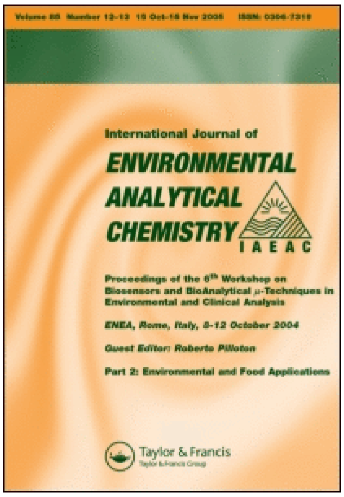

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Significance of Photosensitized Oxidation of Alkanes During the Photochemical Degradation of Petroleum Hydrocarbon Fractions in Seawater

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SIGNIFICANCE OF PHOTOSENSITIZED OXIDATION OF ALKANES DURING THE PHOTOCHEMICAL DEGRADATION OF PETROLEUM HYDROCARBON FRACTIONS IN SEAWATER

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A crude oil hydrocarbon fraction was photooxidized as a surface film on seawater under simulated environmental conditions. After irradiation, gas chromatography and gas chromatography/mass spectrometry analyses allowed to demonstrate the presence of relatively high quantities of compounds deriving from the photosensitized oxidation of *n*-alkanes, pristane and phytane, being among the non-acidic photoproducts of this fraction. The results suggest that the photochemical degradation of alkanes should be considered in studies of the fate of petroleum crudes in the marine environment.

KEY WORDS: Crude oil hydrocarbon fraction, photodegradation, sunlight irradiation, photosensitized oxidation of alkanes, *n*-alkanes, pristane, phytane.

INTRODUCTION

Several studies have shown that photooxidation is an important transformation pathway of petroleum spilled in the marine environment.[1–3] As the saturated hydrocarbons do not absorb solar light directly, many scientists working on the fate of petroleum residues have simply neglected the photochemical degradation of alkanes.

Today, it is known that in the presence of adequate sensitizers these compounds can be photooxidized by radiations above 290 nm.[4,5] Ehrhardt and Petrick,[6] for example showed that irradiation by solar light of *n*-pentadecane in seawater containing traces of anthraquinone as sensitizer results mainly in the formation of different isomeric *n*-pentadecanones. Recently, we have studied these phenomena in the case of branched[7,8] and cyclic alkanes.[9] During these studies we could demonstrate that the photochemical processes act intensively on the tertiary carbons of these compounds, leading to the formation of tertiary alcohols and to different cleavages of the molecules.

In the present study, we intend to prove that the photosensitized oxidation of alkanes constitutes a non-negligible phenomenon during the photooxidation of a crude oil hydrocarbon fraction.

EXPERIMENTAL

Substrate The total hydrocarbon fraction of a crude oil (Asthart) originating from an oil field localized in the Gabes Gulf was used. The separation of this fraction was described in a previous paper.[10]

Photooxidation experiments Pyrex flasks containing 50 ml of seawater collected at 0.5 m depth in the Gulf of Marseille (Mediterranean Sea) were used. 100 μl of hydrocarbons were spread over the surface of the water and were irradiated by sunlight for different times.

Separation of the photoproducts After pH adjustment with potassium hydroxide (pH = 8), the medium was extracted with chloroform. The chloroform extracts were dried on calcium chloride, filtered, concentrated and chromatographed on a wet packed (*n*-hexane) column filled with silica gel (20 cm × 1.5 cm I.D.; Fluka 60 + 5 % H_2O). Three fractions were eluted with 100 ml of *n*-hexane, 100 ml of chloroform and 50 ml of methanol, respectively: F_A, containing residual hydrocarbons; F_B, containing non-acidic photoproducts (ketones, alcohols); and F_C, containing weak acidic photoproducts. The strongly acidic compounds (F_D) were obtained by diethylether extraction of the acidified aqueous phase (pH = 1).

