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Sources of Hydrocarbons and Fatty Acids in Sediment from Hor Al-Hammar Marsh, Shatt Al-Arab, and North-West Arabian Gulf

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Sediment samples taken from different locations of Hor Al-Hammar marsh, Shatt Al-Arab estuary and North–West Arabian Gulf, were analysed to determine origins and sources of hydrocarbons and fatty acids.

In Hor Al-Hammar there are two different sources: one from phytoplankton and zooplankton and the other from aquatic plants dominant in the region. These are characterized by carbon numbers such as C19, C25, C27 for hydrocarbons and C16, C18 for fatty acids. The same patterns were observed in the Shatt Al-Arab estuary, while in the North–West Arabian Gulf, odd and even carbon numbers were observed; these came from different sources such as phytoplankton, especially diatoms, zooplankton, bacteria, and fungi. The input of terrigenous material such as wax of aquatic plants is missing in this area. Transportation from Shatt Al-Arab and Khor Al-Zubair was another source of higher molecular weight compounds to the North–West Arabian Gulf.

The pressure of industrial development and rising populations in the coastal zone is likely to result in increased pollutant loadings to estuaries. Pathways of anthropogenic hydrocarbons into water bodies are diverse. In addition to oil spills, lakes and estuaries receive chronic inputs from a variety of sources including industrial discharge, marinas, urban-runoff, and atmospheric fallout (Bidleman *et al.*, 1990).

In unpolluted areas, hydrocarbons associated with marine sediment are often a mixture of algal and other marine remains, and terrigenous plants. The distribution of hydrocarbons in aquatic sediment, especially the top 0–20 cm, generally shows that most organic matter present in the samples has identifiable sources. The predominance of low molecular weight (smaller than C23) n-alkanes and fatty acids in gas chromatograms is indicative of organic matter derived mainly from algae and partially from zooplankton, bacteria, fungi, and fish. However, a predominance of high molecular weight (larger than C23) is generally considered to be indicative of organic matter originating from land and aquatic plants. Fossil hydrocarbons can enter the aquatic environment through natural and anthropogenic sources (Jeng, 1981). In this paper, sediment from Hor Al-Hammar marsh, the Shatt Al-Arab estuary and North–West Arabian Gulf was taken and their sources of hydrocarbons and fatty acids were identified.

Materials and Methods

Sediment samples were collected from stations shown in Fig. 1, during 1988–1989. A Van Veen grab sampler was used, and undisturbed, uncontaminated, replicate samples were taken. The sediment was sampled with a spatula, and all the samples were kept at −20°C until analysis. For most samples, work was carried out soon after sampling. Precleaning of all equipment and glassware included extensive washings with micro cleaning solution and triple rinsing with deionized water, acetone and methylene chloride and/or combustion at 400°C for 4 h. All solvents were nongrade purity (Burdick & Jakson) and tested by collecting the final rinse and subjecting them to the entire analytical scheme. Blanks were reduced to negligible levels of all parameters monitored.

In the laboratory 100 g of dry homogenous sediment was Soxhlet extracted for 24 h with a 1:1 mixture of methanol and benzene according to the method of Goutx & Saliot (1980). At the end of this period, the extract was reduced in volume to *c.* 10 ml using a rotary evaporator. Then the extract was saponified for 2 h with a solution of 4 N KOH in 1:1 methanol:benzene. After extracting the unsaponified matter with hexane, the extract was dried over Na_2SO_4, concentrated, treated with copper to remove sulfur, and further concentrated by a stream of N_2. 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

