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Hydrocarbons in Seawater, Sediment, and Oyster from the Omani Coastal Waters

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Over half of the world crude oil supply is transported from the Arabian Gulf area via tankers through the narrow Strait of Hormuz, which forms the northern boundary of the Sultanate of Oman. Generally, crude oil tanker traffic off the coast of Oman is relatively heavy and all the vessels entering the Gulf to load at various terminals pass by the coastal line of Oman.

The present work plays an essential part on the Omani marine monitoring program. The purpose of this program was to establish baseline levels of selected heavy metals, chlorinated and petroleum hydrocarbons in some marine species. This study aims to assess hydrocarbons in seawater, sediment and rocky oysters from the different sites along Omani coastal waters.

MATERIAL AND METHODS

The pollutant sampling stations are shown in Figure 1. Rock oysters sites were chosen where rocky outcrops with attached fauna could be seen near beaches surveyed for oil pollution and represented different regions in Omani coastal waters.

Samples of seawater for petroleum hydrocarbons were taken from a depth of 1 m at reference stations following procedures outlined by (ROPME 1983 and UNESCO 1984). Briefly, sub-surface grab seawater samples were collected into 2L amber colored glass bottle previously rinsed 3 times with a mixture of dichloromethane and hexane, (6/4 v/v). If the extraction was not started within 4-6 hours, small amount of seawater was removed and 50 ml of glass redistilled methylene chloride was added to bottle and subsequently stored in dark. Samples should be analyzed during 7 days.

Surface sediments were taken with small stainless steel van veen grab sampler operated by handline. The surface layer (top 1 cm) was carefully removed with a spatula and frozen in glass jars or aluminium foil previously cleaned with dichromate-sulfuric acid, tap water, acetone and rinsed three times with dichloromethane.

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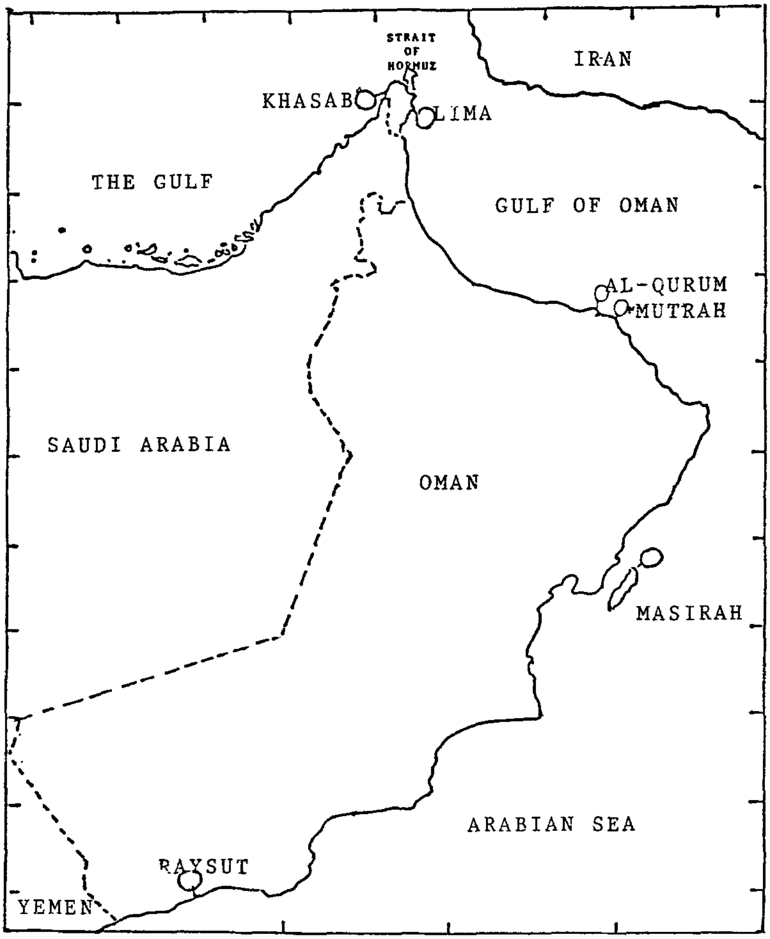

Figure 1. Sampling location in the Sultanate of Oman

Rock oysters Saccostrea cuculata) were opened with knife and hammer and the soft parts scraped into appropriate containers (solven-washed glass bottles for hydrocarbons). In Soutern Oman, mussels (Perna-perna) were also collected.