Gas chromatography was done on a Girdel series 30 chromatograph equipped with a Ross injector and a FID detector. The following conditions were employed: 25 m × 0.3 mm I.D. capillary column coated with SE-52; temperature programmed from 110 °C to 290 °C at 3 °C/min; helium carrier gas pressure, 0.9 bar; detector temperature, 290 °C; injector temperature, 300 °C.

Mass spectra were obtained with a Ribermag R-10-10-C spectrometer (electron energy, 70 eV; source temperature, 120 °C) coupled to a DI 700 gas chromatograph.

HPLC analyses were carried out on a Beckman apparatus using an Ultrasphere ODS column (25 cm × 4.6 mm I.D.). Samples were eluted with a solvent programme from 75 % to 90 % methanol in water (30 min) and then to 100 % in 10 min. The flow rate was 1.5 ml/min.

RESULTS AND DISCUSSION

After sunlight irradiation of the hydrocarbon fraction of Asthart crude oil over 28 days in abiotic conditions, the disappearance of half of this fraction was observed (Figure 1). Concerning the qualitative evolution of alkanes during the irradiation, gas chromatographic analyses showed a decrease of the pristane/*n*-C_{17} and phytane/*n*-C_{18} ratios (Table 1), which confirms the higher photochemical reactivity of branched alkanes.[11,7]

