Marina Mesopotamica 5(1) : 81 - 88 (1990)

# HYDROCARBON RESIDUES IN FISHES FROM KHOR AL-ZUBAIR, NORTH WEST ARABIAN GULF

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## ABSTRACT

The lack of published information on the residues of petroleum hydrocarbons in fish prompted us to initiate an examination of the background of petroleum hydrocarbons (PHC) in the tissues of 14 fish species, which collected from Khor Al-Zubair area, North-West of the Arabian Gulf.

Petroleum hydrocarbons were present at low concentrations in *Johnieops sina* 8.3 ugg-1 which can accumulate low quantities of fat in the musculature (2.1%) , while high concentrations observed in *Hilsa ilisha* 40.6 ugg-1 which accumulate (6.2%) of fat. A more result analysis by gas chromatography shows that the presence of PHC in the fishes due to different sources.

## INTRODUCTION

Khor Al-Zubair is a north-west extension of the Arabian Gulf (Figure 1). The environmental conditions in this area are more or less similar to those in the Gulf region. The ichthofauna of Khor Al-Zubair is, to a great extent , similar to that of the Arabian Gulf except for some fish species which do not enter the area. Fishes from Khor Al-Zubair are mostly pelagic except for some species which are bottom feeders. They are widely distributed in this area and some species make their appearance seasonally.

Hydrocarbons in the marine environment are mainly derived from four different sources: (1) biosynthesis by living organisms in the water, on the sea floor and the

