# Distribution and source identification of petroleum pollutants, particularly PAH, in the Northeastern Mediterranean

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## Abstract

The distribution and composition of petroleum hydrocarbons, particularly of polynuclear aromatic hydrocarbons (PAH) and paraffins, in the various compartments of the southern coast of Turkey, were investigated. The study area covered the coastal and offshore between Turkey and Cyprus, including one of the largest and most productive bays in Turkey, i.e. Iskenderun Bay.

The coastal waters provided a concentration range of 0.5-3.5 µg/l with an average of 1.5 µg/l, whereas the area midway between Cyprus and Turkey, (35° - 36° N) was characterised by higher concentrations of PAHs, within a range of 2.0-6.0 µg/l. The effect of mixing and shipping activity on both ranges were examined.

The PAHs in sea-water, organisms and sediments from Iskenderun by exhibited ranges from 0.7 to 7.0 µg/l(ppb), 0.04 to 7.3 µg/g(ppm) and 0.04 to 0.68 µg/g, respectively. The relatively higher concentrations of PAHs in sea-water and sediments from the north and west coasts of the bay were correlated to probable sources of shipping activity originating from an oil pipe terminal, an iron-steel plant and a busy harbour.

The bimodal paraffinic pattern of hydrocarbons in gas chromatograms of sediments, traces of smoothly distributed n-paraffins in fish tissues, and pyrene, PAHs dominated by chrysene and ovalene especially in fish and sediment extracts, indicate a possible source of pollution from fossil fuel was traced.

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## Introduction

Although many investigations have been attempted in the central and western Mediterranean Sea, only a few measurements were taken from the eastern Mediterranean (SHEKEL 1977) and almost none have been obtained for the north-eastern Mediterranean coasts of Turkey.

The aim of this work is to determine the distribution and source of petroleum hydrocarbons, particularly of Polynuclear Aromatic Hydrocarbons (PAHs) in the various compartments, e.g. sea-water, fish and sediments, of the marine environment.

Recent investigations for the source identification of petroleum hydrocarbons were mainly based on the analysis of oil slicks (KAWAHARA 1970) whilst a few concerned the analysis of tar balls (SHEKEL 1977, ALBAIGES 1979). The fingerprintings of petroleum hydrocarbons by passive tagging methods (SLEETER 1978) including the analytical techniques such as Fluorescence Spectroscopy, Gas Chromatography (GC) and Gas Chromatography/Mass Spectrometry (GC/MS), whose details can be found elsewhere (SUNAY 1982), have led to the determination of the probable source crude oils of tar balls on beaches and sea-water, as well as the source of PAHs in organisms and sediments.

## Experimental

Sampling: The reference crude oils were obtained from the Atas refinery in Mersin (Turkish, Basra and Kirkuk crude oils), British Petroleum Co. in the UK (Iran and Kuwait crude oils) and Warren Spring Lab. Inc., UK (S.Arabia, Libya, A.Dhabi Qatar, N.Sea, Venezuelan, Peruvian and Nigerian crude oils).

Figure 1 shows locations of sea-water, fish, sediment and tar ball samples. Water, fish and sediment samples were exhaustively extracted with $CCl_4$, hexane and benzene-methanol, respectively. Tar ball and crude oil samples were prepared as described elsewhere (BALKAS 1980).

Table 1: Source Crude Oils of Tar Balls collected from the Southern Coasts of Turkey and Cyprus

| Tar Ball | Source Crude Oil |
|---|---|
| Campus | Any type of Middle East crude oils (particularly Turkish or Basra) |
| Cyprus | Kuwait |
| Seyhan | Turkish or Kirkuk |
| Iskenderun bay | Any type of Middle East crude oils |
| S-13 (Seyhan, floating) | Libya |
| S-6 (Tarsus) | Kirkuk |
| Floating (Campus, offshore) | Iran (light) |
| S-4 (Tırtar) | Turkish |
| S-5 (Atas) | Kirkuk or Iran |
| S-8 (Seyhan, sunken) | Iran |
| S-9 (Cyprus, Girne) | Kirkuk or Kuwait |