The photooxidation reactions result in the formation of numerous photopro-

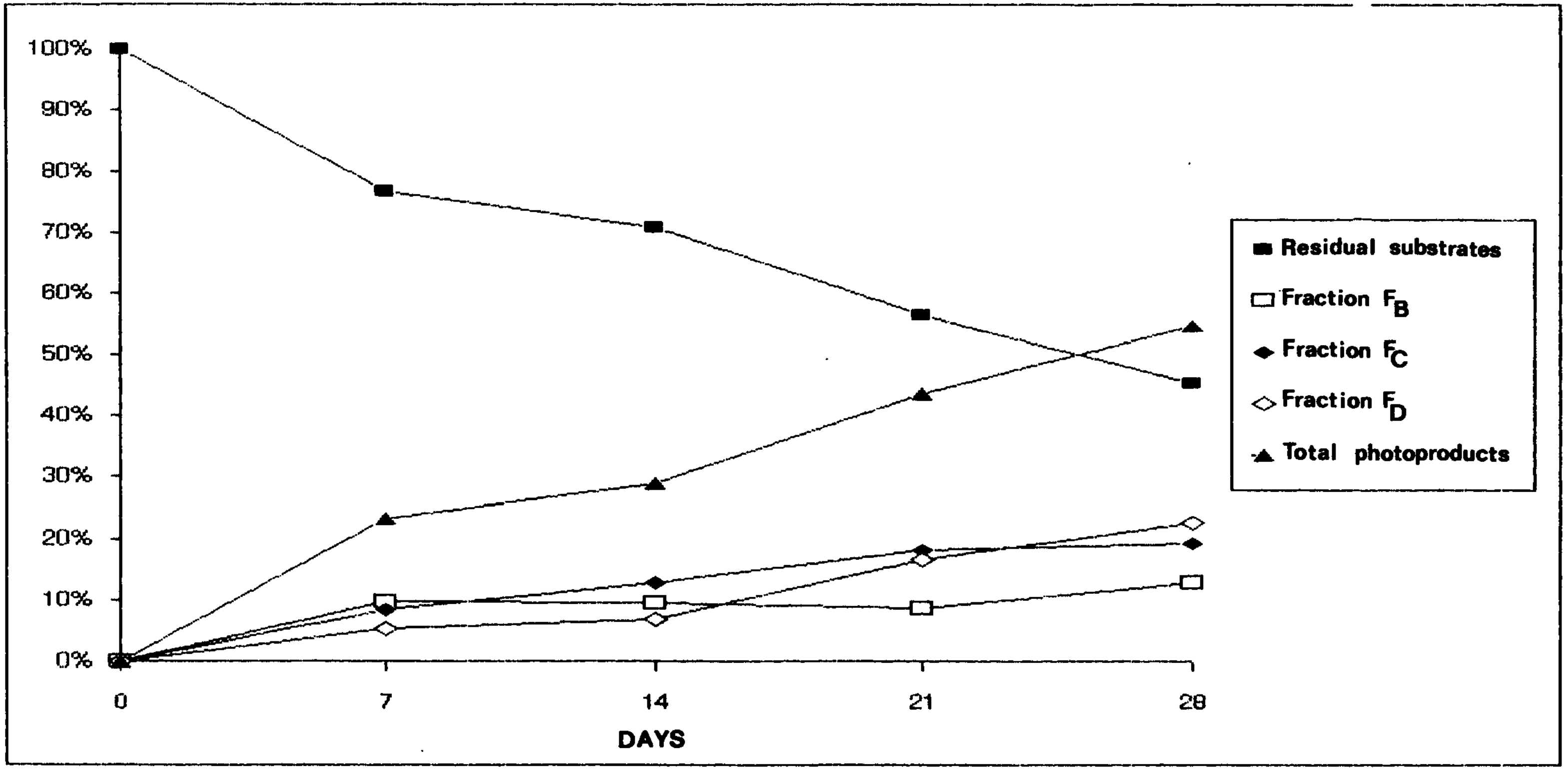


Figure 1 Photodegradation of Asthart crude oil hydrocarbon fraction by sunlight.

Table 1 Qualitative evolution of the hydrocarbon fraction during sunlight irradiation

Days	*Pristane/n-C_{17}*	*Phytane/n-C_{18}*
7	0.51	0.42
14	0.42	0.41
21	0.38	0.40
28	0.34	0.40

ducts which have been separated in three fractions (F_B, F_C and F_D) according to their polarity.

In order to identify alkanes photoproducts, we have studied more precisely fraction F_B which contains the non-acidic compounds. In the gas chromatogram of this fraction (Figure 2A), a homologous series of relatively well defined groups of peaks lying on top of an important UCM can be recognized. The comparison of their retention times and mass spectra with those of different standards (example, Figure 2B) allowed us to attribute these groups of peaks to straight-chain ketones coming from the photosensitized oxidation of *n*-alkanes.[6]

Moreover, gas chromatography/mass spectrometry of this fraction permitted the identification of 6,10,14-trimethylpentadecan-2-one (no. 1), 2,6,10,14-tetramethylpentadecan-6-ol (no. 2) and 2,6,10,14-tetramethylpentadecan-2-ol (no.-3)—compounds, whose production during the photosensitized oxidation of pristane has been demonstrated.[7]

The production of 6,10,14-trimethylpentadecan-2-one (no. 1) from pristane is a minor process because it involves the removal of an unstable methyl radical.[7] The relatively high quantity of this photoproduct present in fraction F_B (Figure 2A) can be explained by photochemical production from phytane (Figure 3), which is a more thermodynamically favoured pathway (formation of an ethyl radical during the β-cleavage I). The other main photoproducts of phytane co-elute with the isomeric *n*-octadecanones (Figure 2A). These various results show that alkane photoproducts are important constituents of fraction F_B.

During the photoinduced oxidation of alkanes, sensitization involves an abstraction of hydrogen atoms by an excited sensitizer molecule.[4–8] In the present cases, during the sunlight irradiation of the Asthart crude oil hydrocarbon fraction, its main aromatic components[13] (Figure 4A) can undergo direct photooxidation yielding several carbonyl compounds[14,15] (Figure 4B) known as voracious hydrogen atoms abstractors when they are electronically excited.[15] After abstraction of $H^{\bullet}$ by these excited triplet state sensitizers on alkanes molecules, the alkyl radicals formed lead to the formation of alkoxy radicals according to well known mechanisms.[4–6] These radicals may play a key role in the photodegradation of alkanes,[16] leading mainly to straight-chain ketones in the case of *n*-alkanes,[6] and to different branched ketones and alcohols in the case of isoprenoid alkanes.[7] Consequently, in studies on the fate of petroleum in the marine environment, it will be important to take into account the photosensitized oxidation of alkanes, which is, as is demonstrated in the present work, a non-negligible phenomenon.

