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# *CONCENTRATION OF PETROLEUM HYDROCARBONS IN FISH,MUSSELS AND SEDIMENT SAMPLES FROM THE RED SEA – COAST OF YEMEN*

By

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## *ABSTRACT*

*This investigation involves the utilization of spectrofluorometric analysis to estimate petroleum residues in fish and fish food from the Red Sea Coast of Yemen. The result, confirmed that all the site are contaminated to some extent with petroleum hydrocarbons. The concentration of petroleum hydrocarbons in the muscles samples ranged from 15.7 ug/g at station RS-I to 63.9ug/g.at station RS-IV, whereas sediment samples ranged from 1.2ug/g at station RS-I to 6.94ug/g at station RS-VI dry weight, expressed as kuwait crude oil equivalent. In order to characterize the extracted hydrocarbons some of the extracts were analyzed by capillary gas chromatography.*

*The chromatograms showed that muscles and sediment extracts contained degraded hydrocarbons in addition to biogenic hydrocarbon components. It was concluded that the Red Sea fishes are subjected to the same point-source pollution of oil contamination as the life sentinel muscles. This pollution is a consequence of localized oil operations and or heavy ship traffic.*

## *INTRODUCTION*

The Gulf of Aden and the Red Sea are among the busiest tanker rout. Most of the produced oil in the region is exported via Sea and pipe lines while local refineries and consumption are located in the coastal area. The oil pollution in the Red Sea is not surprising (Wennink & Nelson-Smith, 1979; Dicks 1987). Although enough data are not available for the Red Sea, probably the pattern may be similar to that of the Arabian Gulf, which suggest that the impacts from tanker and ship traffic are most important (linden *et al.*, 1990). It is important to make distinction between chronic and catastrophic oil pollution. Chronic refers to long-term but constant low Level seepage of oil into the marine environment from shipping, deballasting, etc, and may not be immediately apparent. catastrophic events refer specifically to accidental oil spill which may contaminate either open oceans or coastal shores .

The Yemeni coaste in both the Red Sea and the Gulf of Aden contain a variety of ecosystems which interact to varying degrees and which are ultimately dependent upon each other. Furthermore, there are various critical habitats along the Yemeni coasts, such as seagrass beds, mangrove stand, coral reefs, soft- bottomed lagoons and offshore islands (TMRU 1987). These habitats are especially, important to management of fisheries and to the conservation of valuable species, due to their high organic production and they represent spawing, breeding or nursery grounds for many species of commercial and/or scientific value. Accordingly, both the Red Sea and the Gulf of Aden are designated "special areas" under the international MARPOL convention. This means that operational discharges from shipping are restricted.

However, it was found that oil pollution from these sources has a far greater effect on the marine environment than accidentals spills. An example of a Chronic oil pollution source on the Yemen coast is the authorised discharge of ballast water effluent of the SAFER super-tanker storage at Ras Isa. Similar problems occur in the Gulf of Aden with vessels deballasting at the Aden refinery. However, the problem of passing vessels deballasting in the Gulf of Aden or the Red Sea appears to be the greater cause of oil pollution in R.O.Y. waters. There are two power stations supplied by underwater pipelines, Ras Kathenib and Al-Mocha. Both receive heavy fuel oil via pipeline. The public electricity corporation informed us that frequent accident occur to the pipeline and loading hoses when tankers are subjected to strong winds. The over all severity effects depends on the nature and quantity of oil spilled in conjunction with other factors such as wind speed and direction. water movements, & temperature.

Animals at particular risk include surface swimmers and feeders, marine reptiles and marine animals in case of oil spill. oil pollution into the coastal area has .seriously, endangered the Red Sea coastal ecosystem along the Saudi Coast (Behairy & Saad, 1984).

The Red Sea Coast of Yemen is also expected to have been affected. A preliminary survey along the Red Sea coast of Yemen showed that oil-related pollutants concentrated in regions, especially around oil loading terminals and some industrial areas. While beach tar is widespread along Yemen coast (Rushdi *et al.*, 1991).

To the best of our knowledge, there is almost no available information's concerning the quantity and the extent of oil spills, although oil spills and oil sheens have been observed and reported several times by local fishermen and citizens along the shore line and the inter-tidal-sediments.

The present paper is undertaken to fill the lacuna in our knowledge on the present status of oil contamination in the Red Sea Coast of Yemen.

