

**Distribution and sources of fatty acids in sediment cores from
Al-Hammar marsh, southern Iraq**

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Abstract

The distribution and concentration of fatty acids in sediment cores from two stations , in the beginning (core 1) and in the end (core 2) at Hor Al-Hammar marshes Southern Iraq, were measured by high resolution capillary gas chromatography. Core was dated by employing Pb-210 method. Other relevant parameters were measured in core section including total organic carbon, C: N and carbonates in addition to grain size analysis. The sedimentation rate at the sampling station was found to be 0.7 cm/y. Thus the core sampled represents the period from 1960 to 1988.

The average concentration of fatty acids in core sections were ranged from 42.25 to 10.66 µg/g dry weight for core 1 and from 30.44 to 2.43 µg/g dry weight for core 2. Chromatography exhibit a bimodal distribution, with maximum at C16 and C26 a strong even to odd carbon number predominance, typical of biogenic source (phytoplankton, terrigenous plant wax and microbial sources).

Introduction

Iraqi marshes are fresh water wetland of unique ecosystem. The biomass mostly include the plant, and the many animals, which inhabit this rich environment. The values of include the plants are numerous, including rich flora and fauna, livestock grazing field, fish and other wildlife breeding places. Marshes are also know to be farmland for rice, and cultivation areas for some other crops. Species lists, classification, specific characteristics, water chemistry and some physical factors of the area can be sought in number of studies (UNEP, 2001; Douabul et.al.,2012 and Douabul et al.,2013)

Marshes are crucial ecosystem, which influences, and also are influenced by many natural forces and human activities. They are crucial as incubators for fish and invertebrates, and play a vital roles as habitat for majority waterfowl. On the other hand, they are a critical factor in the complex web of life for both; Shatt-Al-Arab Estuary, the Gulf, and the surrounding land ecosystems. It is, therefore, very important that remaining marshes be protected, and that their health enhanced, wherever possible this is important for the surrounding environment, and for people who share this part of Iraq, in particular (NGN,2006; Al-Maarofi et al., 2012)

Many important sedimentary deposits have accumulated under freshwater environments. Knowledge of modern equivalents of organic matter sources and of early geolipid diagenesis is valuable in deciphering the geochemical histories of these deposits. In particular, carbon skeleton chain-length

distributions of geolipids have often been utilized to provide such information (Richardson and Hussain, 2006; Bedair and Al-Saad,2007 and Mollenhauer and Eglinton,2007)

Fatty acids are used to characterize the sources of organic matter in marine sediments (Carrie et al., 1998; Mudge et al., 1998; Fahl and Stein, 1999). However, their utility as quantitative tracers of the different organic carbon sources is complicated by many factors. Ambiguities in source are common (Wakeham, 1999) and individual fatty acids may differ in their diagenetic susceptibility during particle settlement through the water column (Harvey and Macko, 1997b) and after deposition (Sun et al., 1997). Diagenetic alteration of individual fatty acids, in turn depends upon environmental factors such as water temperature (Fileman et al., 1998) and the dissolved oxygen concentration (Harvey and Macko, 1997b). Many studies have described the relative distributions of the different sources of fatty acids in vertical profiles of aquatic sediments (Colombo et al., 1996; Laureillard et al., 1997; Gong and Hollander, 1997; Stefanova and Disnar, 2000).

Only Al-Timari and Al-Saad (1990) and Al-Saad and Al-Timari (1993) were studies the distribution of fatty acid in recent sediments of Al-Hammar marshes. In this report, fatty acids were determined in different sections of sediment cores from marsh land of Iraq in order to obtain a better understanding of depositional processes occurring in the area, and to provide a record of historical input of pollutant, which could support other benchmark data for this area.

MATERIALS AND METHODS

Sediment core samples were taken from Hor Al-Hammar during the period 1988.