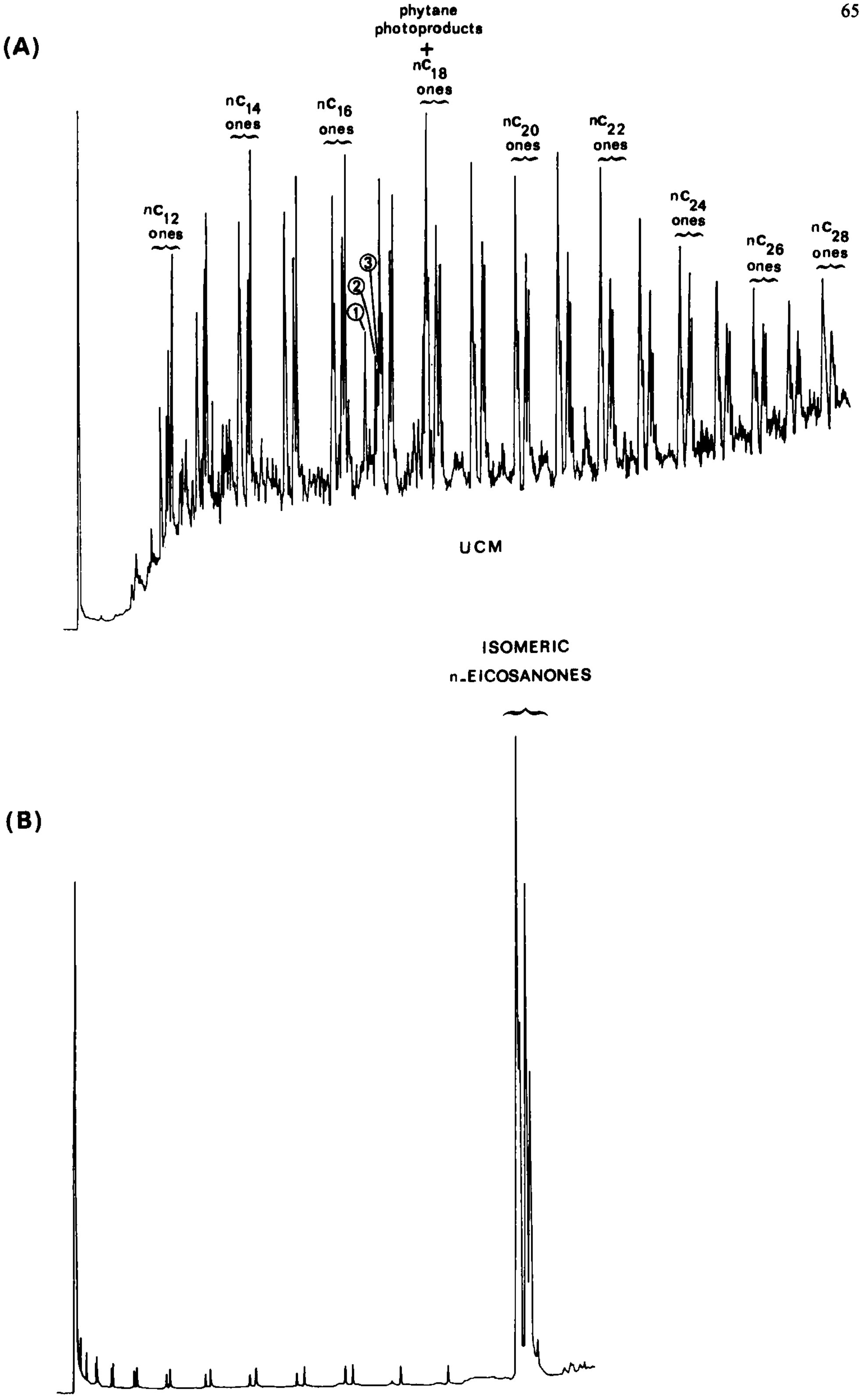