## *MATERIAL AND METHODS*

The study was carried out on a coastal area of Al-Hodeydah city, during 1994 .Two sites to the north of the city were chosen according to the suitability of getting the fishes, and to the importance of the site itself. The first site was in front of the power station at Ras-Kathnib, whereas the second was further north to Al-Salif port (Figure 1).To the south of AL-Hodeydah city another site AL-Taif, aremat fishermen village was chosen. Fish samples were also taken from fishermen fishing off Al-Hodeydah coast. After collection, the fish samples were wrapped in aluminium foil, stored in a cool box, and frozen upon return to the city center. A composite samples of fish, having similar size (length and weight) were chosen from each species. Liver and gill were removed and fixed separately in 10% neutral buffered formaline. Edible tissues (muscles only) of each of the species were taken and extracted according to the procedure given in the following section.

The shrimp *Penaeus siemisulcatus* was taken from Al-Salif, where a composite sample of the same length and weight was used for petroleum hydrocarbon analysis. The integument. (exoskeleton) and the digestive tracts were removed, and homogenized samples were used for hydrocarbon analysis. Based upon the foregoing facts the snail *Strombus tricornis was* sampled from Al-Hodeydah in order to correlate the distribution patterns of petroleum hydrocarbons found in them with that of the fish, consequently it will be possible to pinpoint the origin of contamination/s i.e. wither it is local or transported. Furthermore, mussels were also collected to assess damage to these resources. The whole samples were used for petroleum hydrocarbon analysis after removing the shells, and the tissues were washed with distilled water to remove any traces of sand.

The aquatic sediments can thus provide not only a historic record of sedimentary environment, but also reserve the features of average sedimentary environmental constituents. Besides they are *vice versa,* also a possible source of chemical in waters. Therefore sub-tidal sediment samples were collected from Al-Hodeydah area as well as further remote area (which serve as a reference “RF”) (Figure 1).

The extraction method was based upon that of Wade *et aL*, (1988). A total of 10g tissues or of 100g of dried sediment was Soxhlet-extracted with methylene chloride and concentrated in Kuderna-Danish tubes. The extracts were fractionated by alumina:silica gel (80-100 mesh) chromatography. The extracts were squentially eluted from the column with 50ml of hexane (aliphatic fraction) and 200ml of 1:1 hexane-dichoromethane (aromatic fraction) and concentrated for instrumental analysis. The determination of petroleum residues was carried out following the spectrofluorometric method based upon that adopted for the IGOSS Project (IOC, 1982). For the present work a Perkin-Elmer spectrofluorometer was used. Blank determinations were carried out by repeating the procedure with pre-extracted samples.

In order to characterize the extracted hydrocarbons (McKay & Latham, 1972), some of the samples were analyzed by Gas Liquid Chromatography (HP-5980) in the splitless mode with flame ionization detection (FID).

The samples were injected onto a 30 m x 0.25 mm (O.32um film thickness) DB-5 fused silica capillary column at an initial temperature of $60^0$C and temperature programmed at $12^0$C/min to $300^0$C and held at the final temperature for 6min.

## *RESULTS & DISCUSSION*

It is well documented that fishes are capable of metabolizing-aliphatic hydrocarbons (detoxification mechanism) which allows effective removal of these compounds from fish tissues, for this reason fish extracts were not analyzed for aliphatic hydrocarbons. However, in order to gain some information's on the present status and the main sources of oil pollution in the Red Sea, mussels, shrimps and sediment samples (Fish-Food) were taken from stations along the Red Sea coast of Yemen and analyzed for petroleum hydrocarbons. The results of the analyses (Table 1) represents the average concentration from at least six determinations. The concentration of petroleum hydrocarbons in the mussels samples ranged from 15.7 ug/g at station RS-I to 63.9ug/g at station RS-IV, whereas sediment samples ranged from 1.2 ug/g at station RS-I to 6.94ug/g at station RS-VI. dry weight, expressed as Kuwait crude oil equivalent. From the result presented here it is evident that all the site are contaminated to some extent with petroleum hydrocarbons. Samples collected from reference station "RF" contained negligible amounts (<0.12 ug/g).

