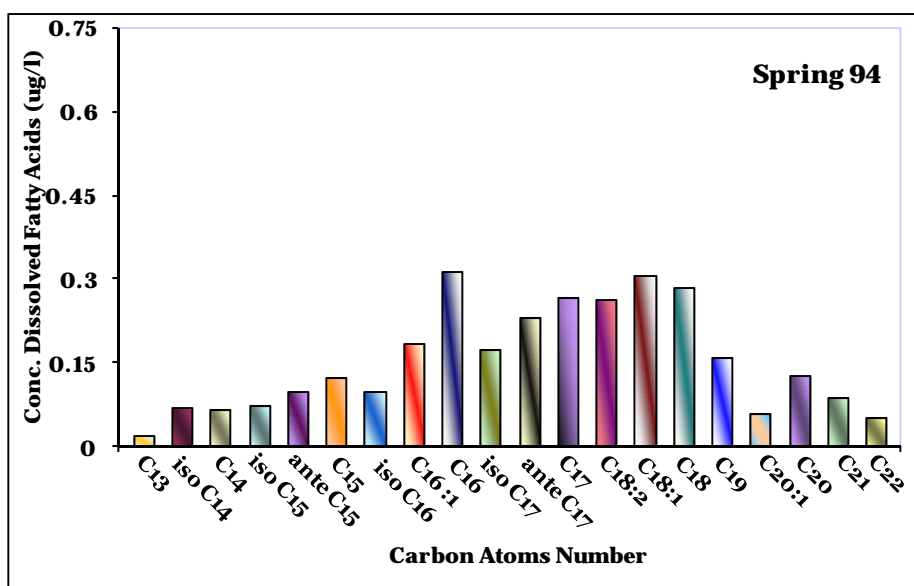


Fig. 5: Mean concentration of dissolved fatty acids ($\mu\text{g/l}$) in the study area during spring 1994.

Table (5). Concentration of dissolved fatty acids ($\mu\text{g/l}$) in water of Shatt Al-Arab estuary and North - West Arabian Gulf during summer 1994.

Carbon Number	Station						
	1	2	3	4	5	6	7
C ₁₃	ND	ND	ND	0.01	ND	ND	0.01
iso C ₁₄	ND	ND	0.02	0.01	ND	0.02	0.02
C ₁₄	ND	0.19	0.34	0.03	0.16	0.04	0.08
iso C ₁₅	ND	0.02	0.07	0.26	0.04	0.20	0.02
ante C ₁₅	ND	0.03	0.06	0.04	0.07	0.04	0.03
C ₁₅	0.02	0.07	0.12	0.06	0.09	0.06	0.07
iso C ₁₆	0.03	0.04	0.18	0.08	ND	0.09	0.06
C _{16:1}	0.05	0.22	0.28	0.13	0.16	0.09	0.08
C ₁₆	0.24	0.78	0.34	0.22	0.38	0.12	0.07
iso C ₁₇	0.26	0.06	0.09	0.18	0.06	0.08	0.04
ante C ₁₇	0.22	0.07	0.14	0.03	0.03	0.06	0.05
C ₁₇	0.18	0.04	0.06	0.03	0.05	0.08	0.07
C _{18:2}	0.29	0.28	0.22	0.05	ND	0.12	0.07
C _{18:1}	0.18	0.94	0.38	0.16	0.18	0.14	0.08
C ₁₈	0.22	0.31	0.25	0.21	0.12	0.10	0.07
C ₁₉	0.07	0.06	0.06	0.18	ND	0.02	0.01
C _{20:1}	0.02	0.03	0.03	0.05	ND	ND	0.02
C ₂₀	0.04	0.02	0.02	0.02	0.06	ND	0.01
C ₂₁	0.01	0.04	0.01	0.02	ND	ND	0.02
C ₂₂	0.14	0.12	0.11	0.26	0.11	0.09	0.06