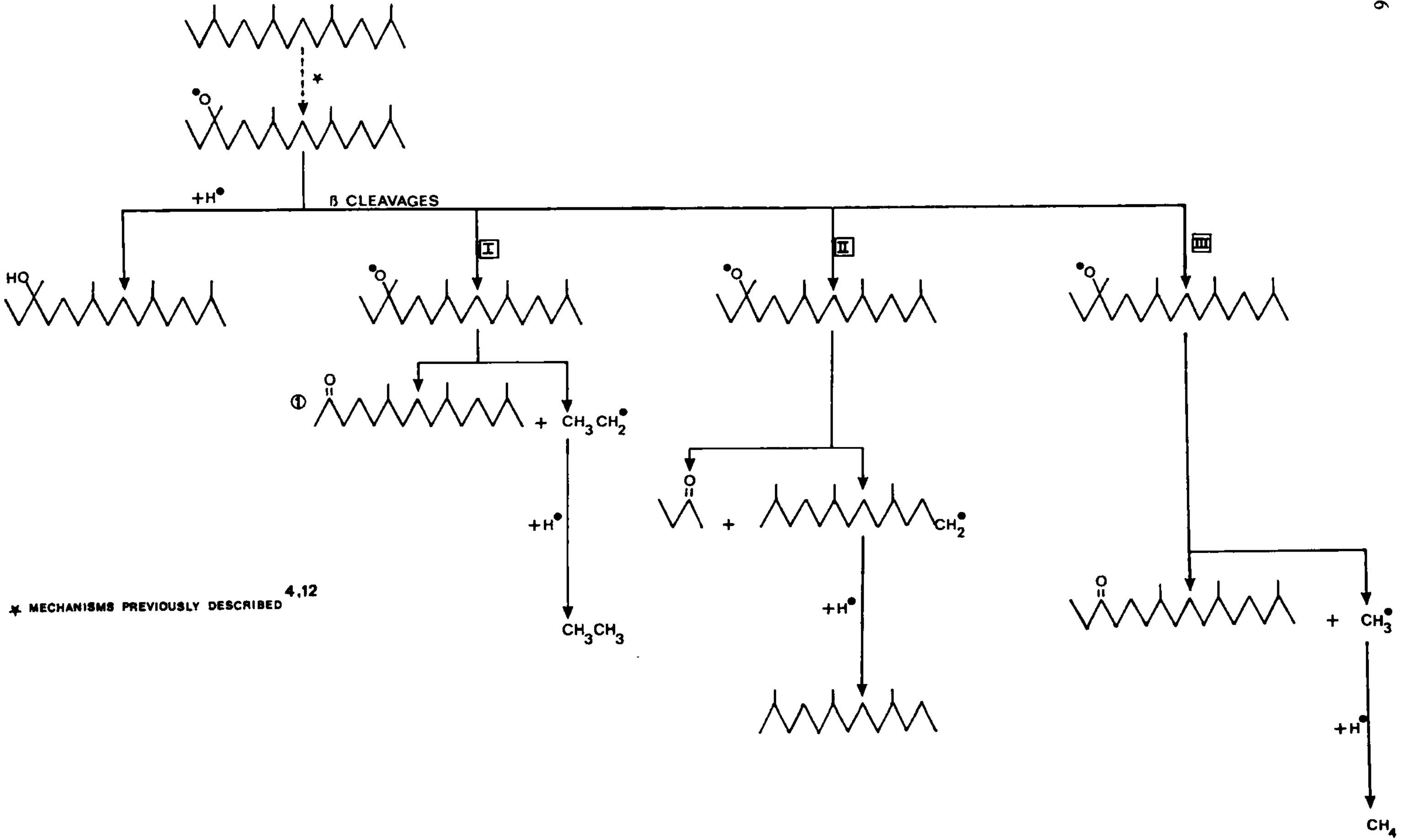