Sediment samples were collected from stations shown in fig.1. Using an aluminum

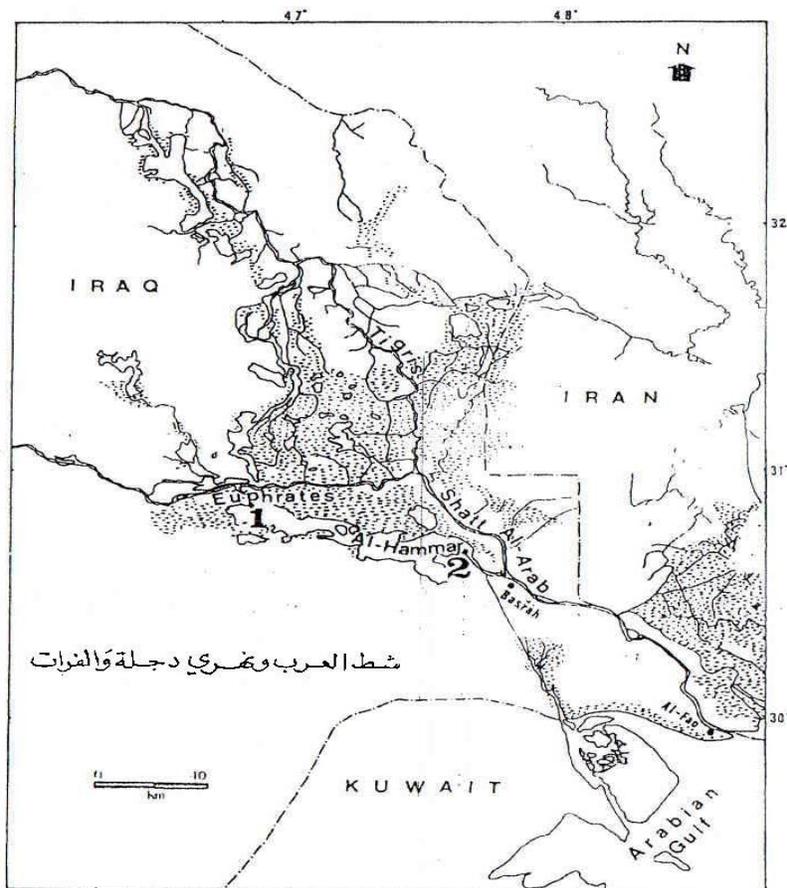


Fig. 1: Map of the Tigris-Euphrates Marsh system, Shatt Al-Arab and the Arabian Gulf, showing location of sampling site.

cylindrical core 3cm i.d. 1m length equipped with a stainless steel handling apparatus. Undisturbed, uncontaminated and replicate samples were taken. The core was worked from the bottom to the surface to prevent contamination of the deeper areas, the

sediment sampled with a spatula and the was carried out soon after sampling. Precleaning was done for all equipments and glassware including extensive washing with micro cleaning solution and triple rinsing with de ionized water, acetone and

methylene chloride and/or combustion at 400°C for 24h. Throughout this work a nano-grade purity (Burdick and Jackson) solvents were used and cleaning procedures were tested by collecting the final rinse and subjecting them to the entire analytical scheme. Blank were reduced to negligible levels for all parameters monitored.

In the laboratory 100g of dry homogenous sediment was Soxhlet extracted for 24h with a 1:1 mixture of methanol and benzene according to the method of Goutx and Salot (1980). At the end of this period, the extract was reduced in volume to ca. 10 ml using a rotary evaporator. Then the extract was saponified for 2h with a solution of 4 N KOH in 1:1 methanol:benzene. After extracting the unsaponified matter with hexane, the extract was dried over Na₂SO₄, concentrated, treated with copper to remove sulfur, and further concentrated by a stream of N₂. The concentrated extract was cleaned up by a column chromatography on 5% deactivated florisil. An aliphatic fraction was eluted with 50 ml of hexane. The saponified material was used to release free fatty acids by acidifying with 6N HCl and extracted with ether. The fatty acid extracted was then methylated by a solution of 14% BF₃ in methanol according to Metcalfe and Schmitz (1961). Quantitative and qualitative analyses of compounds were performed on a

Perkin-Elmer sigma 300 capillary gas chromatography with splitless injection flame ionization detector using SP2100, WCOT column 25 m with He as a carrier gas (1.5 ml/min), temperature was programmed from 50°C for 2 min to 300°C for 30 min at rate 4°C/min. Recovery efficiency of sediment samples exceeded 90% for all compounds. Total Organic Carbon (TOC) was determined by treating subsamples with phosphoric acids to remove carbonates, then dried at 60°C to constant weight and combusted using a Perkin-Elmer model 240B Elemental analyzer. Grain size analysis was done by using 15g dried sample, Then wet sieving was carried by sieve of 230 mesh (Folk, 1974). The fine grain (<63µm) were passed through the Sedigraph ET-5000 instrument.

