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FATTY ACIDS IN RECENT SEDIMENTS OF THE MARSHES, SOUTHERN IRAQ

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ABSTRACT

Fatty acids have been isolated and quantitatively determined from the surface and at 10 cm depth of the sediment of the southern marshes of Iraq.

The fatty acids identified by gas chromatography exhibit a bimodal distribution, with maximum at C_{16} and C_{26} and a strong even to odd carbon number predominance, typical of biogenic source (phytoplankton, terrigenous plant wax and microbial sources).

Grain size analysis and TOC% of these sediments was also determined. A comparison of the sediment types in each station does not show a direct correlation with the fatty acid and with the organic carbon concentrations.

INTRODUCTION

The organic compounds found in sedimentary deposits are derived from a variety of sources, knowledge of which can give valuable information on the environmental conditions existing during sediment deposition. Thus, the sediment acts as a long - term record of the water column history. Area where there has been a high organic input to the sediment are particularly suitable for organic geochemical studies, since this situation frequently results in good preservation of the organic content, and

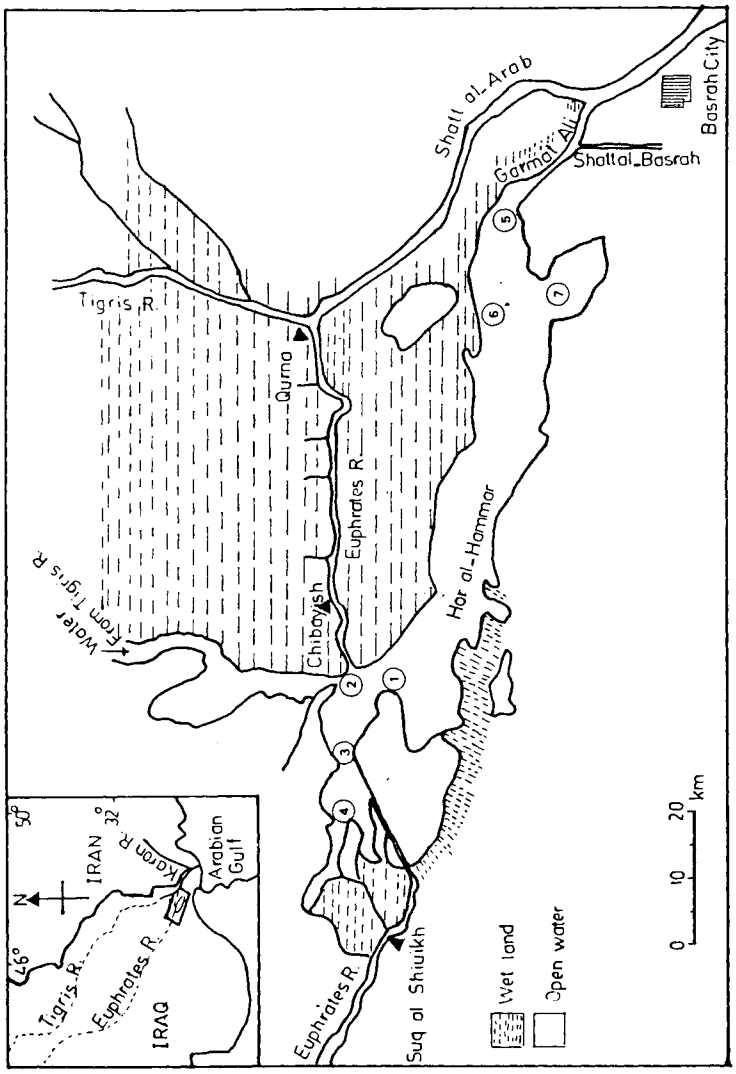

Figure (1) : Sample locations.

Lemna , *Utricularia* & *Salvinia* often occur between the reeds. Common submerged angiosperms, water - lilies are abundant in open waters and *Potamogeton* species are wildspred (Maulood et al., 1981). Al-Saadi et al. (1981) provide some chemical and physical data , total phyto-plankton contents and a general vegetation description from the marshes of Iraq. In their study, they recorded that diatoms were the most dominant phytoplankters , followed by the green, blue green dianoflagellate and the euglenoid species. Also Al-Zubaidi (1985) found that the most abundant phytoplankton group in these marshes is the diatoms.