Petroleum hydrocarbon concentration found in mussels and sediments were reported by other workers and compared to our data in Tables 2 & 3. Goldberg (1975) has reported that the unpolluted open ocean sediments contain 1-4ug/g. dry weight hydrocarbons, less than 100ug/g in coastal sediments and up to 12000 ug/g in highly polluted areas. However, it should be borne in mind that the efficiency of hydrocarbons absorbance onto sediment particles are governed mainly by its grain size and total organic matter content. The sandy nature of the Red Sea coast of Yemen sediments coupled with its very low content of organic matter (<0.1% TOC) render its low capacity for hydrocarbons adsorption. Thus it may be suggested that although the extent of oil pollution in the region may be severe, however, it is not reflected accurately by its sub-tidal sediments.

Table (1): Total Hydrocarbon Concentrations in Environmental Samples from the Red Sea.

| ***Station*** | ***Sample Type*** | ***MV at 360nm*** | ***Petroleum hydrocarbon concentrations ug/g dry weight (API Kuwait crude oil equivalent*** |
|---|---|---|---|
| RS-I | Sediment | *22.5* | 1.21 |
| RS-II | Sediment | 67.7 | 3.68 |
| RS-III | Sediment | 33.0 | 1.78 |
| RS-IV | Sediment | 78.0 | 4.24 |
| RS-V | Sediment | 108.4 | 5.91 |
| RS-VI | Sediment | 127.5 | 6.94 |
| RF | Sediment | 2.6 | 0.12 |
| | | | |
| RS-I | Mussels | 29.1 | 15.7 |
| RS-II | Mussels | 39.6 | 21.4 |
| RS-III | Mussels | 60.8 | 33.0 |
| RS-IV | Mussels | 117.4 | 63.9 |
| RS-V | Mussels | 30.7 | 16.5 |
| RS-VI | Mussels | 33.5 | 16.5 |
| RF | Mussels | 3.0 | 0.13 |
| | | | |
| Composite Sample | Fish | 38.1 | 20.6 |
| | | | |
| Composite Sample | Shrimp | 48.7 | 26.4 |

Table (2): Comparison of hydrocarbon Content in Muscles Collected from Different Region of the World

| *Area* | *Concentration (ug/g)* | *Source* |
|---|---|---|
| Western Port Bay(Australia) | 0.0-23.0 | Burns & Smith (1977) |
| Scottish Coast | 19.0-71.0 | Mackie *et aL.* 1980 |
| Northeast Gulf of Alaska | 21.0 | Wise *et al.*. ( 1981) |
| The Sound of Copenhagen | 11.0-47.0 | Jenesen (1981) |
| Antarctica | 0.0-124.0 | Clark & Law 1981 |
| Arabian Gulf | 13.1-34.6 | Al-Saad & DouAbul 1987 |
| Red Sea | 15.7-63.9 | Present Study |

Table (3): Comparison of Hydrocarbon Content in Sediment Collected from Different Region of the World

| *Area* | *Concentration (ug/g)* | *Source* |
|---|---|---|
| Narragansett Bay (USA) | 50.0-120.0 | Farrington & Quinn (1973) |
| Eastern Passage, Nova Scotia (Canada) | 5.0-37.0 | Hargrave & Phillips (1975) |
| Scotian Shelf (Canada) | 1.0-94.0 | Keizer *et al.*, ( 1978) |
| Ghadira Bay (Malta) | 22.0 | Sammut & Nickless (1978) |
| St. Paul's Bay (Malta) | 37.8 | Sammut & Nickless (1978) |
| Baffin Bay (Canada) | 1.25-33.75 | Levy ( 1979 ) |
| Falmouth Bay (UK) | 48.0 | Law ( 1981 ) |
| Carmarthen Bay (UK) | 34.0 | Law ( 1981 ) |
| Liverpool Bay (UK) | 29.0 | Law ( 1981 ) |
| Coast of Oman | 0.8-19.0 | Burns *et al.*. ( 1982) |
| Arabian Gulf | 0.4-44.0 | DouAbul *et al.*. ( 1984) |
| Red Sea | 1.21-6.94 | Present Study |

The complexity of hydrocarbon composition of environmental samples made the relative ranking of importance of various diffuse urban/industrial sources difficult. Thus the differences in hydrocarbon composition between various ecosystem components imply the importance of biogeochemical processes acting on hydrocarbons discharged to coastal waters. However, the degraded nature of the oil in most samples made it difficult to rank the relative importance of various input sources. Nevertheless we shall discuss below the most probable source of hydrocarbons encountered in environmental samples from the Red Sea.