Sedimentation rate in Al-Hammar marsh was done by Pb²¹⁰ activity (dpm/gm). Fig.2 show the Pb²¹⁰ as a function of depth in sediment from station 1 from this figure, the activity at the half life is dpm/gm which corresponds to a sediment of 15.9 cm. Since the half-life of Pb²¹⁰ is 22.3 years then sedimentation rate is:

$$15.9 / 22.3 = 0.7 \text{ cm/yr}$$

Thus the sampled represented the period from 1960 to 1988 (Abaychi, 1995).

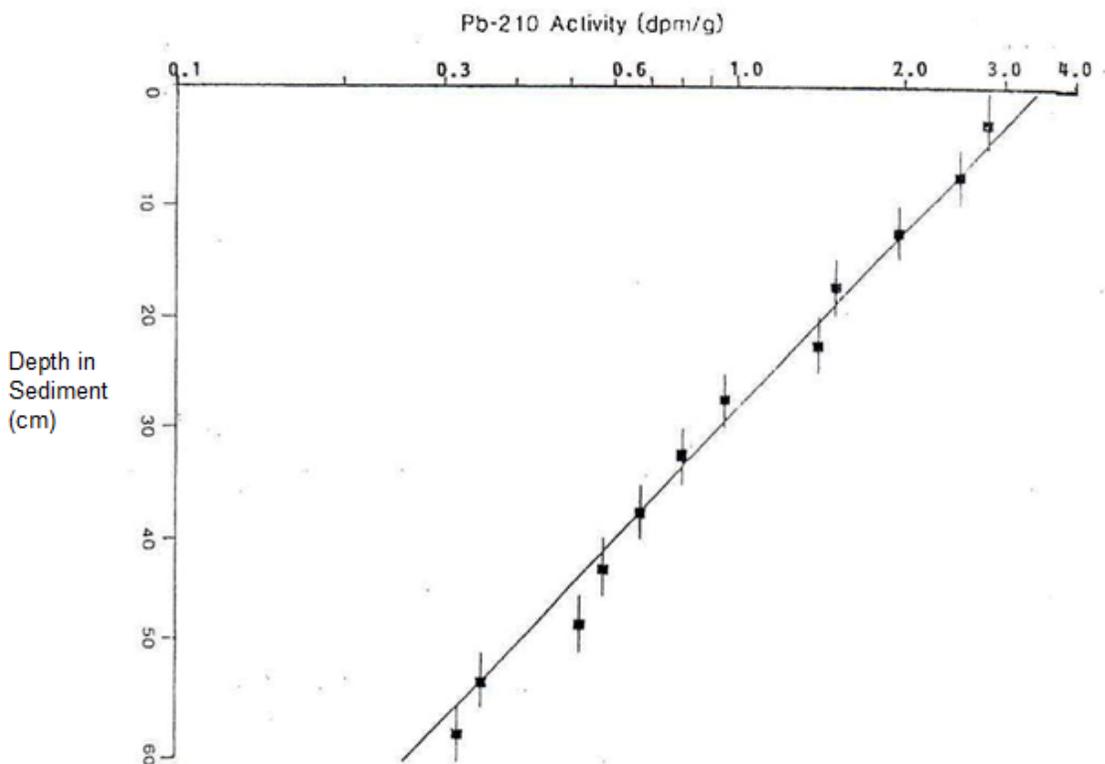


Fig. 2: Pb-210 Activity in Al-Hammar Marsh sediment as a function of depth from Abaychi(1995)

RESULTES AND DISCUSSION

the result of a core taken in the beginning and at the end of the marshes (station 1 and 2 in Fig.1) are summarize in Figs.3 and 4. The fatty acids content has been analyzed

as a function of depth in two cores in order to relates its vertical distribution to recent history of the marshes.