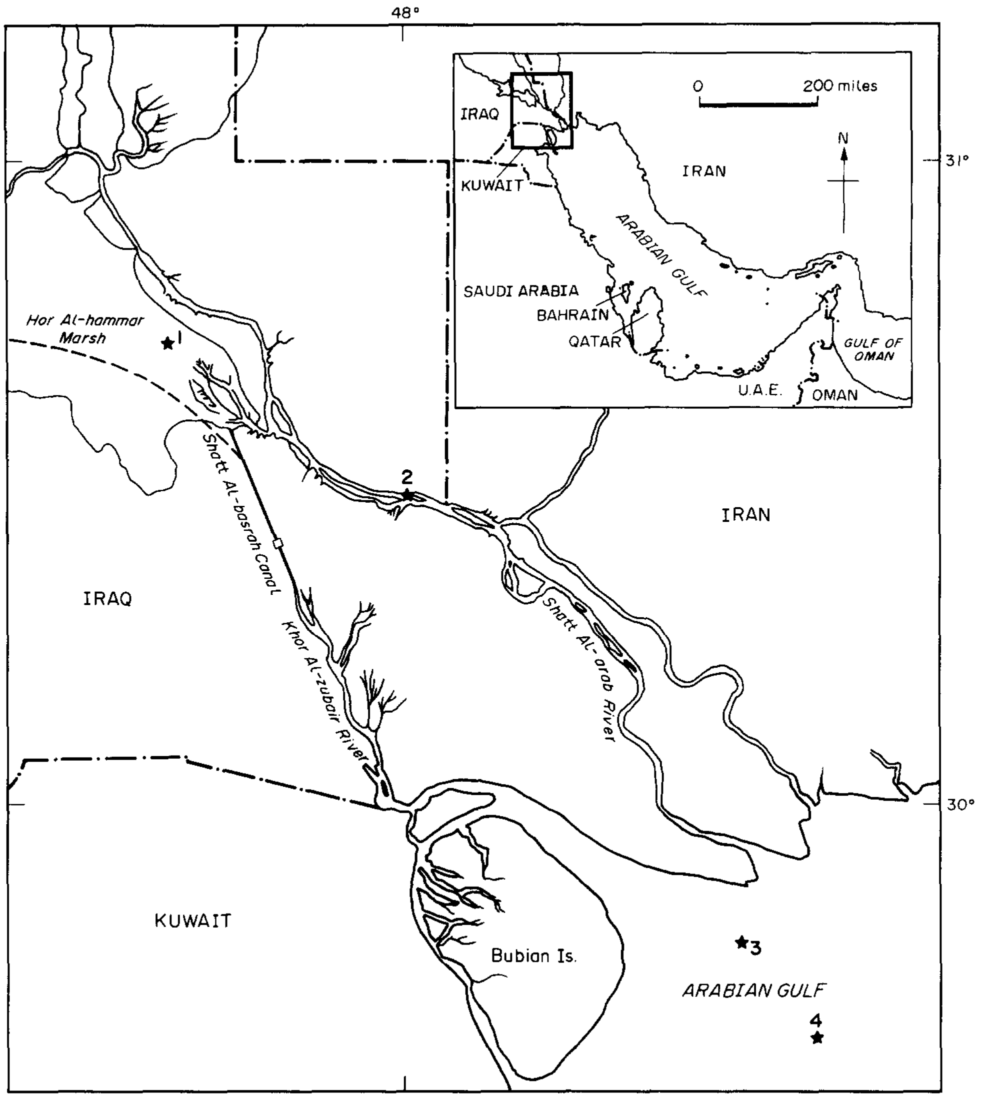

Fig. 1 Sampling locations.

methylated by a solution of 14% BF_3 in methanol according to Metcalfe & Schmitz (1961). Quantitative and qualitative analyses of compounds were performed on a Perkin–Elmer sigma 300 capillary gas chromatography equipped with splitless injection flame ionization detector using a SE30 WCOT column 50 m with He as a carrier gas (1.5 ml min^{-1}). Temperature was programmed from 70°C for 4 min to 300°C for 30 min at rate 4°C min^{-1} for hydrocarbons analysis. For fatty acid analysis using SP2100 WCOT column 25 m with He as a carrier gas (1.5 ml min^{-1}) splitless injection, temperature was programmed from 50°C for 2 min to 300°C for 30 min at rate 4°C min^{-1}. Recovery efficiency of sediment samples exceeded 90% for all compounds. Total organic carbon was determined using the oxidation with potassium dichromate, the excess oxidant was titrated against ferrous ammonium sulphate using diphenylamine as indicator. The sediment was weighed before and after oxidation (El-Wakeel & Riley, 1957).