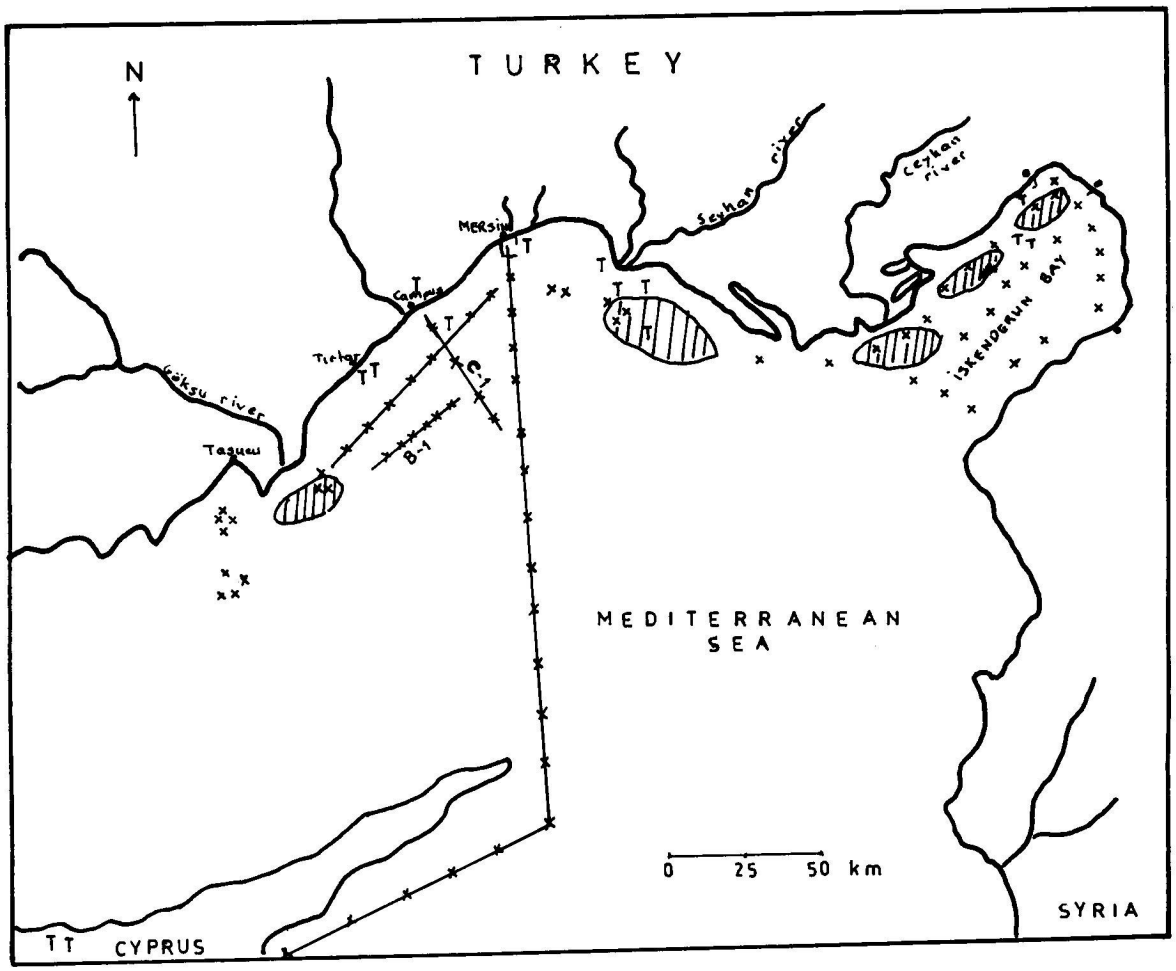



Figure 1. Sampling locations (X: sea-water samples, T: tar ball samples, shaded regions denote fishing areas).