MATERIALS and METHODS

The sediment samples were taken on May 1986 from 7 stations of the marshes of southern Iraq, by mean of Van Veen grap sampler. As soon as the sample were taken they were kept in glass jar and stored at 20 ^{o}C until analysis. All possible precaution were taken during sampling and handling to avoid contamination. Fatty acids analyses of both surface and bottom (10 cm depth) samples were done following procedure described by Goutx & Saliot (1980). The sediment sample were freeze - dried, ground and passed through a 1 mm metal sieve. Fifty gram of dry weight sediment were extracted for 24 hours in a soxhlet apparatus using a 1:1 mixture of benzen and methanol, then the extract saponified for two hours with a solution of 4 N KOH in 1:1 methanol : benzen. After extracting,the free fatty acids were released by 6 N HCl extracted with ether. The acid extract was then methylated by a solution of 14% BF_3 in methanol (Metcalfe & Schmitz, 1961).

Total organic carbon determined using the oxidation with potassium dichromate. The excess oxidant was titrated against ferrous ammonium sulfate using diphenylamine as indicator. The sediment were weight before and after oxidation (El-Wakeel & Riley, 1957). Grain size analysis was done according to combined dry sieve and pipette method (Folk, 1974).

Analysis of fatty acids were carried on a Perkin -

Elmer sigma 300 capillary gas chromatography with flame ionization detector (FID) using SP 2100 WCOT column 25 m with He as a carrier gas (1.5 ml/min) splitless injection. Temperature program from 50 ^{o}C for 30 min at rate 4 ^{o}C / min.

Recovery observations with sediment samples have indicated that recovery efficiency exceeded 90% for all fatty acids compounds.

Procedural blank consisting of all reagents , glassware and samples during the analysis were periodically determined.

RESULTS and DISCUSSION

Grain size analysis (Table 1) showed a high percentage of clay in station 4 while station 5 a high percentage of sand prevailed in the sediment. These result were expected due to the water current prevailing. However other stations represent an anomaly by having a lower sand and clay content.

Organic carbon content of the sediment exceed 1% only in station 4 & 6, where high content of fatty acids were recorded. The total fatty acids concentrations at the surface sediment range from 1.827 ugg^{-1} at station 7 to 2.985 ugg^{-1} at station 4, while the concentration in 10 cm depth ranged from 1.559 ugg^{-1} at station 7 to 2.350 ugg^{-1} at station 4 (Table 2). Based on the concentration gradient of fatty acids in the sediment it appears that the saturated fatty acids with higher molecular weight (> 20) are more stable than the lower molecular weight saturated C_{12} - C_{19} and all members of the unsaturated fatty acids in the biologically active layer of the sediment. A comparison of the sediment type in each sample of the marshes does not show a direct correlation with the fatty acids and with the total organic carbon concentration.

The biologically active layers of recent sediments contain saturated and unsaturated fatty acids. They are probably a part of a pool of organic matter which is cycled by micro-organisms at a rapid rate relative to the

Table (1) : Granulometric analysis , organic carbon content and total fatty acid concentations in the sediment of the marshes of Iraq.

Station		Sand%	Silt%	Clay%	Textural class	Md O	TOC%	Fatty acid conc. (ugg^{-1} dry weight)
1	A	8.50	51.97	39.53	mud	7.10	0.69	2.358
	B	29.98	30.28	39.74	sandy - mud	7.00	0.64	2.005
2	A	12.90	53.83	33.27	sandy mud	6.85	0.58	2.056
	B	12.90	53.83	33.27	sandy mud	6.85	0.37	1.722
3	A	4.86	46.97	48.13	mud	7.90	0.79	1.910
	B	5.57	58.56	39.74	mud	7.65	0.63	1.559
4	A	27.01	32.14	40.86	sandy mud	6.10	3.62	2.985
	B	16.75	56.09	27.15	sandy mud	5.70	2.12	2.350
5	A	52.26	21.99	26.53	mudy sand	3.20	0.95	2.504
	B	51.77	23.99	24.24	mudy sand	4.20	0.83	2.016
6	A	22.50	41.34	36.16	sandy mud	6.20	1.38	2.595
	B	23.62	34.30	42.08	sandy mud	8.00	1.23	2.125
7	A	23.08	42.12	34.12	sandy mud	7.00	0.45	1.827
	B	47.52	23.57	28.91	sandy mud	4.30	0.33	1.559

Table (2) : Fatty acid composition (ugg^{-1} dry weight) in the sediment of the marshes of Iraq.