ND: Not Detected

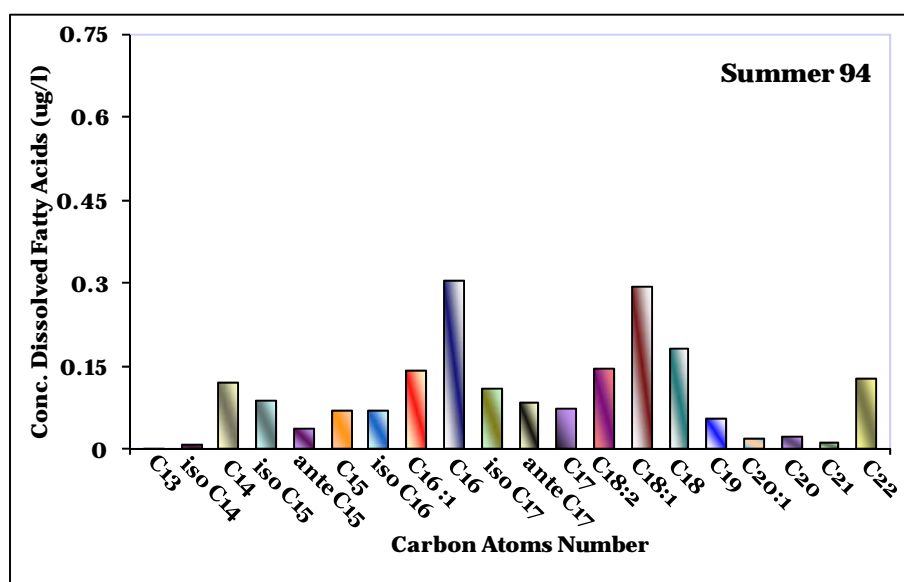
Fig. 6: Mean concentration of dissolved fatty acids ($\mu\text{g/l}$) in the study area during summer 1994.

Table 6: Concentration of total fatty acids (TFA) ($\mu\text{g/l}$) in dissolved fraction in the Shatt Al-Arab estuary and North-West Arabian Gulf.

Seasons	STATIONS							Regional Average
	1	2	3	4	5	6	7	
summer 93	1.68	3.49	2.93	2.15	1.31	1.27	0.85	1.95
autumn 93	5.35	7.98	6.74	5.30	4.00	3.89	2.08	5.05
winter 93	6.83	12.74	7.46	5.93	4.82	4.28	3.17	6.46
spring 94	2.82	5.91	3.19	2.95	2.47	2.23	1.85	3.06
summer 94	1.97	3.32	2.78	2.03	1.51	1.35	0.94	1.99
Seasonal Average	3.73	6.69	4.62	3.67	2.82	2.60	1.78	

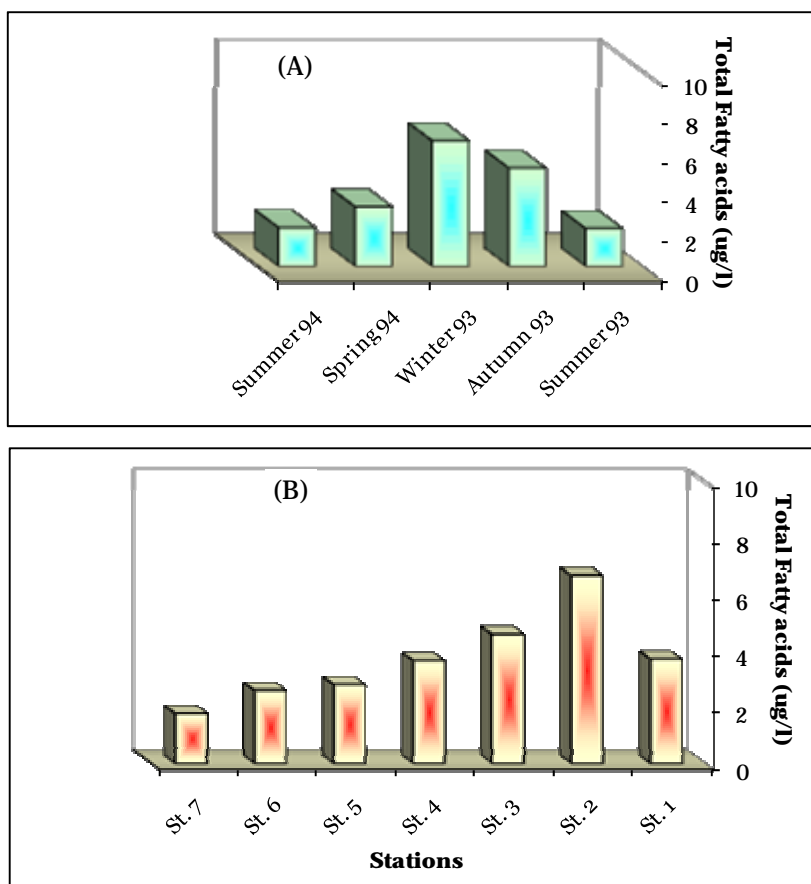


Fig. 7: Regional (a) and seasonal (b) averages of total fatty acids ($\mu\text{g/l}$).