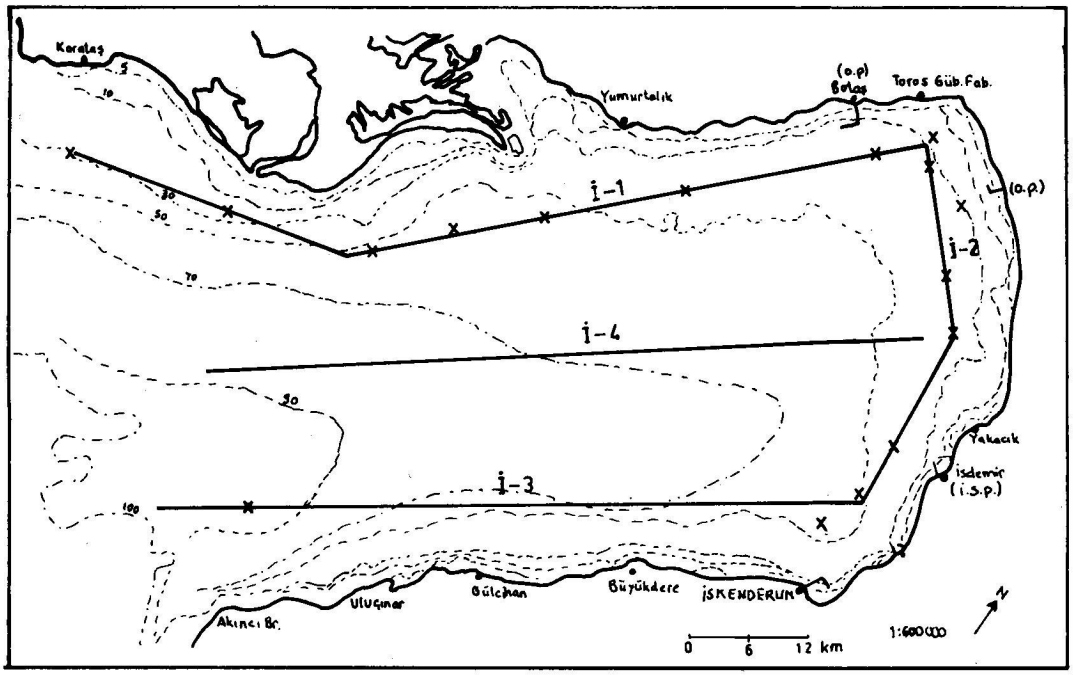



Figure 2. Location of the sediment samples in Iskenderun bay (o.p.: oil pipe).

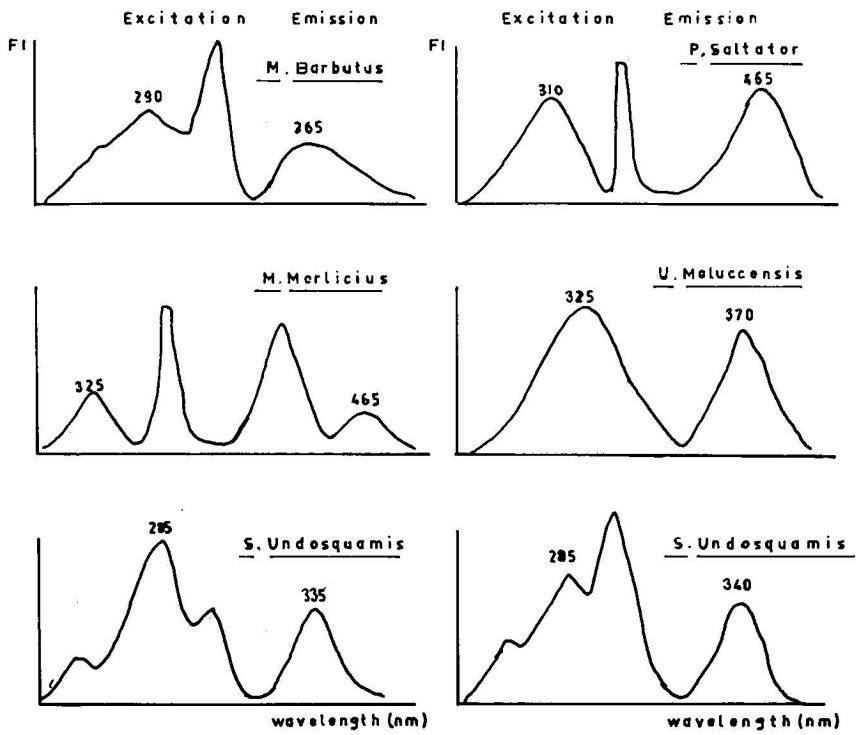



Figure 3. Fluorescence excitation and emission spectra of fish liver extracts (F.I.: Fluorescence Intensity, the numbers on the peaks are excitation and emission maxima).