Hydrocarbons found in recent aquatic sediments reflect natural and anthropogenic inputs from the water column by transport and sedimentation, as well as the diagenetic processes taking place within the sediment *N*-Alkanes generally constitute the major fraction of saturated hydrocarbons, and their distribution patterns are characterized by carbon-number ranges and predominance's depending on the nature of the source material and its microbial or geochemical alteration. In this respect it has been recognized that distributions exhibiting odd carbon-number predominance's in the $C_{15}$-$C_{21}$ and $C_{25}$-$C_{31}$ ranges are characteristic of autochthonous and allochthonous natural inputs, respectively. (Tissot et *al.*, 1975), whereas slight even carbon-number predominance's or smooth distributions in the $C_{20}$-$C_{30}$ range have been invoked for reduction or bacterial diagentic processes. Finally, fossil (petroleum) *n*-alkanes are characterized by a low carbon preference distribution generally concurrent with an unresolved complex mixture of branched and cyclic saturated hydrocarbons (Farrington & Meyer, 1975).

In order to characterize the extracted hydrocarbons (McKay & Latham, 1972) some of the extracts were analyzed by capillary gas chromatography. The chromatograms showed that the sediment extracts contained degraded hydrocarbons in addition to biogenic

hydrocarbon components. Figure 2 is illustrative of the gas chromatograms of sediment sampled from the Red Sea Coast of Yemen. These chromatograms demonstrate the wide-range complex mixture which encountered in all crude oils and many oil products. They also indicate a high level of unresolved materials which must be attributed to a mixture of iso- and cycloalkane. It is important to note the presence of *phytane* (2,6,10, 14-tetramethylhexadecane) peak, which is used as a marker compound for petroleum, as it has not been shown with certainty to occur naturally in aquatic organisms (Avigan & Blumer, 1968). However, a more precise distinction between hydrocarbons of biogenic origin and those of fossil origin will be possible only after a detailed investigation of plankton of the Red Sea.

In the light of the above reasoning we may thus conclude that : The Red Sea fishes, mussels and sediment are subjected to same point-source of oil contamination. The pollution is a consequence of localized oil operations and / or heavy ship traffic.

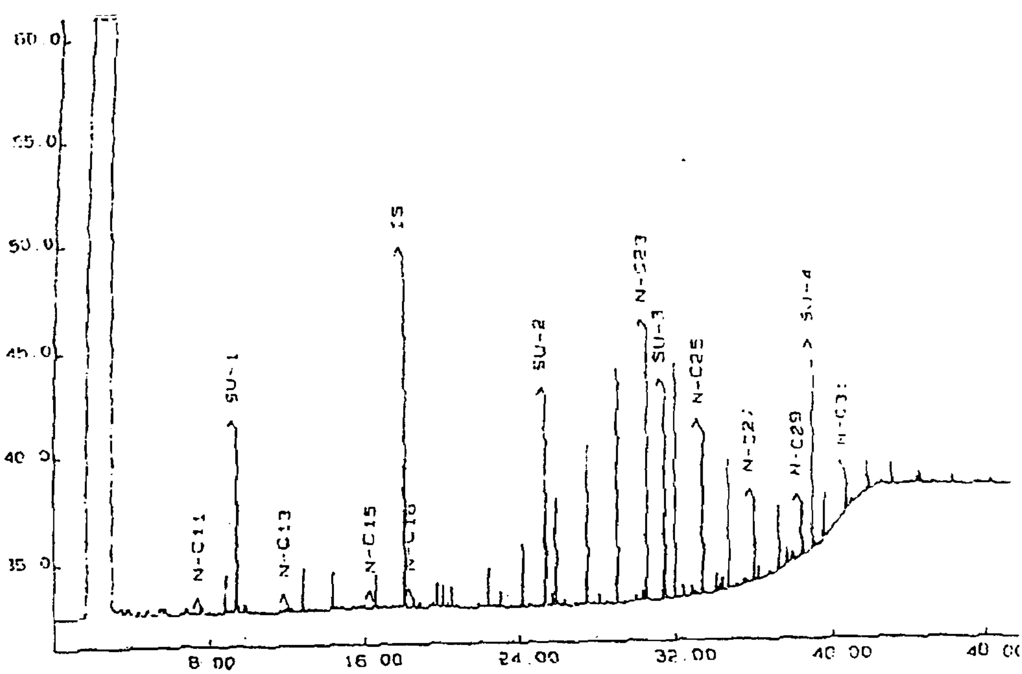


**Fig. (2): GC chromatograms of sediment sample (aliphatic fraction)**

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