the major fatty acids in marine bacteria, cyanobacteria, eukaryotic algae, it has also been found to be the major fatty acid in sea foam, in the sea surface micro-layer, in dissolved and particulate matter and in sewage (Goutx and Saliot, 1980; Matsumoto, 1981 and Parrish, 1988). The dissolved fraction of fatty acids is classified into three groups; the largest, consisting mostly of hydrocarbons and this reflects the anthropogenic inputs, the second was composed of some C15 - C20 fatty acids and represented the biogenic autochthonous inputs, especially those of algal origin, a third group was formed by the C21 - C30 and corresponded to the terrigenous distribution (Gomez-Belinchon *et al.*, 1988). Micro-algae contain many of the major lipids classes and fatty acids found in other organisms. However, they are also the principal precursors of some polyunsaturated fatty acids (Behrens and Kyle, 1996). The increases of dissolved fatty acids may be due to intensified decay and decomposition of phytoplankton cells with a higher proportion of fatty acid containing lipids (Kattner *et al.*, 1983).

The concentration of total fatty acids that were given in Table (6) ranged from 0.85 µg/l at station 7 during summer 1993 to 12.74 µg/l at station 2 during winter 1993. Also, regional average of total fatty acids ranged from 1.95 µg/l in summer 1993 to 6.46 µg/l in winter 1993, while seasonal average of total fatty acids ranged from 1.78 µg/l at station 7 to 6.69 µg/l at station 2 (Fig. 7). The salt content and lower temperature of most gulf waters would significantly reduce the solubility of lipid compounds (Parrish, 1988). The seasonal changes in fatty acids were related to 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 decrease of unsaturated fatty acids in some stations is probably due to decomposition by photolytic and oxidizing processes (Goutx and Saliot, 1980). Saturated fatty acids are more resistant to the photolytic and chemical degradation (chemically stable) than their unsaturated counterparts.

It can be concluded that the source of the dissolved fatty acids in the water samples are mainly biogenic from phytoplankton, zooplankton and bacteria. Levels of palmitic acid, palmitoleic acid, heptadecanoic acid, stearic acid, oleic acid and linoleic acid were higher in winter than in summer. The concentration of fatty acids was acceptable in comparison with other similar parts of the world.

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أصل وتوزيع الأحماض الدهنية الذائبة في مصب شط العرب وشمال غرب الخليج العربي

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المستخلص جمعت عينات مائية من عمق واحد متر لسبعة مواقع اختيرت على امتداد مصب شط العرب وشمال غرب الخليج العربي لمدة أربعة عشر شهراً خلال الفترة بين شهر حزيران 1993 وشهر تموز 1994. حلت عينات الأحماض الدهنية الذائبة لتحديد نوعية المياه. بعد ترشيح العينات، شخّصت الأحماض الدهنية الذائبة في الكلوروفورم باستخدام جهاز كروماتوغرافيا الغاز. سجل حامض الستياريك أعلى تراكيز الأحماض الدهنية المشبعة يليه حامضي الهيبتاديكانويك والبالمتيك. بينما سادت أحماض الباليميتوليك والأوليك واللينوليك على بقية الأحماض الدهنية غير المشبعة. أظهرت الأحماض الدهنية المشبعة وغير المشبعة الأخرى تراكيز بين المتوسط والقليل. أبدت الأحماض الدهنية الكلية اختلافاً معنوياً في تراكيزها، إذ تراوحت معدلاتها الموقعية من 1.95 مايكروغرام/لتر خلال الصيف 1993 إلى 6.46 مايكروغرام/لتر في الشتاء 1993، في حين تراوحت معدلاتها السنوية من 1.78 مايكروغرام/لتر في الموقع (7) إلى 6.69 مايكروغرام/لتر في الموقع (2).