Results and Discussion

The composition of the n-alkanes and fatty acids extracted from all sediments was relatively consistent (Table 1, 2), exceptions are Hor Al-Hammar marshes (station 1) whose samples predominantly showed abundant high molecular C23, C25, C27, C29, C31, C36 n-alkanes (Fig. 2) and fatty acids such as C16, C18, C22 (Fig. 3). The n-alkanes distribution in sediments from the North-West Arabian Gulf has the most abundant components of odd carbon number C17, C19, C21 and even carbon number C18, C20, C22 (Fig. 2). This peculiar predominance of even numbered n-paraffins can be encountered occasionally, sometimes even in very fresh samples. As examples, a predominance of even number n-paraffins in the range from C13 to C31 was first observed in several sediment samples (of an age span from 2000 to 9000 years) from the Arabian Gulf by Welte & Ebhardt (1968). Simoneit (1977) also reported one sediment section of a core sample taken from the Black Sea which exhibited a maximum peak of C18 n-alkanes with a strong even to odd predominance (overall CPI = 0.77). It is suggested that a transformation of fatty acids into saturated n-alkanes might have given rise to this phenomenon. In this study, however, samples are the most recent sediments since they were taken from the surface layer; therefore age could not possibly be responsible for the even-carbon predominance. In the light of the above

TABLE 1

Concentration of Hydrocarbons (μg g^{-1} dry wt) in sediment samples from Hor Al-Hammar, Shatt Al-Arab, and North–West Arabian Gulf.

Carbon numbers	Stations 1	2	3	4
C11		0.18	0.32	0.34
C12		0.34	0.23	0.68
C13	0.01	0.16	0.31	0.57
C14	0.04	0.49	0.64	0.66
C15	0.07	1.08	0.85	0.93
C16	0.08	1.47	1.20	1.54
C17	0.22	1.86	1.44	1.68
C18	0.20	1.28	0.89	0.97
C19	0.09	1.05	0.53	0.65
C20	0.07	0.84	0.74	0.58
C21	0.31	1.98	0.45	0.38
C22	0.03	0.76	0.13	0.17
C23	0.04	0.69	0.21	0.28
C24	0.06	0.84	0.12	0.37
C25	0.09	0.43	0.20	0.29
C26	0.06	0.56	0.13	0.11
C27	0.22	0.37	0.12	0.10
C28	0.09	0.28	0.21	0.21
C29	0.29	0.73	0.10	0.13
C30	0.03	0.38	0.10	0.28
C31	0.09	0.18		
C32	0.03	0.20		
C33	0.04	0.21		
C34	0.02	0.32		
C35		0.10		
C36	0.01	0.11		
Total	2.20	16.89	8.92	10.92
Pristane	0.13	1.45	0.93	0.67
Phytane	0.09	1.18	0.42	0.48
Squalane	0.04	0.64	0.35	0.26
CPI	2.05	1.14	1.03	0.96
UCM	2.30	3.20	1.32	1.63
TOC%	0.90	0.76	1.90	2.40

TABLE 2

Concentration of fatty acids (μg g^{-1} dry wt) in sediment samples from Hor Al-Hammar, Shatt Al-Arab, and North–West Arabian Gulf.

Carbon numbers	Stations 1	2	3	4
C6	0.01	0.09	0.11	0.06
C7	0.05	0.34	0.23	0.31
C8	0.07	0.30	0.16	0.18
C9	0.02	1.19	0.31	0.43
C10	0.03	0.10	0.29	0.54
C11:1	0.02	0.45	0.12	0.03
C11	0.03	1.86	0.10	0.71
C12	0.06	0.46	1.10	1.92
C13	0.08	0.83	0.32	0.10
isoC14	0.09	0.64	0.41	0.45
C14	0.13	1.84	2.78	1.45
isoC15	0.06	0.78	1.63	1.23
anteC15	0.04	0.90	0.74	1.87
C15	0.07	0.86	0.68	1.94
isoC16	0.06	0.46	0.89	0.71
C16:1	0.08	0.79	1.21	1.42
C16	0.15	1.89	1.89	1.86
isoC17	0.05	0.82	0.63	0.73
C17	0.06	0.64	0.52	0.41
C18:2	0.10	0.80	0.43	0.72
C18:1	0.15	0.92	0.56	0.51
C18	0.15	1.52	0.68	0.64
C19	0.03	0.85	0.12	0.12
C20:1	0.01			
C20	0.03	0.56	0.10	0.09
C21	0.03	0.42	0.09	0.04
C22	0.16	0.38	0.06	0.02
C23	0.03	0.31	0.04	0.01
C24	0.11	0.30	0.03	0.03
C25	0.03			
C26	0.13			
C27	0.03			
C28	0.12			
C29	0.05			
C30	0.01			
C31	0.03			
C32	0.03			
C33	0.03			
C34				
C35				
C36	0.02			
Total	2.50	22.1	16.64	19.07