Fatty acid	1		2		3		4		5		6		7	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
C6	0.012	0.022	0.013	-	0.022	0.010	0.031	0.012	0.010	0.010	0.028	0.022	0.026	-
C7	0.011	0.031	0.022	0.011	0.041	0.040	0.042	0.031	0.052	0.032	0.042	0.041	0.068	-
C8	0.014	0.023	0.025	0.011	0.033	0.031	0.053	0.020	0.073	0.061	0.063	0.081	0.111	0.021
C9	0.022	0.024	0.014	0.022	0.026	0.023	0.042	0.028	0.021	0.026	0.014	0.010	0.018	-
C10	0.043	0.032	0.018	0.010	0.028	0.026	0.050	0.030	0.027	0.022	0.016	0.018	0.027	0.028
C11:1	0.052	0.021	0.037	0.034	0.032	0.032	0.028	0.061	0.023	0.033	0.032	0.010	0.034	0.032
C11	0.056	0.026	0.033	0.032	0.031	0.021	0.062	0.023	0.034	0.034	0.033	0.012	0.033	0.033
C12	0.063	0.042	0.041	0.023	0.026	0.032	0.054	0.071	0.054	0.053	0.056	0.042	0.028	0.023
C13	0.031	0.072	0.018	0.034	0.028	-	0.027	0.061	0.082	0.043	0.032	0.021	0.036	0.023
iso C14	0.056	0.034	0.028	0.031	0.042	0.031	0.063	0.047	0.091	0.063	0.092	0.071	0.035	0.042
C14	0.121	0.092	0.068	0.083	0.064	0.062	0.093	0.112	0.132	0.116	0.136	0.092	0.053	0.086
iso C15	0.047	0.029	0.083	0.052	0.037	0.026	0.036	0.026	0.048	0.026	0.023	0.012	0.043	0.026
anteC15	0.073	0.032	0.055	0.042	0.023	0.012	0.042	0.018	0.036	0.025	0.053	0.031	0.032	0.046
C15	0.096	0.084	0.053	0.096	0.053	0.035	0.087	0.115	0.075	0.064	0.084	0.053	0.056	0.084
iso C16	0.038	0.026	0.031	0.030	0.045	0.072	0.082	0.031	0.065	0.042	0.082	0.062	0.085	0.062
C16:1	0.092	0.121	0.072	0.018	0.083	0.062	0.062	0.051	0.082	0.061	0.092	0.042	0.091	0.072
C16	0.210	0.128	0.121	0.231	0.192	0.167	0.235	0.162	0.152	0.102	0.263	0.201	0.163	0.125
iso C17	0.031	0.030	0.037	0.028	0.035	0.023	0.031	0.015	0.046	0.024	0.043	0.028	0.023	0.021
C17	0.063	0.054	0.053	0.034	0.078	0.036	0.074	0.125	0.063	0.060	0.073	0.042	0.031	0.020
C18:2	0.043	0.113	0.093	0.086	0.084	0.042	0.162	0.183	0.097	0.076	0.095	0.197	0.086	0.062
C18:1	0.084	0.091	0.113	0.091	0.043	0.061	0.071	0.090	0.145	0.131	0.193	0.182	0.063	0.045
C18	0.064	0.052	0.067	0.035	0.013	0.086	0.091	0.071	0.156	0.127	0.182	0.102	0.092	0.071
C19	0.036	0.035	0.032	0.031	0.016	0.012	0.026	0.041	0.026	0.023	0.023	0.028	0.031	0.026
C20:1	0.025	0.013	0.052	0.041	0.043	0.021	0.046	0.018	0.012	0.026	0.034	0.032	0.051	0.043
C20	0.048	0.041	0.076	0.052	0.052	0.036	0.028	0.046	0.029	0.046	0.047	0.035	0.062	0.089
C21	0.018	0.042	0.012	-	0.012	0.010	0.020	0.042	0.028	0.017	0.026	0.031	0.011	0.010
C22	0.048	0.052	0.046	0.152	0.093	0.012	0.225	0.112	0.164	0.052	0.084	0.072	0.043	0.053
C23	0.063	0.035	0.062	0.053	0.034	0.030	0.065	0.047	0.031	0.030	0.032	0.030	0.051	0.042
C24	0.093	0.042	0.065	0.044	0.101	0.123	0.195	0.158	0.118	0.076	0.128	0.109	0.062	0.060
C25	0.138	0.192	0.075	0.072	0.043	0.032	0.030	0.059	0.038	0.032	0.036	0.061	0.038	0.027
C26	0.129	0.123	0.063	0.031	0.116	0.092	0.291	0.158	0.132	0.191	0.141	0.116	0.057	0.073
C27	0.058	-	0.076	0.063	0.026	0.031	0.029	0.036	0.025	0.024	0.031	0.021	0.025	0.027
C28	0.075	0.095	0.031	0.042	0.071	0.092	0.181	0.101	0.125	0.063	0.172	0.093	0.035	0.062
C29	0.031	-	0.082	-	0.026	0.041	0.017	0.036	0.052	0.041	0.026	0.021	0.043	0.085
C30	0.087	0.064	0.027	0.025	-	-	0.037	-	0.015	0.024	-	-	-	-
C31	0.026	-	0.023	-	0.031	0.032	0.086	0.026	0.031	0.049	0.032	0.030	0.037	0.030
C32	0.058	-	0.062	-	0.021	-	0.027	-	0.028	0.019	-	-	-	-
C33	-	0.031	0.058	0.030	0.018	-	-	-	0.031	-	-	-	0.037	-
C34	0.038	-	-	-	0.036	0.034	0.043	0.032	-	0.021	-	-	-	-
C35	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C36	0.029	-	0.036	0.034	0.028	0.029	-	0.023	0.021	0.010	-	0.031	-	-
Σ	2.358	2.005	2.056	1.722	1.910	1.559	2.350	2.350	2.504	2.016	2.595	2.125	1.827	1.559