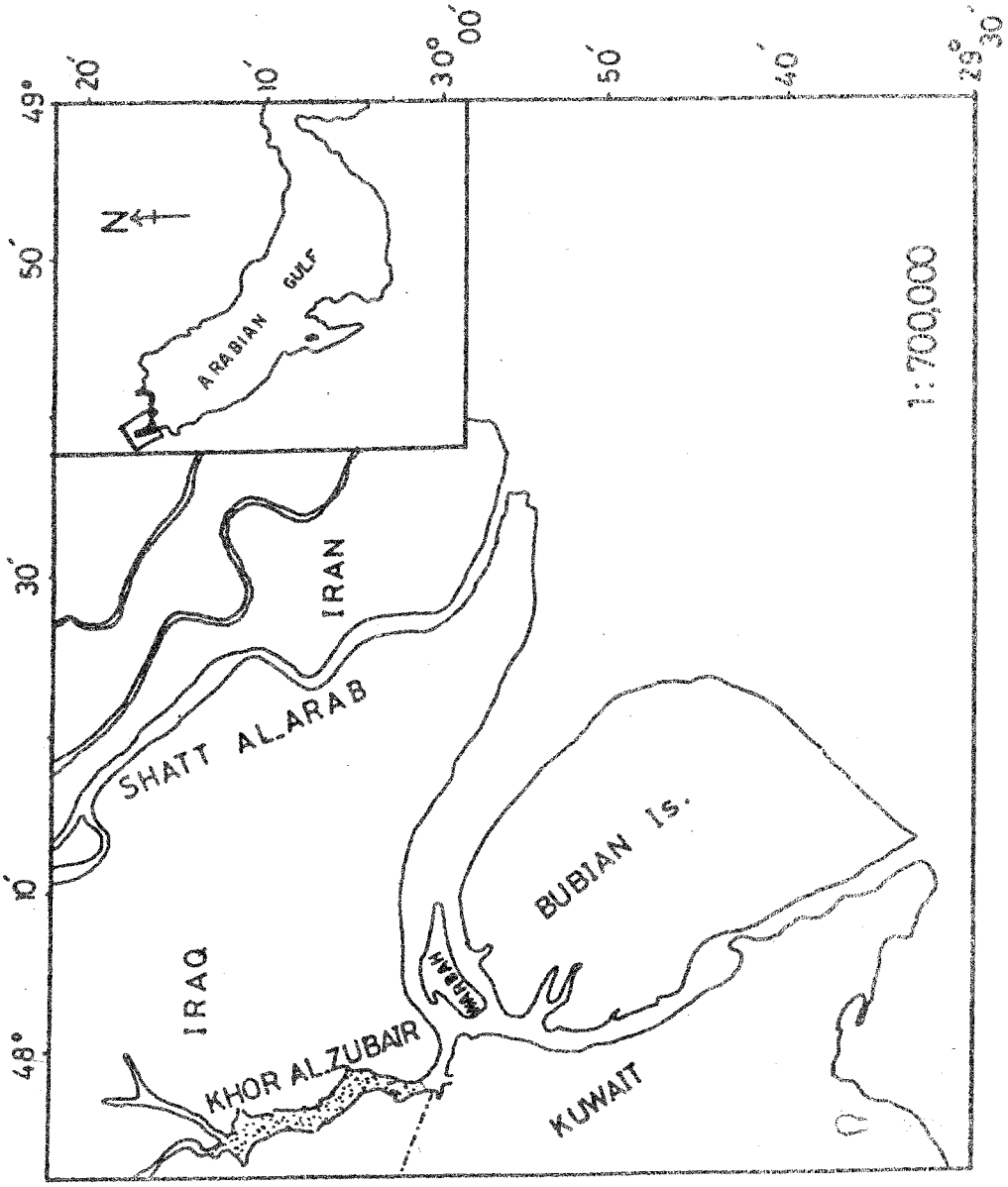


**Figure (1) : Map of Khor Al-Zubair, north west region of the Arabian Gulf.**

sediments ; (2) advection through land run - off ; (3) precipitation from the atmosphere; and (4) accidental and intentional release of fossil fuels during production , transportation and use (Ehrhardt & Heinemann 1975).

Since the fishes are widely distributed in Khor Al-Zubair, they can be considered as appropriate organisms to monitor hydrocarbon pollution in this area. The aim of this work is to analyse commercially exploited species of fish, taken along the Khor Al-Zubair, for petroleum hydrocarbon residues in order to evaluate the present state of concentration and also to serve as baseline for a monitoring program in the future. This study provides valuable information for forthcoming researches.

## MATERIALS and METHODS

Samples of 14 species of fish were collected from Khor Al-Zubair area. The samples were stored at -20 °C before the analysis. Fish samples , at least (10) individuals (muscles only), were freeze-dried, ground and sieved through 1 mm metal sieve. A replicate of ten gm of dried fish muscles were placed in pre - extracted cellulose thimble and soxhlet extracted with methylene chloride. At the end of extraction , the extract was transferred to a storage flask and the sample was further extracted with fresh solvent. The combined extracts were reduced in volume by arotory evaporator. Lipids content determined according to DouAbul et. al (1987) and then it was separated by florisil column chromatography (supelco 60/100 mesh florisil ; activated 130 °C for 12 h; deactivated with 0.5% water equilibrated for at least 15 h ; 16 cm florisil column 2.2 cm i.d.). Columns were packed dry and then rinsed with 200 ml hexane to remove potential contamination present in the florisil ; the samples were applied in hexane , the fractions were collected eluting F1 with 150 ml of hexane for Alphatic , and F2 with 200 ml of 30% Methylene chloride in hexane for Aromatic (Risebrough et al. 1983). All the solvent used were of high purity. The determination of petroleum residues was carried out using SHIMADZU RF 540 Spectrofluorometer. Emission spectra (excitation 310 nm) were recorded for each sample , and fluorescence intensities were measured at (360 nm). Blank determination were achieved for each sample. Kuwait crude oil, supplied by American Petroleum Institute (API), was chosen as an arbitary standard for comparison. Chrysen

standard were employed to calibrate the spectroflurometer and to check quantification of the analytical result for characterizing the extracted hydrocarbon (Mazurek & Simoneit 1984; Saliot et al. 1981). Some of the samples were also analyzed by gas liquid chromotography. For this purpose , a Perkin Elmer model 300 capillary gas chromotography with flame ionization detector (FID) was used in this case a wall-coated open tubular (WCOT) fused silica capillary column (10x0.25 mm. i.d.) with 0.22 u film thickness coated with SE 30 was used. Helium used as a carrier gas. Splitless injection , temperature programmed from 50 °C for 2 min to 280 °C for 30 min at rate 4 °C min was employed.