reasoning it would seem logical to expect that a direct input from marine plankton is a more likely source of even-carbon n-alkanes (Al-Saad & Al-Timari, 1990). The presence of longer chain C23–C36 alkanes is evidence that there is a terrigenous input to these sediments, since such compounds are characteristic of higher plant wax (Simoneit 1978), and because the marshes of Iraq contain many grass and aquatic plants. Higher molecular weight n-alkanes with a great predominance of odd carbon number such as C21, C25, C27, C29, C31 are widely distributed in these sediments (Fig. 2). Besides, the n-alkanes from photosynthetic and nonphotosynthetic bacteria range in chain length from C13 to C31. In our samples the C17 is the predominant odd carbon number and it was known that the widespread sulphate reducing bacteria *Desulfovibrio desulfuricans* biosynthesize this alkane, suggesting a possible source from these bacteria.

Diatoms are the most dominant group of phytoplankton in Hor Al-Hammar (Al-Saadi & Al-Mousawi, 1988) and in the Shatt Al-Arab (Al-Saboonchi & Al-Saad, 1988) and in the North–West Arabian Gulf generally (Al-Handal 1988), they are a major and common source of autochthonous organic matter in the region (Tynni, 1983) which suggests that diatoms are responsible for even carbon n-alkanes in these sediments. Fatty acids containing from 12 to 22 carbon atoms probably originate from marine algae, plankton and microorganisms (Cranwell, 1974). However, they can also have a terrigenous source. For station 3 and 4, the fatty acid distributions show a predominance of even carbon number components C14, C16 and C18 (Fig. 3) with unsaturated fatty acids in the range C18 to C24 being major components of marine plankton (Volkman *et al.*, 1980). A presence of low amounts of odd number carbon acids in the range C13–C19 (Fig. 3) may indicate the presence of bacterial activity (Saliot *et al.*, 1980). The absence of higher molecular weight odd and even carbon number fatty acids in the range C24–C32, shows that inputs of terrigenous materials such as cuticular waxes of higher plants are negligible in this area (Al-Timari & Al-Saad, 1990).

The fatty acids in the marshes exhibit a bimodal distribution with maximum C16, C18 and C22, C26 and a strong predominance of even to odd carbon number, which is typical of biogenic sources (Table 2, Fig. 3) derived from plankton, terrigenous runoff, benthic organisms, water grasses and marsh plants (Al-Timari & Al-Saad, 1990).

The fatty acids (both free and bound) from Hor Al-Hammar marsh sediment consisted of three major