Table 2: PAHs in Seawater (μg/l) (Samples collected between January 1080 and February 1982)

| Location | Depth (m) | Conc. (μg/l) range | Average(μg/l) |
|---|---|---|---|
| Taşucu (15 km. offshore) | 1 | 1.6 - 2.6 | 2.2 |
| Campus offshore (Cl-line) | 1 | 1.3 - 2.5 | |
| | 25 | 0.7 - 1.0 | 1.4 |
| | 50 | 1.1 - 1.4 | |
| | 75 | 1.0 - 2.3 | |
| Taşucu (2-3 km. offshore) | 1 | 0.8 - 1.2 | 1.1 |
| Mersin - Magosa line | 1 | 0.3 - 3.5 | 1.9 |
| Bl-line (20 km.offshore) | 1 | 0.1 - 0.8 | |
| | 10 | N.D. - 2.1 | |
| | 100 | N.D. - 0.7 | |
| | 150 | N.D. | |
| Cl-line (30 km.offshore) | 1 | N.D. - 0.7 | |
| | 50 | N.D. - 0.5 | |
| | 100 | N.D. - 0.5 | |
| | 150 | N.D. | |
| | 200 | N.D. | |
| | 300 | N.D. | |
| Mersin - Taşucu line | 1 | 0.3 - 1.6 | 0.9 |
| Iskenderun bay (east coast and center) | 1 | 0.7-1.8 | 1.0 |
| Iskenderun bay (north and west coasts) | 1 | 0.9 - 4.9 | 2.0 |

N.D.: not detectable

Instrumentation: Fluorescence measurements were made with a Turner Model 430 UVF spectrometer. Chrysene was used as the reference.

Gas chromatographic peaks resolved by a PYE UNICAM Model 304 gas chromatograph with a glass capillary column were identified by a VG MICROMASS 12/12 mass spectrometer using 70 eV ionization voltage at about $10^{-6}$ mm Hg.

**Results and discussion**

The distribution and the densities of tar balls on southern Turkey coasts have been discussed elsewhere (SUNAY 1978). The crude oil sources of these residues were determined by seven basic analytical techniques and are listed in Table 1. This Table shows the major source of tar balls on Turkish beaches to be Middle East and Libya crude oils.

The largest contributors of spilled petroleum hydrocarbons are considered to be the oil pipe-line terminals in the area, which supply Kirkuk and Turkish crude oils. However, many other tar balls were formed from Kuwait, Iran and Libyan crudes which are not supplied by the pipelines and are not refined in the study area. Thus pollution is arising from both local nonlocal sources. The time taken to form the tar balls estimated on the principles desribed by previous workers (SHAKEL 1977) was found to vary from two weeks to one month. The surface currents of the north-east Mediterranean have an average velocity of 10 cm/sec (UNLUATA 1980). The transport of tar balls from points outside the study area even from the south of Cyprus or the Suez Canal would take much longer than one or two months and does not seem to occur.

PAHs in sea-water: Concentration of PAHs in surface waters between Turkey and Cyprus generally varied between 0.5 and 3.5 µg/l (average 1.5 µg/l) with the exception of some slightly higher concentrations (2.0-6.0 µg/l) found near the midway point between Mersin and Cyprus (35° - 36° N). The heaviest ship and tanker traffic density in this region might have caused the higher concentration. The PAH concentration in sea-water from Iskenderun bay lay in the range of 0.7-7.0 µg/l with overall averages of 2.0 and 1.0 ug/l (Table 2) on the northern and southern coasts, respectively. There was no change of PAH concentration with depths to 150m as measured about 10km offshore, either in summer or in winter. The uniform distribution of hydrocarbons with depth may indicate efficient mixing in the north Levantine basin.

PAHs in fish: The concentration of PAHs in fatty tissue of Mullus barbatus, Upeneus molluccensis, Mugil cephalus, Solea solea, and Ephinephalus aeneas lay in the range 0.04 to 7.3 µg/g (Table 3). The overall average concentration of PAHs in fish flesh and livers were 0.13 and 0.79 µg/g, respectively. These values are much below the tolerable levels, considered hazardous when they reach $\geq$ 1-10 µg/g varying with species (FAO 1977, UNEP 1978).

The PAHs quantified by UVF (Figure 3) were also identified by GC and GC/MS (Figures 4 and 5). Chyresene and pyrene together with traces of paraffinic hydrocarbons and phthalic esters were the main features identified on gas chromatograms and mass spectra.

It has been found in this work that Mullus barbatus and Saurida undosquamis species were generally polluted by Iran crude oil whose major PAH component is chyresene. Mugil cephalus and Upeneus molluccensis were found to be polluted by pyrene-dominated Kirkuk and Turkish crude oils. The presence of longer fluorescence emission wavelength hydrocarbons, e.g. ovalene, in a few samples of Pomatomus saltator indicated a possible change in the composition of the original spilled oil in the digestive tracts of fish.