## RESULTS and DISCUSSION

Total hydrocarbons concentration (Kuwait crude oil equivalents)found in the present study are summarized in Table 1. The amount of oil residues in fish samples is ranged from 8.3 $ugg^{-1}$ in (*Johnieops sina* ) to 40.6 $ugg^{-1}$ in ( *Hilsa ilisha* ). Form this result, it is evident that all fish species are contaminated , to some extent , with petroleum hydrocarbons.

The analysis of fish samples reveal its ability to contain hydrocarbons in their lipid pool. On the basis of differing hydrocarbon concentration observed in fishes along Khor Al-Zubair, it is observed that a direct relationship exists between petroleum hydrocarbons and lipid content (Fat %) ($r = 0.932$). Smillar findings were reported by Gravedi and Tulliez 1982 .

The detection of polluting hydrocarbons in marine organism is also complicated , since marine organism can also synthesize hydrocarbons. So the total amount of petroleum hydrocarbons in these organism cannot be taken as an index of pollution by petroleum products only. This makes the tracing of hydrocarbon pollution in marine environment is difficult since the hydrocarbons originating from crude oils are found together with hydrocarbon produced recently by marine organisms, and hence analysis by gas chromatography allows a distinction between hydrocarbons typically for recent production by marine organisms and hydrocarbons from oil pollution. Comparison of some gas chromatograms of fish species against typical blank establishes that this is not an artifact of the analytical procedures nor can it be attributed to blending of the liquid phase during the programmed temperature analysis.

Table (1) : Petroleum Hydrocarbons (PHC) concentrations in fishes from Khor Al-Zubair North West Region of the Arabian Gulf with their fat percentage.

| Species | PHC ugg-1 dry weight (API Kuwait Crude Oil Equivalents) range | mean | * FAT% range | mean |
|---|---|---|---|---|
| *Tylosurus strongyhirus* | 12.6 - 14.2 | 13.7 | 2.4 - 2.6 | 2.6 |
| *Eleutheronema tetradactum* | 18.1 - 22.6 | 20.2 | 2.8 - 3.1 | 2.9 |
| *Pomadasys argenteus* | 16.9 - 20.0 | 18.6 | 2.4 - 2.5 | 2.5 |
| *Cynoglosus arel* | 13.9 - 16.7 | 15.1 | 4.5 - 4.6 | 4.6 |
| *Platycephalus indicus* | 8.6 - 10.5 | 9.7 | 2.1 - 2.2 | 2.1 |
| *Ilisha elongata* | 19.8 - 25.9 | 22.4 | 4.0 - 4.3 | 4.1 |
| *Thryssa hamiltonii* | 23.2 - 27.6 | 25.3 | 5.6 - 5.7 | 5.7 |
| *Arius thalassinus* | 28.9 - 32.5 | 29.1 | 5.6 - 5.9 | 5.8 |
| *Acanthopagrus luteus* | 34.1 - 40.6 | 37.3 | 5.8 - 5.9 | 5.9 |
| *Johnieops sina* | 6.5 - 10.7 | 8.3 | 2.0 - 2.1 | 2.1 |
| *Liza dussumeiri* | 28.5 - 31.6 | 30.3 | 5.7 - 6.0 | 5.9 |
| *Hilsa ilisha* | 39.5 - 43.9 | 40.6 | 6.1 - 6.2 | 6.2 |
| *Nematalosa nasus* | 29.7 - 35.6 | 32.1 | 5.9 - 6.0 | 6.0 |
| *Otoliths argenteus* | 33.2 - 40.7 | 37.5 | 6.0 - 6.1 | 6.1 |

* Adopted from DouAbul et.al (1987)

The presence of the resolved peaks in fish species is identified by retention time , including pristane, phytane and the n-alkane;n- $C_{15}$, $C_{17}$, $C_{18}$,$C_{21}$, $C_{27}$ See (Figure 2) which have been previously reported to be derived from phytoplankton , zooplankton, bacteria and benthic marine algae (Youngblood et al. 1971 ; Farrington et al. 1983). It is regarded as normal occurrence related to the food chain and most of these fishes feed on phytoplankton , zooplankton , other animals resource and detritus. Khor Al-Zubair is rich of such food (Salman et.al 1984 ; Hadi & Al-saboonchi 1984). This indicates that the pollutant hydrocarbon present in the fish species is a biogenic origin. The presence of hydrocarbone in the area may be due to the industrial character of the area where many plants were built in which