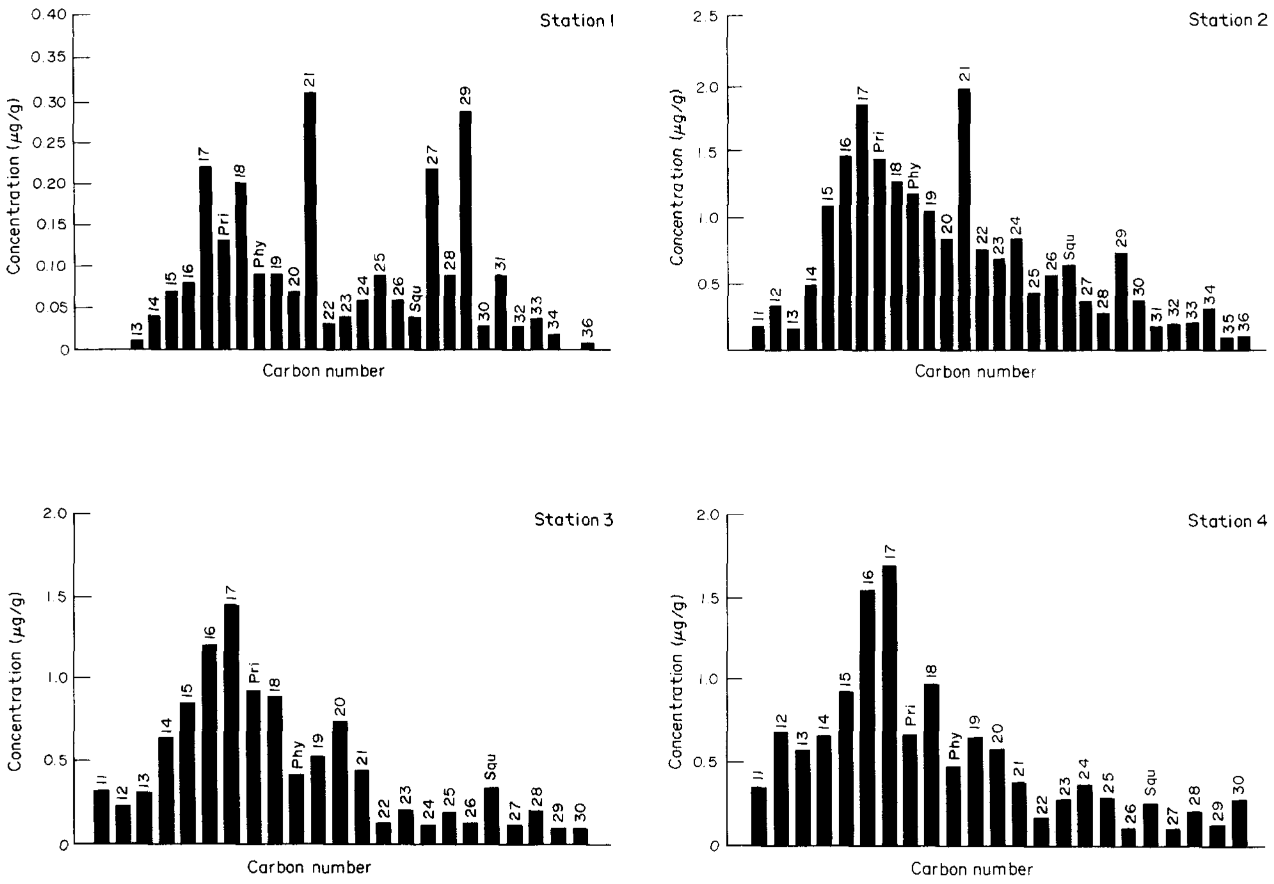

Fig. 2 Distribution histograms for n-alkanes.