PAHs in sediments: The bimodal paraffin profile and the unresolved complex mixture shown by gas chromatograms (Figure 6) indicated contamination by hydrocarbons of fossil fuel origin. The concentration of oil-derived PAHs in sediments collected from Iskenderun bay (Figure 2) are given in Table 4. The concentrations range between 0.04 and 0.68 µg/g with an overall average of approximately 0.24 µg/g. Even the highest values obtained in this work may be considered low compared with those reported from other regions of the Mediterranean (SAMMUT 1978).

Most of the sediment samples were contaminated by pyrene-dominated Turkish or Kirkuk crude oils and pollution probably originated from local sources, e.g. pipe-lines in Iskenderun bay. To a lesser extent some of the sediment samples were found to be contaminated by chyresene-dominated Iran and anthracene-dominated Imeg (Iran) and Libyan crude oils, i.e. from non-local sources contributed through tanker deballasting operations.

Table 3: PAHs in Fish (µg/g)

| Fish | Tissue analyzed | Conc.range (µg/g) | Average(µg/g) |
|---|---|---|---|
| Epinephelus aeneus (white grouper) | Flesh | 0.04 - 0.32 | 0.11 |
| " " | Liver | 0.35 - 0.69 | 0.55 |
| Mugil cephalus (grey mullet) | Flesh | 0.44 - 4.63 | * |
| Mullus barbutus (red mullet) | Flesh | 0.03 - 0.25 | 0.09 |
| " " | Liver | 0.38 - 1.39 | 0.75 |
| Upenus moluccensis (stripped mullet) | Flesh | 0.32 - 0.50 | * |
| " " | Liver | 0.79 - 7.29 | * |
| Solea solea (sole fish) | Flesh | 0.04 - 0.17 | * |
| | Liver | 0.66 - 2.15 | * |

Overall average: Flesh : 0.13
(all fishes)
Liver : 0.79

* insufficient data for the estimation of a precise average

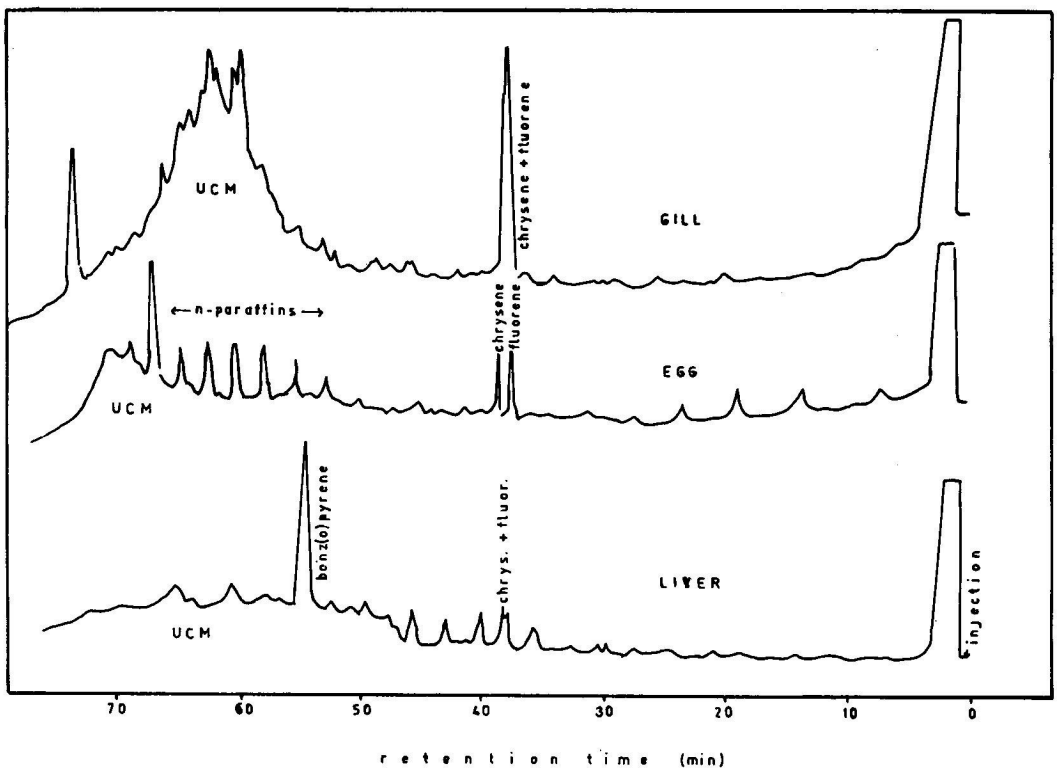



**Figure 4. Gas Chromatograms of hexane extracts of fish organs and eggs.**

Table 4: PAHs in Sediments (µg/g)