Sediment cores of the marshes were taken in an attempt to a good geochemical record of the pollution history for the marshes. The marsh sediment are subjected

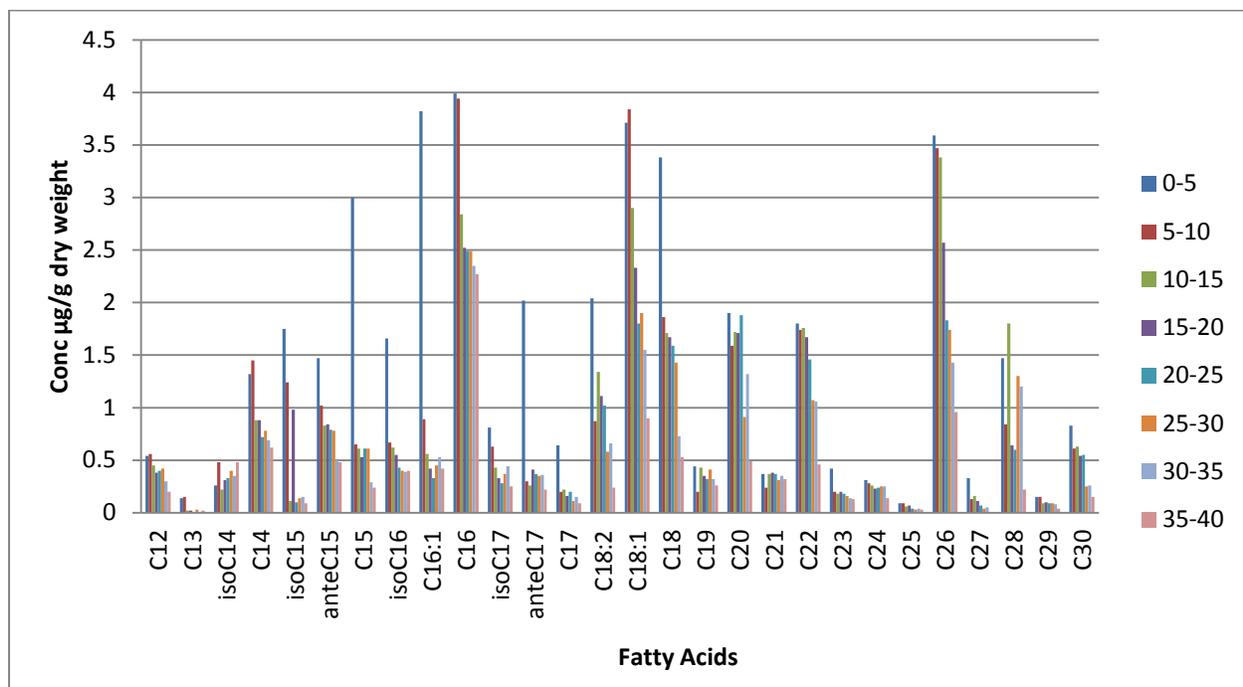


Fig.3 Fatty acids profiles in core1(st.1)