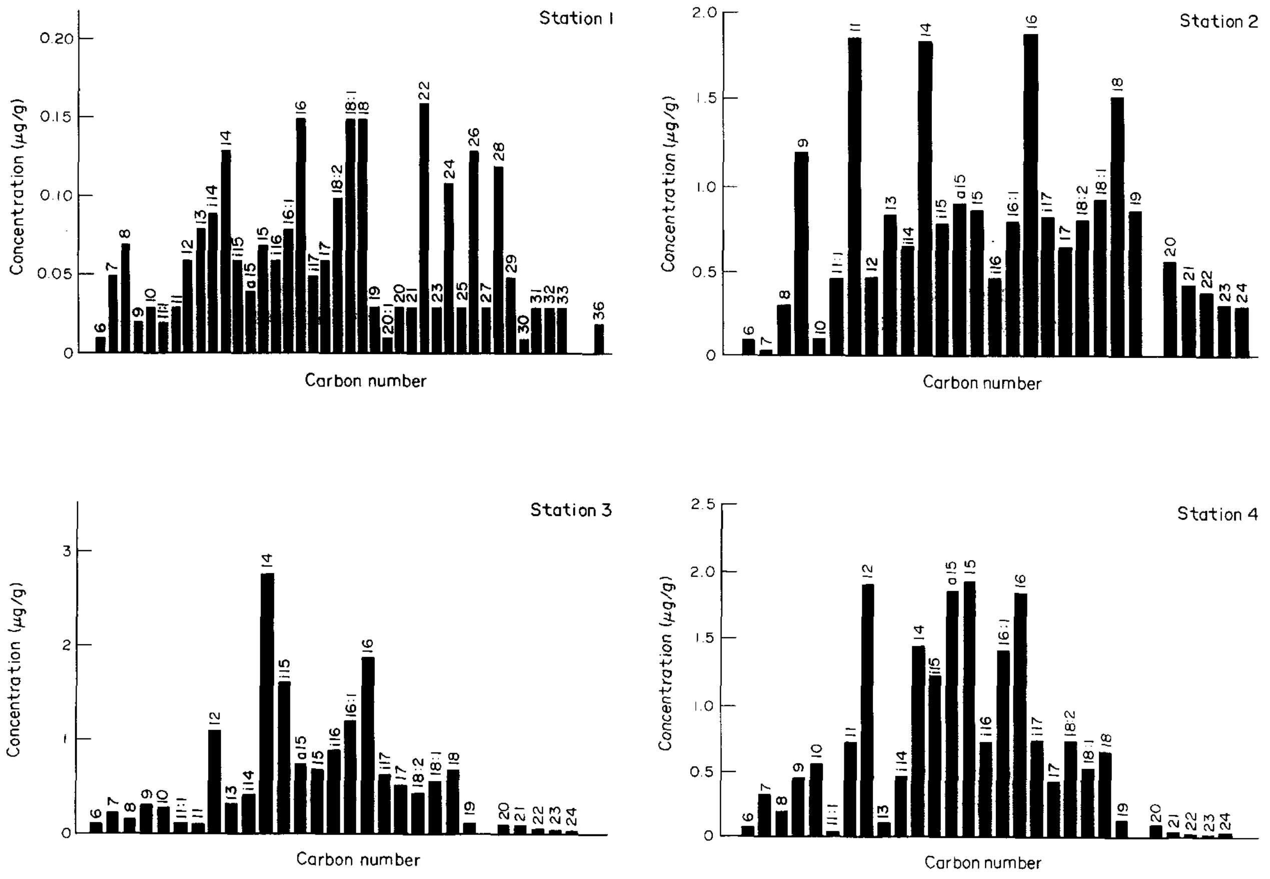

Fig. 3 Distribution histograms for fatty acids.

components namely, straight chain C14:0, C16:0 and C18:0 (Al-Timari & Al-Saad, 1990), implying that fatty acids with more than C21 generally are of terrestrial origin, and they are a major constituent of plant and insect wax. However, the presence of iso and anteiso fatty acid in marsh sediment confirms the presence of bacterial activity (Al-Timari & Al-Saad, 1990).

Carbon preference index (CPI) for hydrocarbons is expressed as a summation of odd carbon number homologs over a range divided by a summation of even carbon number homologs over the same range (Simoneit, 1978). As shown in Table 1, CPI in station 1 and 2 (odd/even preference) was substantially greater than one, which indicates more complex biogenic sources, while in station 3 and 4 the pattern is easily obscured by petroleum contamination which tends to reduce CPI to unity.

The most common isoprenoids, pristane and phytane, have been found in all sites (Table 1; Fig. 2). Pristane can originate from zooplankton (Blumer *et al.*, 1963) or from decomposition of algae (Simoneit, 1978). Phytane may originate from several types of bacteria or from decomposition of algae, which is generally a major attributed source. Also the presence of squalane (Table 1 and Fig. 2) in all the samples has a different origin which might have originated from living organism or from artificial sources (Al-Saad, 1990).

The sediment samples also contain Unresolved Complex Mixture (UCM) (Table 1 and Fig. 5). The measureable amount of UCM in these sediment could originate from a number of possible sources (Brook *et al.*, 1977). As shown in Fig. 4, it is evident that all the stations studied are contaminated to some extent with hydrocarbons and fatty acids, the higher concentration were always observed at Shatt Al-Arab estuary (station 2), while the lowest were at Hor Al-Hammar (station 1), indicating that pollution of the Shatt Al-Arab estuary has diverse sources, e.g. oil refinery discharges, municipal and industrial effluent and urban run-off (DouAbul & Al-Saad, 1985).

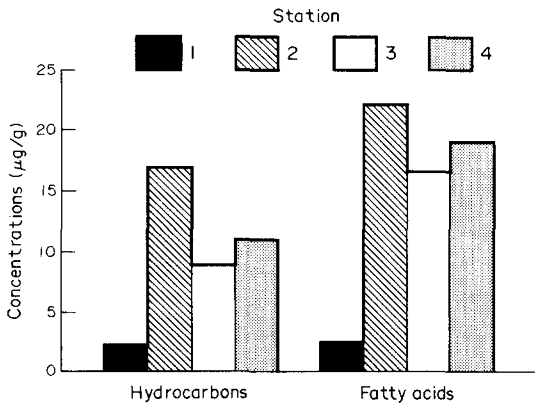

Fig. 4 Distribution histograms for total hydrocarbons and fatty acids.