| Location | Concentration range (µg/g) | Average (µg/g) |
|---|---|---|
| İ-1 line | 0.04 - 0.27 | 0.16 |
| İ-1 line | 0.04 - 0.21 | 0.11 |
| İ-2 line | 0.11 - 0.60 | 0.39 |
| İ-2 line | 0.07 - 0.68 | * |
| İ-3 line | 0.11 - 0.68 | * |
| İ-4 line | 0.09 - 0.68 | * |

* insufficient data for estimation of a precise average

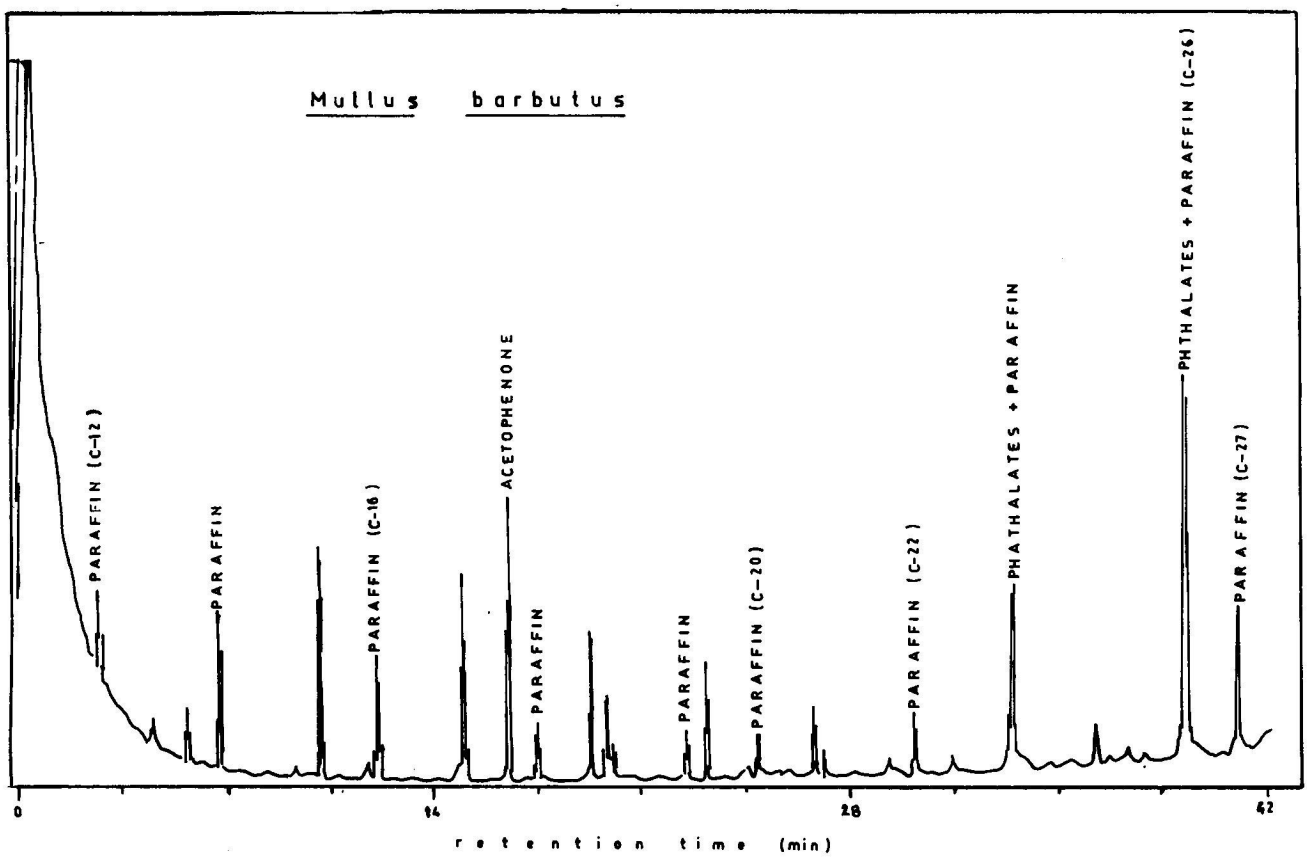
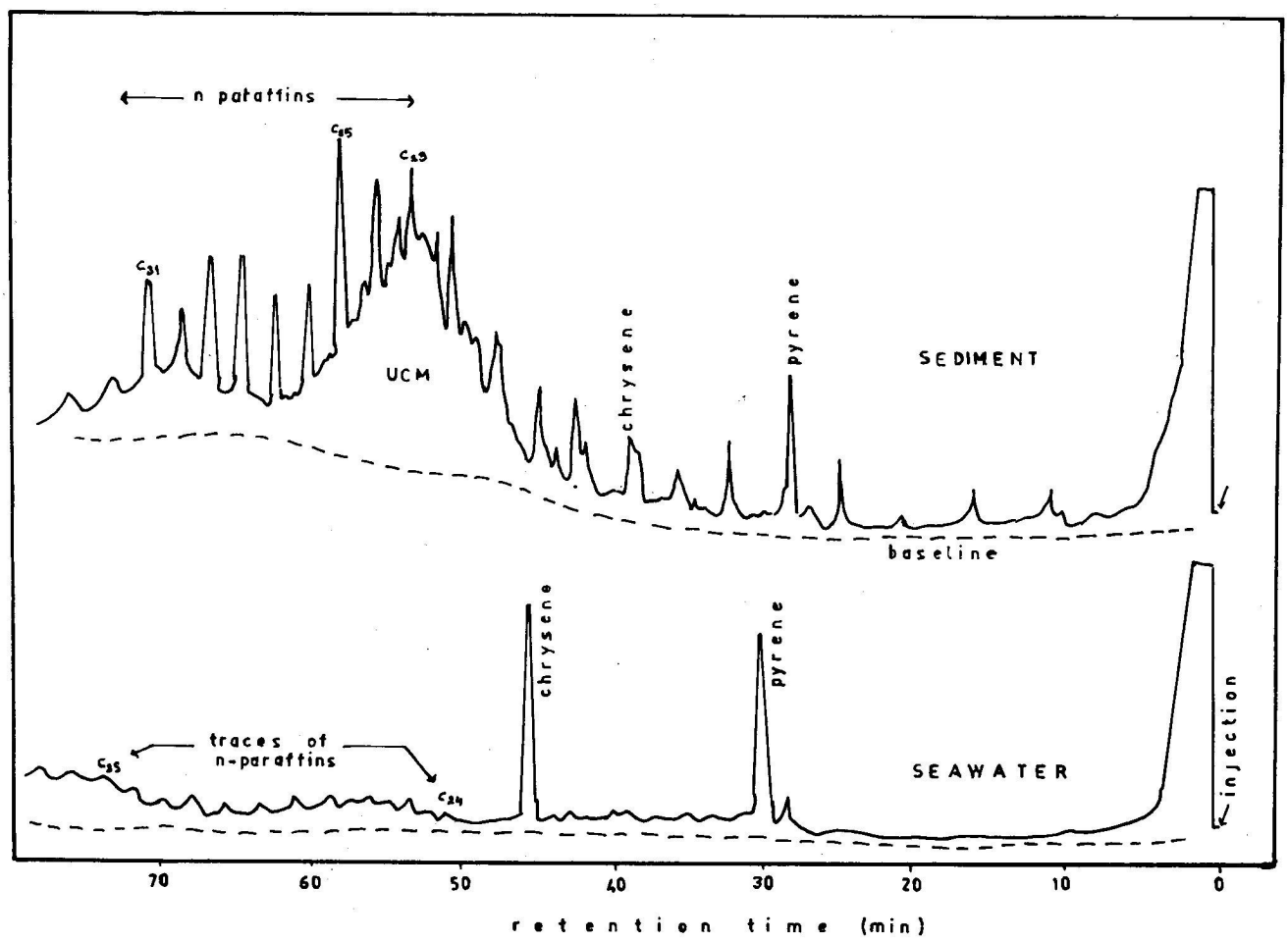



Figure 5. TIC (Total Ion Current) chromatogram of hexane extract of Mullus barbatus liver.

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