Frozen aliquots of sediment and biota samples were subsequently freeze-dried. Sediment samples were sieved and fractions less than 63 um were used for extraction. 10 g of freeze-dried sediment and 5g of biota samples were Soxhlet extracted with a mixture of 15% dichloromethane in hexane and methanol (1:1) and the extract partitioned between dichloromethane-hexane layer and methanol-water layer. The lipids in the dichloromethane-hexane layer were saponified. Elemental sulfur present was removed by reaction with activated copper. The sulfur free non-saponifiable lipid extracts were then separated into two main fractions using a column of alumina packed over silica gel (both 5% deactivated with water). The fraction 1 (F1) included alkanes, alkenes and cycloalkanes, was eluted with one column of pentane. Fraction 2 (F2) contained alkenes, aromatic and polyaromatic hydrocarbons was eluted with one column of 10% benzene in pentane followed by one column of 20% benzene in pentane (Farrington and Tripp 1977).

Shimadzu RF-5400 spectrophotometer was used for the analysis of total hydrocarbons. Quantification was made with excitation at 310 nm and emmission at 360 nm. Estimation of oil type was based on examination of emmission spectra at 310 nm excitation and synchronous excitation-emmission scan with wave length difference of 20 nm.

The quality assurance program included the following steps: 1- A blank was run with each set of analysis. 2- The calibration program was verified on each working day by the measurement of one or more standards. 3- A random sample was run in triplicate. Quality control sample was analysed with each series of actual samples. The relative standard deviations ranged between 10% to 15% of the mean.

RESULTS AND DISCUSSION

The UV fluorescence analytical technique was selected for assessing the petroleum hydrocarbon levels in seawater, sediment and biota. The method is simple and is sufficiently sensitive to detect very low concentrations of polycyclic aromatic hydrocarbon constituents of mineral oils. The disadvantage of this method is that it measures a signal from a mixture of compounds; the fluorescence units are measured and then converted to an arbitrary scale of petroleum units. Taking this into account it is important that the results be reported in terms of standard reference material. In the present analysis chrysene as well as Kuwait crude oil (ROPME 1983) are used as standards with excitation at 310 nm and emmission at 360 nm.

Total petroleum hydrocarbons (THC) levels in seawater samples collected from Omani coastal waters (Figure 1) in all periods of surveys, October 1985-October 1988, were measured by fluorescence spectrofluoremetry and represented in Table 1. The results showed that the samples from Masirah and Raysut harbor appeared to be relatively contaminated by oil and the mean concentrations were 8.69 and 14.44 ug/L, respectively, when chrysene is used as reference, while the levels were reported to 19.7 ug/L at Masirah and 32.96 ug/L at Raysut when ROPME crude oil was used as standard. In contrast, samples from Mutrah harbor near oil bunkering terminal was relatively clean.

A comparison of the data in Table 1 with levels of THC in other areas of the world oceans suggests that with one exception of Raysut harbor, current levels of petroleum hydrocarbons at these sites are not exceptionally high and are within the range as reported in other areas of the world oceans. For example, Faraco and Ros (1979) found that the concentrations of THC in Western Mediterranean sea ranged from 1-12.3 ug/L with an average of 9.8 ug/L. Monitoring studies carried out in the North Atlantic off the coast of Canada show average levels of approximately 4.9 ug/L and ranged from

Table 1. Total hydrocarbons in seawater (ug/L)

Site	Chrysene standard		Crude oil standard	
	Range	Mean	Range	Mean
Musandam (Khasab)	0.15- 2.37	1.15	0.50- 3.00	1.64
Mutrah	0.37- 6.53	2.56	0.86- 19.50	6.53
Masirah	0.09- 23.6	8.69	0.23- 71.00	19.70
Raysut	0.31- 66.0	14.44	0.70-152.00	32.96

1.6-10.8 ug/L (Gordon and Keiser 1974). The mean concentrations measured at several stations in the present survey ranged between 1.15 to 14.44 ug/L with an average of 5.71 ug/L.