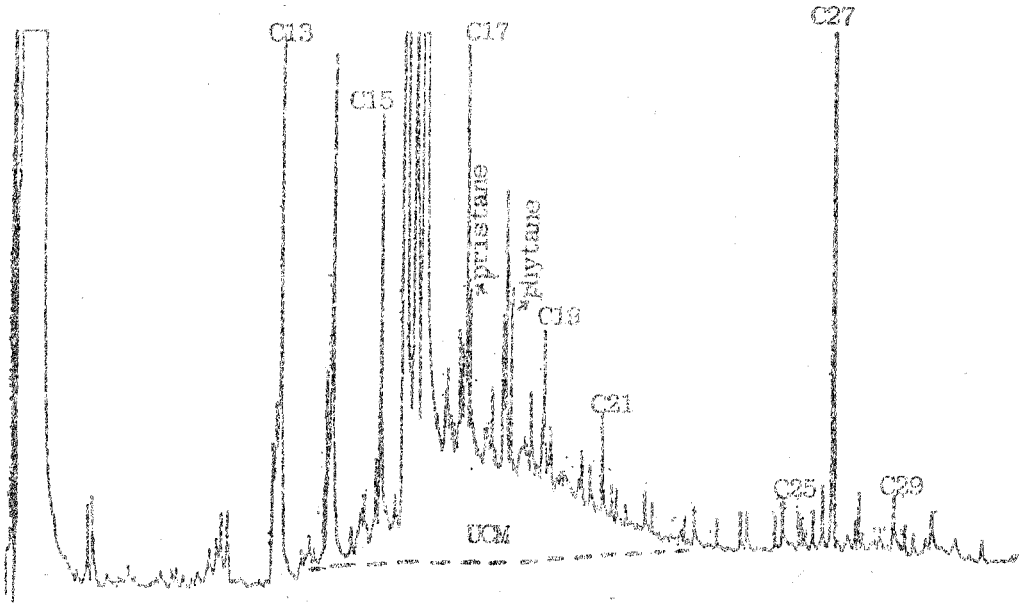


Figure (2) : FID chromatogram of the saturated fraction extract of fishes from Khor Al-Zubair (Eleutheronema tetradactum).

they expell reasonable amount of pollutants to this area . Al-Hashimi & Salman 1985 suggested that Khor Al-Zubair was subjected to maintenance dredging which expose deeper layer at probably higher organic contents to the surface beside the possible contamination due to shipping activities. The chromatograms at saturate fraction from these fishes are influenced strongly by petroleum, and contain an unresolved complex mixture (UCM) pattren (Figure 2) as described by (Risbrough et al. 1980 ; 1983). This represents a complex mixture of hydrocarbons, principally of petroleum nature.

Higher concentration of hydrocarbons is UCM and this generally reflects petroleum contamination ( Farrington et al. 1983).

As a conclusion, these fishes are found to be contaminated with petroleum hydrocarbons and the main source of these hydrocarbons are biogenic and anthropogenic.

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## مخلفات الهيدروكاربونات في اسماك خور الزبير ، شمال غرب الخليج العربي

### المستخلص

بالنظر لنقص المعلومات المتوفرة حول تراكيز مخلفات الهيدروكاربونات النفطية في الاسماك، دعت الحاجة الى دراسة ١٤ نوع من الاسماك المتواجدة في منطقة خور الزبير شمال غرب الخليج العربي لمعرفة مستوى بقايا الهيدروكاربونات النفطية المتواجدة فيها . وجدت اقل التراكيز للهيدروكاربونات النفطية في اسماك الطمطمعوه حيث بلغت ٨,٣ مايكروغرام/غرام التي كانت نسبة الدهن فيها ٢,١ % بينما اعلى تركيز ظهر في اسماك الصبور حيث بلغت ٤٠,٦ مايكروغرام/غرام وكان مستوى الدهن فيها ٦,٢ % .

بينت نتائج تحليل العينات لجهاز الغاز السائل الكروموتوغرافي بان مصادر الهيدروكاربونات النفطية في هذه الاسماك متعددة .