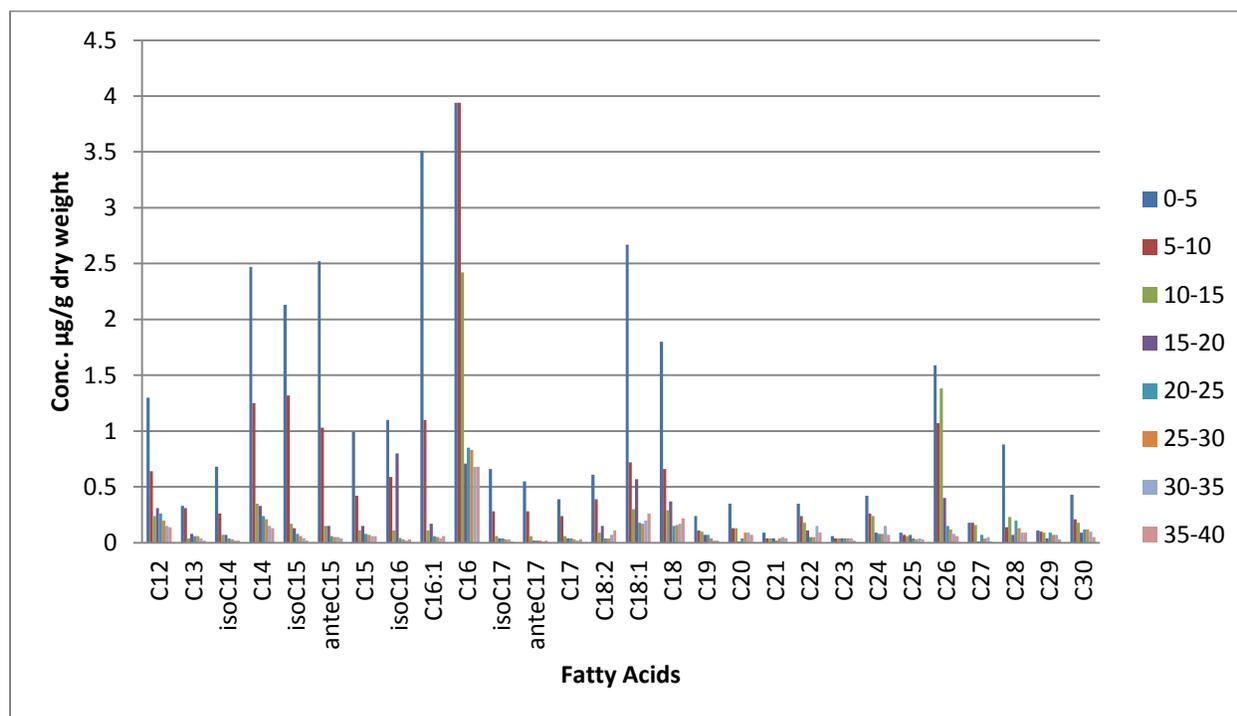


Fig.4 Fatty acids profiles in core2 (st.2)

to a great deal of physical mixing and in order to obtain a good sedimentation record, the area from which the core were taken should not be disturbed by bioturbation or physical mixing and ideally, should have a constant rate of sedimentation over the period of interest (Abaychi, 1995). It is also desirable to confirm the analytical data with historical data on the effluent discharge. The sediment from the area of study are anoxic (Al-Saad and Al-Timari, 1993), this will prohibit the development of microfauna and thus avoid the problem of bioturbation. Recently, Lead-210 (Pb^{210}) has been used to date cores in aquatic environment to get a date for deposition of pollutants (Aqrawi, 1993 and Abaychi, 1995). The obtained sedimentation rate in different marsh sediment measured by employed Pb^{210} technique (Smith and Hamilton, 1985). The relatively high value of sedimentation rate

obtained could be attributed to the huge amount of particulate matter carried by Euphrates river most which settle down in the marshes (Al-Saad and Al-Timari, 1989). This high sedimentation rate is further substantiated by the large amount of terrigenous fatty acid present at some depths and absent in others (Figs.3 and 4).

The chemical and sedimentological parameters (Tables 1 and 2 and Figs.5 and 6) provide an idea of the nature of sediments in the area (Aqrawi, 1993 and Abaychi, 1995). Calcium carbonates represented 39-51% of sediments in different skeletal-rich zone. Profiles of TOC % in the two cores are shown in Table 1 and Fig. 7. TOC concentrations at the top of cores are 2.66% and 1.44% for Station1 and Station 2 respectively, and decrease to be 0.8% and 0.15% in the bottom layer of the studied sections (35-40-cm) . The same conclusion

has been reached by Aqrawi (1993). It is known that the behavior of TOC in a sedimentary profile can be controlled by factors such as: (1) grain-size (surface area), (2) environmental conditions in the water column including primary productivity, water depth, temperature, oxygen content, etc., and (3) sedimentation rates (Sun et al.,

1997; Tyson, 2001). we believe that the observed low TOC% probably caused by an intense degradation of organic matter in the water column before deposition.

The average concentration of fatty acids in core sections were ranged from 42.25 to 10.66 for core 1 and from 30.44 to 2.43 µg/g dry weight for core 2(Fig.7) .

Table -1-

Percentage of CaCO₃, TOC, N, C and C:N ratio sediment cores from Hor Al-Hammar *

	CaCO ₃ %	TOC%	N%	C%	C:N
	Station (1)				
Depth(cm)					
0-5	42	2.66	0.94	4.59	4.88
5-10	43	2.34	0.7	4.1	5.85
10-15	45	1.95	0.95	3.54	3.72
15-20	51	1.57	0.7	3.2	4.57
20-25					
25-30	41	1.21	0.36	2.05	5.69
30-35	41	1.23	0.41	2.1	5.12
35-40	39	0.84	0.41	1.38	3.36
	Station (2)				
0-5	47	1.44	0.81	2.72	3.35
5-10	41	1.13	0.24	1.92	8
10-15	44	0.41	0.77	0.74	0.96
15-20	35	0.21	0.71	0.33	0.46