A = surface sediment

B = 10 cm depth sediment

rate of burial. Fatty acids can be derived from plankton, terrigenous runoff, benthic organisms, water grasses and marsh plant (Rodier & Khalil, 1982).

The n-fatty acids exhibited a bimodal distribution , with maximum C_{16} and C_{26} and a strong even to odd carbon number predominance typically of biogenic source (Figure 2).

The fatty acids present can partly accounted for by the known input of phytoplankton, especially diatoms. These are known from microscopy and mineralogical data, to constitute an important part of the sedimentary material. Indeed, a comparison of this sedimentary fatty acid distribution with those reported for various species of plankton (CHu & Dupuy, 1980; Volkman et al., 1980) show a high degree of similarity.

The highly unsaturated fatty acids such as C_{20} and the polyunsaturated C_{16} and C_{18} acids are characteristic of many planktonic algae (Farringhton & Quinn, 1973 ; CHu & Dupuy, 1980 and Volkman et al., 1980). In addition the relative abundance of these compounds in this sediment are comparable to those found in living phytoplankton (CHu & Dupuy, 1980 , Volkman et al., 1980). Table (2) shows the concentration of fatty acids with lower and high molecular weight in two sediment layers. The C_{12} - C_{18} n - saturated and unsaturated fatty acids are of plankton origin. In general blue green algae usually have 16 : 0 or 16 : 1 as their major fatty acids component while green algae have an unsaturated C_{18} as their major fatty acid. The fatty acids (both free and bound) from the sediments of the marshes of Iraq consisted of three major component : a striaght chain of C_{14} : 0 a straight chain of C_{16} : 0 and a straight chain C_{18} : 0 . The fatty acid with more than C_{21} atoms generally of terrestrial origin (Farringhton & Quinn, 1973), they are known to form the major constituent of wax covering plant and insects (Brown et al., 1972).

Branched chain fatty acids in particular have been considered to reflect bacterial origin. Iso and anteiso branched chain acids are common to many bacteria and account for up to 60% of the total fatty acids in many *Bacillus* species (Kaneda , 1967).