Figure 2 Gas chromatogram of (A) fraction F_B, and (B) *n*-eicosane photoproducts (obtained in the presence of anthraquinone)[6].



★ MECHANISMS PREVIOUSLY DESCRIBED[4,12]

Figure 3 Proposed pathway for the photosensitized oxidation of the carbon-14 of phytane.

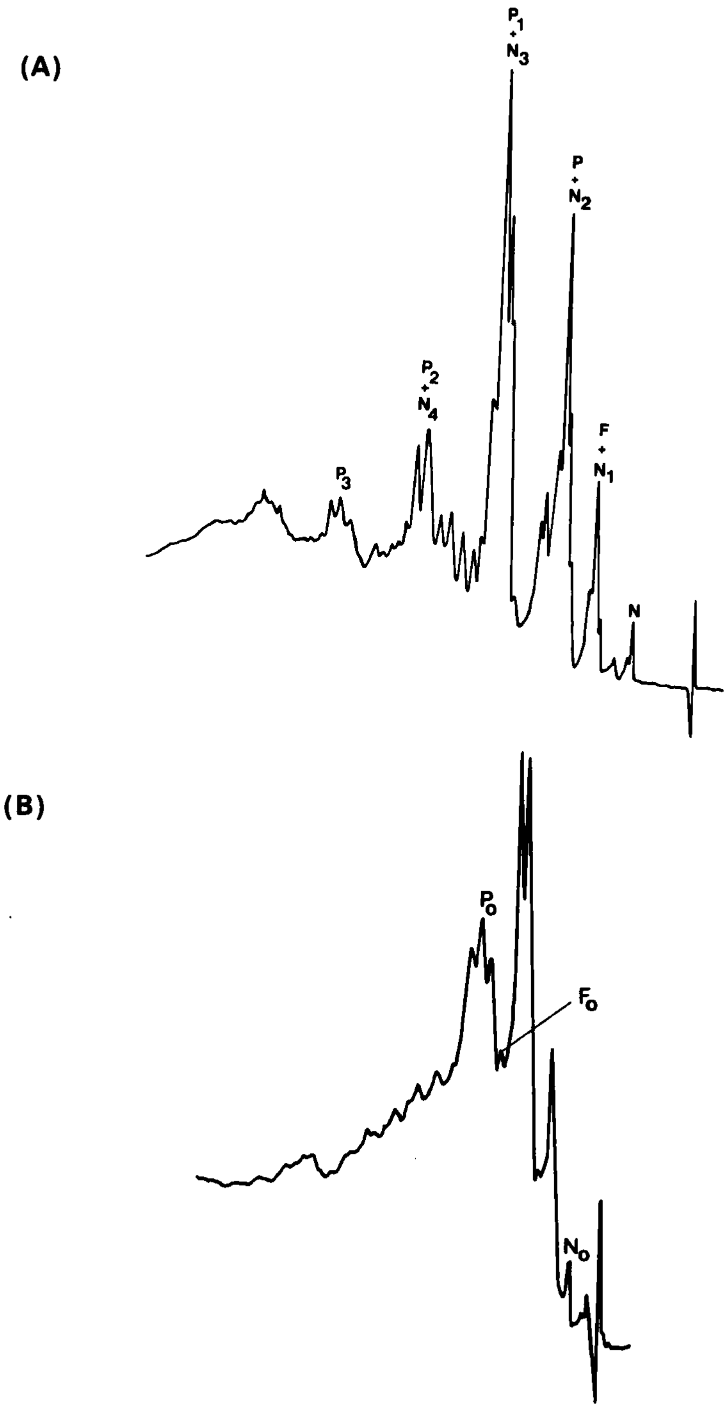


Figure 4 HPLC chromatograms. (A) Asthart crude oil hydrocarbon fraction, detection at 254 nm; N: naphthalene; N_X: alkyl-naphthalenes; F: fluorene; P: phenanthrene; P_Y: alkylphenanthrenes. (B) fraction F_B, detection at 254 nm; N_O: 1,4-naphthalenedione; F_O: 9-fluorenone; P_O: 9,10-phenanthrenedione.

It is interesting to note that these processes considerably influence both branched[7,8] and cyclic[9] alkanes, which are said to be biologically recalcitrant.[17,18] Although easily degraded by marine bacteria,[19] *n*-alkanes can also be photodegraded in the marine environment, especially at low temperatures (i.e. below 10 °C), when the rate of biotic degradation is very low.[20]

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