20-25	40	0.19	0.5	0.32	0.64
25-30	32	0.24	0.82	0.36	0.41
30-35	33	0.13	0.7	0.2	0.28
35-40	34	0.15	0.95	0.23	0.24

Table-2-

Grain size analysis of sediment core of Hor Al-Hammar*

Depth (cm)	Sand%	Silt%	Clay%
0-5	63.5	9.9	26.6
5-10	55.8	2.7	41.6
10-15	48.9	20.5	30.7
15-20	24.9	31.5	43.5
20-25	29.2	29.7	41.1
25-30	52.1	20.6	27.3
30-35	62.4	14.3	32.3

* = Adpoted from Al-Abaychi(1995).

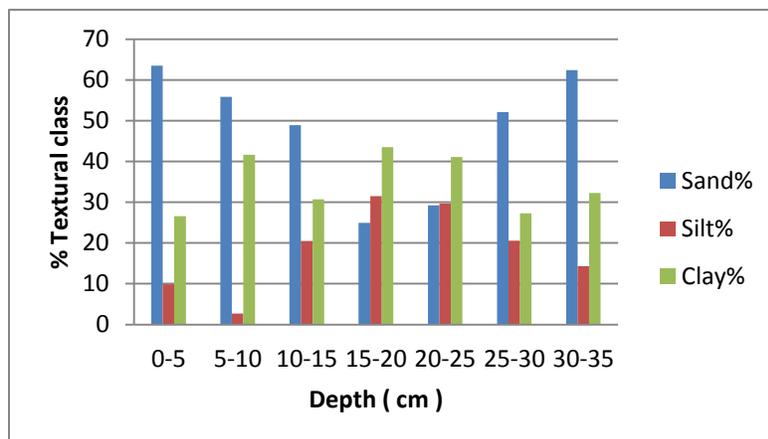


Fig.5 Grain size profiles of sediment core of Hor Al-Hammar

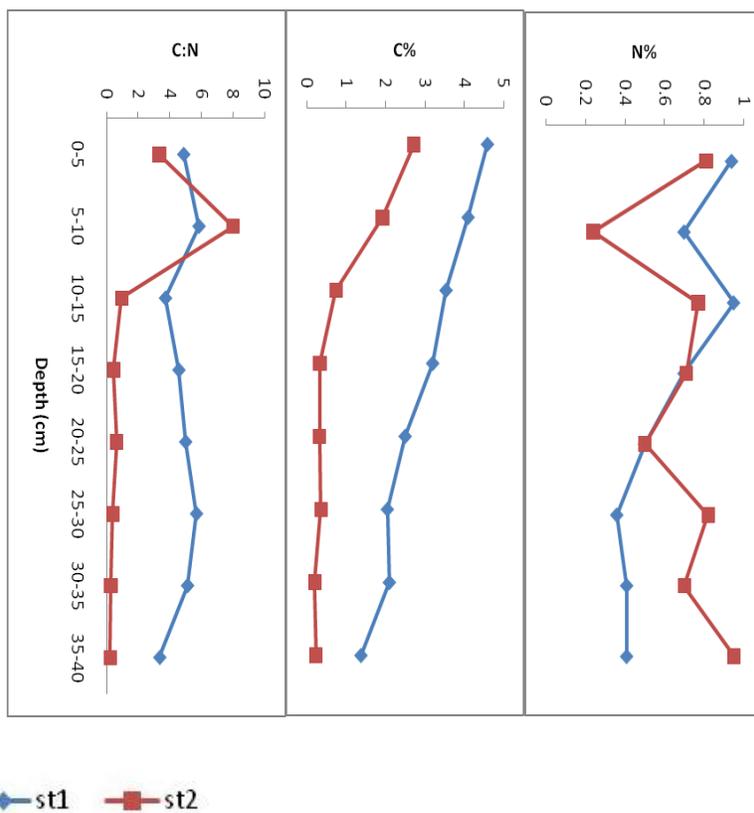


Fig.6 Percentage of N, C and C:N ratio sediment cores from Hor Al-Hammar

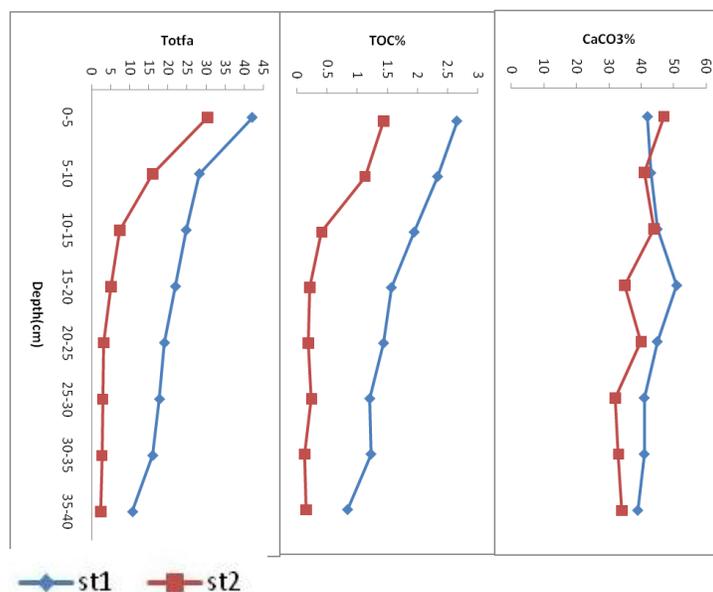


Fig.7: Percentage of CaCO₃, TOC and total Fatty acids in sediment cores from Hor Al-Hammar

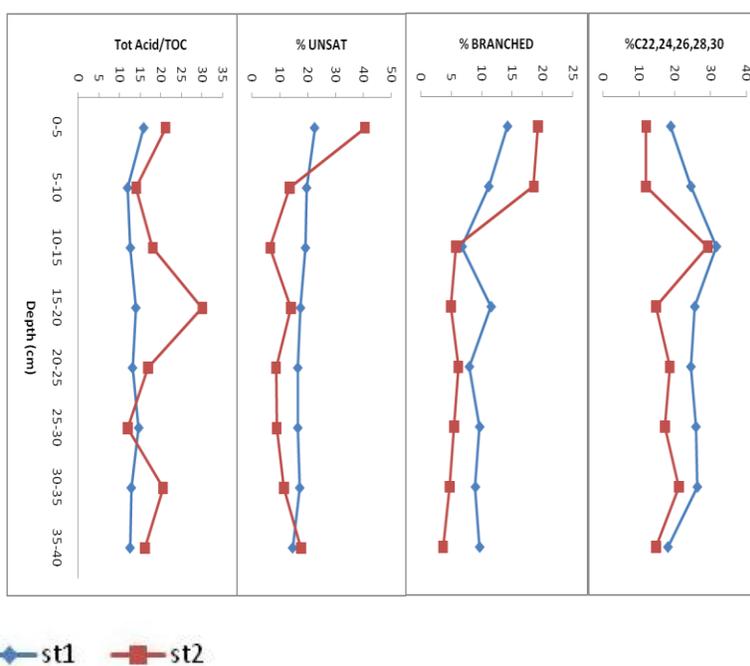


Fig.8: Ratio of fatty acids to TOC in per% TOC, unsat is the sum of the relative abundance of the planktonic acids, branched is the sum of bacterial branched acids (iso-15:0, anteiso-

15:0, iso-17:0 and anteiso-17:0), and the sum of terrigenous acids is (22:0,24:0, 26:0, 28:0 and 30:0)

Profiles of individual fatty acid concentration in the two cores are shown in Figs. 3 and 4. Chromatography exhibit a bimodal distribution, with strong even to odd carbon number. In general, the most abundant of the 27 identified fatty acids are 16:0 16:1 18:0 18:1 and 26(3.99-2.27),(3.82-0.42),(3.38-0.53),(3.71-0.9) and (3.59 - 0.96) $\mu\text{g/g}$ dry weight respectively in core 1 and (3.94-0.68), (3.51-0.06),(1.8-0.22),(2.67-0.26) and (1.59-0.06) $\mu\text{g/g}$ dry weight respectively in core 2.