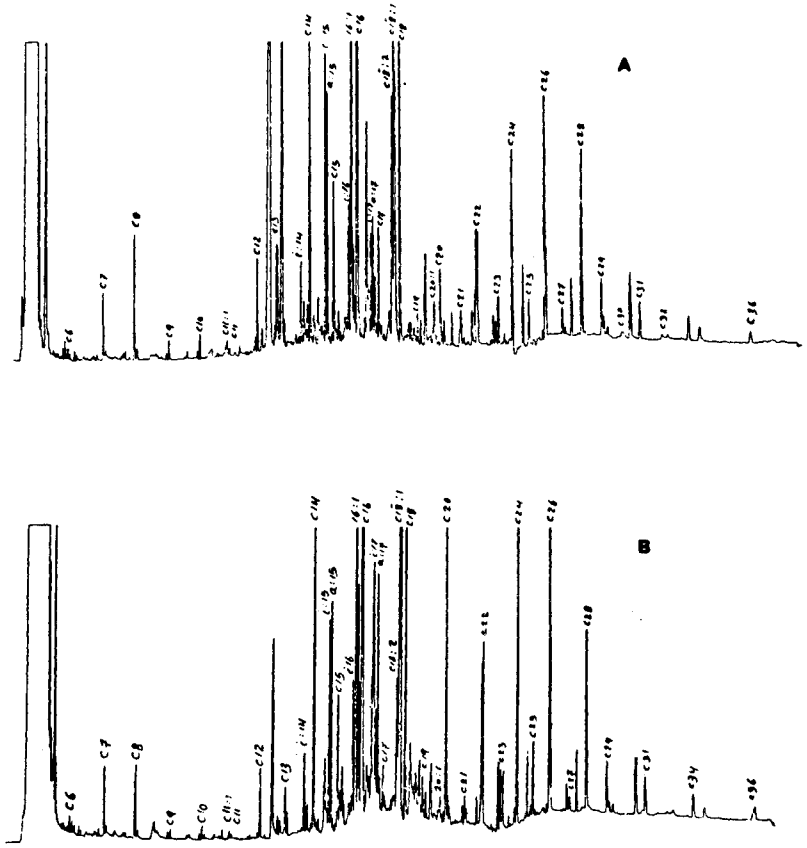

Figure (2) : Gas chromatogram of the total fatty acids from station 5.
A = Surface sediment.
B = 10 cm depth sediment.

The presence of iso and anteiso-fatty in aquatic sediment have been considered by many authors as possible marker for bacterial lipid contribution. Copper & Blumer (1968); Perry et al., (1979) concluded that the predominance of anteiso C_{15} and C_{17} fatty acids in marshes sediment confirm the presence of a bacterial activity. Our results show a decrease in the total fatty acid from surface to 10 cm depth (Table 1). C_{16} and C_{18} is more abundant in surface compared with those at 10 cm. Thus finding is in accordance with that of Cranwell (1974) and Rodier & Khalil (1982), who noticed the rapid decrease in unsaturated fatty acid with the depth and a relative accumulation of C_{12} to C_{16} fatty acids. This may be attributed to non-steady state of deposition and / or scouring (Rodier & Khalil, 1982).

In conclusion, it appears that there are three different possible origins of fatty acids formed in the sediments of the marshes of Iraq :

1. The indigenous plankton flora contributing sizable fraction of the fatty acids in the sediment with C_{16} predominant.

2. Plant wax with abundant long chain saturated fatty acids, their distribution provide evidence for aterrigenous contribution to the sediment.

3. The original biological input which derives principally from a contribution of bacteria.

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الاحماض الدهنيه في الرواسب الحديثه لاهوار جنوب العراق

المستخلص

تم فصل وتعيين الاحماض الدهنيه في الرواسب السطحيه وعلى عمق ١٠ سم من مناطق مختلفه من اهوار العراق .

شخصت هذه الاحماض الدهنيه وتم قياس تراكيزها بجهاز الغاز الكروموتوغرافي وتبين بانّ توزيعها يكون على شكل نموذجين وانّ اعلى التراكيز تظهر في ذرات الكاربون ١٦ و ٢٦ مع زيادة بتراكيز ذرات الكاربون المزدوجه على الفرديه مما يعطي دليلاً على انّ مصادر هذه الاحماض هي الفعاليات البايولوجيه الطبيعيه التي تأتي من (الهائمات، النباتات والفعاليات الميكروبيه) .

تم تحليل حجم الجزئيات وكمية الكاربون العضوي الكلي في هذه الرواسب، وعند مقارنة انواع الرواسب لكل محطه تبين عدم وجود علاقة بين الاحماض الدهنيه وبين هذه الانواع من الرواسب وكمية الكاربون العضوي الكلي .