Sediment samples from four sites exhibited light to heavy petroleum contamination (Table 2). The mean residue levels of THC ranged from 0.77 to 7.87 ug/g dry weight when ROPME crude oil is used as standard. The highest levels were found in sediments at Mutrah harbor. This result is not in agreement with the relatively low levels that have been measured in seawater from the same site. Likewise, sediments from Raysut harbor indicate a relatively low degree of contamination, whereas water at that station was found to possess relatively higher contaminant levels. The reason for this may be attributed to the coarse grained sands at Raysut harbor which are known to be typically poor accumulators of organic pollutants (Burns et al 1982). As a general trend, the THC levels in sediments increased in the following order: Mutrah> Masirah>Raysut>Musandam.

Oyster samples analysis showed the presence of petroleum hydrocarbons pollution at nearly all stations (Table 3). The consistently low levels observed in rock oysters from Southern area at Raysut site are most likely due to biogenic hydrocarbons and indicate a very clean environment in this area. The same observation was reported in a 1980 survey (Burns et al 1982). Another interesting observation is the contrast between the relatively higher levels in oysters and the lower dissolved petroleum concentrations in seawater from the Musandam area (Lima site). This may indicate chronic contamination of the oysters since these bivalves are known to accumulate and integrate over time substances such as petroleum hydrocarbons.

Assuming a uniform distribution of petroleum hydrocarbons in seawater, the accumulation factors (mean concentration in media ug/kg / mean concentration in water ug/L) of 1890, 6179, 543 and 132 for sediments at Musandam (Khasab site), Mutrah, Masirah and Raysut, respectively were obtained. However, the accumulation factors of 9390, 710 and 632 in oysters at Musandam (Lima site), Masirah and Raysut respectively indicate that they act as good indicators of petroleum hydrocarbon accumulation and integration.

Table: 2 - Range and mean of Petroleum hydrocarbons in sedimens from Omani coastal waters (ug/g dry weight)

Site	F_1				F_2				F_1 & F_2			
	Chrysene		Crude oil		Chrysene		Crude oil		Chrysene		Crude oil	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Musandam (Khasab)	0.01- 3.0	0.64	0.01-27.2	4.80	0.30- 7.2	2.17	1.40- 9.2	3.96	ND - 1.8	0.77	0.20- 8.6	3.1
Mutrah (Harbor)	0.04-10.7	2.45	0.15-99.0	22.20	7.20-238.5	52.37	10.52-420.0	100.18	3.20-12.5	7.87	21.50-119.0	40.35
Masirah (Haql)	0.01- 1.0	0.28	0.01-10.6	2.38	1.00- 17.6	5.58	4.18-144.0	33.50	0.10- 8.9	3.24	1.00- 23.8	10.52
Raysut (Harbor)	0.01- 0.97	0.26	0.01- 3.0	0.71	0.78- 6.3	2.65	2.6 - 60.0	17.83	0.20- 6.6	1.83	1.5 - 7.8	4.35

Table: 3 - Range and mean of Petroleum hydrocarbons in oysters from Omani coastal waters (ug/g dry weight)

Site	F_1				F_2				F_1 & F_2			
	Chrysene		Crude oil		Chrysene		Crude oil		Chrysene		Crude oil	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Musandam (Lima)	ND -65.9	13.45	ND -660.0	134.3	4.3 -74.7	42.16	43.2-454.0	201.9	12.2-74.7	37.0	111.0-248.4	154.08
Al-Qurum	0.01- 5.7	1.22	0.03- 53.5	11.12	6.8 -74.5	26.34	22.5-707.0	194.56	3.6-31.1	12.76	22.5-141.5	64.1
Masirah	ND - 0.8	0.24	ND - 7.0	1.92	0.03-13.0	4.99	8.1-124.0	44.24	1.5- 5.5	3.02	8.2- 25.3	14.98
Raysut	ND -14.0	3.1	ND -131.5	29.12	1.2 -13.9	6.52	4.3-132.8	46.78	1.3- 5.7	3.64	4.4- 39.5	20.84

ND = not detected

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