some of the fatty acids can be assigned to dominant sources. Plankton (phytoplankton and zooplankton) is probably the most important source of the monounsaturated acid and the polyunsaturated acids (Zimmerman and Canuel, 2001). Bacteria are typically the dominant sources of odd and branched-chain acids, especially the iso- (i) and anteiso- (a) acids i15:0, i17:0, a15:0 and a17:0 (Gong and Hollander, 1997; Harvey and Macko, 1997a). Long-chain fatty acids 24:0, 26:0, 28:0 and 30:0 in marine sediments are typically associated with terrestrial inputs of organic matter from higher plants (see review by Meyers, 1997). The changes throughout the cores in the relative abundance of each source (defined as the sum of the concentrations of the fatty acids above assigned to each source) within the TFA pool, are shown in Fig. 8. This figure shows that the relative abundance of the planktonic fatty acids (_Plank) within the 0- 5 cm section of the two cores is 40.5-22.6%, and decreases to 17.7-14.6% within the bottom layer 40 cm. At the top of the cores the terrestrial fatty acids (_Terri) show a lower abundance than _Plank, with values between 12 and 19%, however, their relative abundance increases sharply with depth within the 10-15 cm section to values up to

29.6-31.5% The bacterial acids (_Bact), in general, show a lower relative abundance than _Plank and _Terri, and also higher relative abundance of _Terri than _Plank. _Plank show more constant values of between 22.6 and 14.6% down the cores. Sedimenting particles in marine systems tend to show a strong planktonic signal, with reported values of _Plank _32% for Chesapeake Bay, a shallow (15 m) and productive system (Harvey and Johnston, 1995), _27% for particles collected at 110 m in Breid Bay (Antarctic; Hayakawa et al., 1996), and _10–15% in particles collected at 2000 m in the Black Sea (Wakeham and Beier, 1991). In the case of surficial sediments of shallow (<20 m deep) systems, Zimmerman and Canuel (2001) report a value for _Plank _27% for samples from the southern section of Chesapeake Bay, and Canuel and Martens (1996) report a value of _20% for sediments from Cape Lookout Bight; in the case of deeper systems, Colombo et al. (1996) report a value for _Plank of _23% for a sample from a 280 m water depth in the St. Lawrence Estuary, and Wakeham and Beier (1991) report a value _10% for a sediment from a 2200 m water depth in the Black Sea. The abundance of _Bact tends to be lower in shallow systems such as Chesapeake Bay and Cape Lookout Bight (Canuel and Martens, 1996; Zimmerman and Canuel, 2001), where the deposition of fresh planktonic material seems to dominate over the in situ and the external supply of bacterial fatty acids. Sediments (Carrie et al., 1998; Mudge et al., 1998) dominated by planktonic material usually show 18:1/16:1 ratio much lower than 1. By contrast, the 18:1/16:1 ratios in core 1 and 2 are lower than 1 near the surface and increase to 5 and

3 at the bottom of the cores 1 and 2 respectively. The lower ratios near the

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surface indicate that, these cores receive a larger input of fine terrigenous particles

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توزيع ومصادر الاحماض الدهنية في رواسب لبية من هور الحمار- جنوب العراق

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المستخلص

تم قياس توزيع وتراكيز الاحماض الدهنية في رواسب لبية لمنطقتين ، في البداية(1) والنهاية (2) من هور الحمار- جنوب العراق بأستخدام جهاز الغازكروماتوغرافي كذلك تم حساب عمر الرواسب بأستخدام طريقة وحددت مؤثرات اخرى في مقاطع الرواسب وفي الكربون العضوي الكلي والكربون والنيتروجين والكاربونات كما حسب حجم حبيبات الرواسب ، وجد بأن معدل الترسيب في منطقة جمع العينات 0.7 سم/سنة وبذلك فأن عينات الرواسب تمثل الفترة 1960-1988 .

كان معدل تراكيز الاحماض الدهنية في مقاطع العينات اللبية يتراوح بين 42.25 الى 10.66 مايكروغرام/ غرام وزن جاف لعينات المنطقة (1) و 30.44 الى 2.43 مايكروغرام/ غرام وزن جاف لعينات المنطقة (2). بينت الكروماتوغرافي بأن توزيعها يكون على شكل نموذجين وأن اعلى التراكيز تظهر في ذرات الكربون 16 و 26 مع زيادة بتراكيز ذرات الكربون المزدوجة على الفردية مما يعطي دليلا على ان هذه الاحماض من الفعاليات البيولوجية الطبيعية التي تأتي من (الهائمات والنباتات والفعاليات الميكروبية).