The degree of pollution in Hor Al-Hammar was very low and this pollution was mainly from Tigris-Euphrates rivers. In sediment of the Shatt Al-Arab estuary, the larget sources of pollutant contributed by both Tigris-Euphrates river and pollutants came from small spillages of fuel oil as well as direct discharge of boat engine exhaust. In the North-West Arabian Gulf, pollution is greater than in the marshes.

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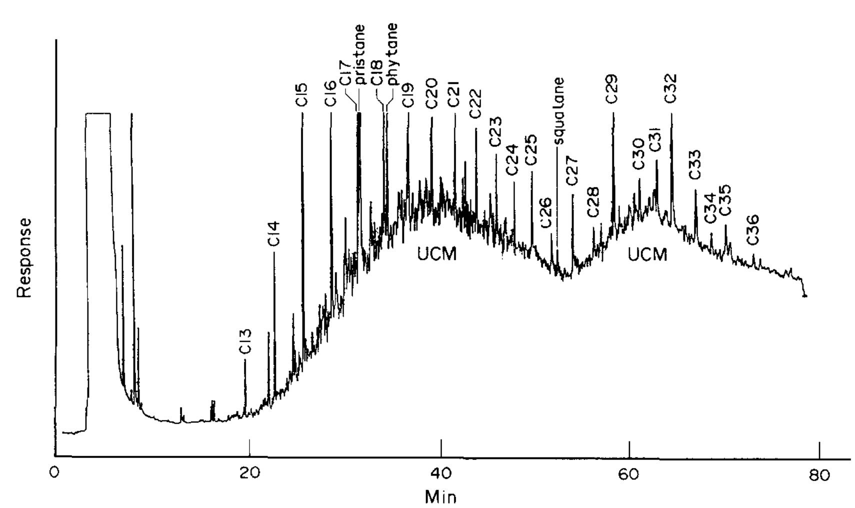

Fig. 5 Gas chromatogram of n-alkanes from station 2.

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Mercury Bioaccumulation by Shrimp (*Penaeus aztecus*) Transplanted to Lavaca Bay, Texas

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A field study was conducted to determine mercury accumulation rates by brown shrimp, *Penaeus aztecus*, transferred to a mercury contaminated estuary, Lavaca Bay, Texas. Mercury levels in the caged shrimp rose from an average baseline value of 347 ± 163 ppb to 1170 ± 107 ppb in 36 days, resulting in an average rate of mercury uptake of 22 ppb per day. Our results show that shrimp rapidly accumulate Hg when confined to a contaminated area, even though the natural population of shrimp in Lavaca Bay is not contaminated.

As much as 29.9 kg day^{-1} of mercury was released into Lavaca Bay, Texas from 1966 to 1970 by waste water from a chlor-alkali plant (Fig. 1). Since 1970 the Texas Department of Health (TDH) has issued periodic health warnings and bay closures due to elevated (>0.5 pm wet wt) Hg levels in Lavaca Bay organisms, only to reopen the bay to fishing when the Hg levels decreased. Portions of the bay closed to commercial and sport fishing of finfish and crabs in 1988 have not been reopened as of this writing. Unlike natural population of oysters (*Crassostrea virginica*) and blue crabs (*Callenectes sapidus*) in Lavaca Bay, no high (>0.5 ppm wet wt) mercury levels in shrimp have been reported by the TDH (Trebatoski & Gooris, 1990) or other researchers who worked in the area (Blanton & Blanton, 1972; Palmer, 1992). Therefore all of Lavaca Bay remains open to shrimping.

Numerous laboratory metal accumulation studies have been conducted using a variety of invertebrates over the years (e.g. King & Davis, 1987; Riisgård & Famme, 1986; Zanders & Rojas, 1992). In the work reported here, instead of a laboratory study, field caging experiments were used to determine the uptake rate of mercury by shrimp confined to a contaminated area of Lavaca Bay. To our knowledge, this is the first time that transplanted shrimp have been used to determine mercury accumulation rates in the field. Although it is impossible to control variables such as temperature, salinity, food supply and turbidity in a field study, the authors felt that a field caging study would better reflect natural conditions than a laboratory study using Lavaca Bay sediment of mercury contaminated food.

Materials and Methods

In July 1991 similarly sized (3.2 ± 0.31 cm rostral length; 3.16 ± 0.31 g wet wt) adult brown shrimp (*Penaeus aztecus*) were collected from Matagorda Bay in a relatively uncontaminated area about 10 km from