



Title	Effects of Water Polluted by Oil on Aquatic Animals : . Quantitative determination of C14-C24 n-paraffins in marine sediments and scallops (Pecten yessoensis)
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Effects of Water Polluted by Oil on Aquatic Animals

IV. Quantitative determination of C_{14} - C_{24} n-paraffins in marine sediments and scallops (*Pecten yessoensis*)

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Abstract

A study was made to determine whether the gas chromatography for quantitative detection was applicable to n-paraffins, and to determine whether the C_{14} ~ C_{24} n-paraffin concentrations could be detected quantitatively in marine sediments. A comparison of the concentrations of n-paraffin composition from C_{14} to C_{24} in marine sediments and in scallops was made also.

The concentrations of the n-paraffins in unknown samples were determined by calculating the areas of the chromatograms and by referring to the standard curve. The area of each peak on the chromatogram has given good correlation with the concentration of n-paraffin (Fig. 1), so the standard curve shown in Fig. 1 could be used for the quantitative determination of n-paraffin concentrations. n-Paraffins from C_{14} to C_{24} were contained in the marine sediments which were collected from the fishing ground of scallops (Fig. 2), and a similar chromatogram pattern was also obtained from the sample of scallops. (Fig. 3).

In a previous paper,¹⁾ a pretreatment in the detection of n-paraffins in marine sediments by gas chromatography was reported. Column and subsequent thin layer chromatographies with suitable developing solvents were found to be effective for separating the hydrocarbons from the lipids and fractionating the n-paraffins from the hydrocarbons.

A great number of papers have reported the analysis of hydrocarbons in sea water, marine sediments, and aquatic organisms. Farrington and Tripp²⁾ have compared analysis methods for hydrocarbons in surface sediments. The three procedures they applied to subsamples of a surface sediment gave similar values of hydrocarbons as detected by gravimetric analysis. Gas chromatographs of the alkane-cycloalkane portion of the hydrocarbons exhibited a very complex mixture of hydrocarbons with a wide molecular weight range extending from C_{14} to beyond C_{31} . May et al.³⁾ have analysed hydrocarbons in marine sediments and sea water by gas chromatography, while Hunter et al.³⁾ have reported the determination of hydrocarbons in marine organisms and sediments by thin layer chromatography. Warner⁴⁾ has determined quantitatively the hydrocarbons in oyster tissues which were extracted and fractionated on silica gel, and the hydrocarbons were then determined by gas chromatography. Recovery was 90% at the 0.2 $\mu\text{g/g}$ level. Individual aromatic hydrocarbons were also determined in clam tissue by chemically ionization mass spectrometry. Farrington et al.⁵⁾ have found

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that the hydrocarbon concentrations in a single tuna meal sample could be 18.9, 13.1, 26.0, or 21.3 $\mu\text{g/g}$ according to the analyses of 4 different laboratories, while pristane concentrations were 1.9, 3.0, 5.7 and 2.0 $\mu\text{g/g}$, respectively. Clark and Finley⁶⁾ have studied uptake and loss of petroleum hydrocarbons by the mussel in laboratory experiments. They found that petroleum paraffin hydrocarbons from C_{14} to C_{37} were rapidly incorporated into the mussel in a laboratory system that simulated tides.

The aim of the present investigation was to determine whether the gas chromatography for quantitative detection was, in the first instance, applicable to n-paraffins, and, secondly, to determine whether the C_{14} - C_{24} n-paraffin concentrations could be detected quantitatively in marine sediments. It was also thought of interest to compare the concentrations of each n-paraffin composition from C_{14} to C_{24} in marine sediments and in scallop (*Pecten yessoensis*) in order to learn of possible correlations between the hydrocarbons of aquatic animals and of their living environment.

Experimental

Materials

The samples of marine sediments and scallops (*Pecten yessoensis*) were collected as reported in a previous paper.¹⁾ The sediments and the scallops were frozen at -20°C until required. A hundred grams each of the thawed sediments and the scallops were weighed.

Analytical Procedures

The preliminary treatment and gas chromatography was carried out by the method as described earlier.¹⁾ The operating details of the gas chromatography are as follows.

Chromatograph	Hitachi Type 063
Column	1.5% silicone SE-30 on Chromosorb W AW DMCS 60/80 mesh
Column dimensions	Stiles steel tube 3 i.d. \times 2,000 mm
Detector	Hydrogen flame ionization
Temperature	Column 80°C to 280°C Detector 340°C Injection 320°C
Program rate	$5^{\circ}\text{C}/\text{min}$
Carrier gas	Nitrogen
Flow rate	Carrier gas 30 ml/min Hydrogen $0.8 \text{ kg}/\text{cm}^2$ Air $1.2 \text{ kg}/\text{cm}^2$

Quantitative Estimations

Estimations of the concentrations of the identified compounds in the samples were carried out as follows: n-paraffins of C_{14} , C_{16} , C_{17} , C_{18} , C_{20} , C_{22} , and C_{24} were applied to the gas chromatography within the range from 0.25 to 1.0 μl at 0.25 μl intervals. A standard curve of each n-paraffin concentration was prepared by plotting the areas of the chromatograms corresponding to the concentrations. The concentrations of the n-paraffins in unknown samples were determined by calculating the areas of the chromatograms and by referring to the standard curve.

Results and Discussion

The area of each peak on the chromatogram has given good correlation with the concentration of n-paraffin (Fig. 1), so the standard curve shown in Fig. 1 could be used for the quantitative determination of n-paraffin concentrations both in marine sediments and scallop.

It was found that n-paraffins from C_{14} to C_{24} were contained in the marine sediments which were collected from the fishing ground of scallops (Fig. 2), and a similar chromatogram pattern of n-paraffins was also obtained from the sample of scallop. (Fig. 3).

In Clark and Finley's experiments⁶⁾, the mussels were exposed to those hydrocarbons encountered in the environment after an oil spill. After 14 days in clean sea water, they had lost most of the hydrocarbons from the fuel oils; however, detectable traces of one particular fuel oil still remained after 35 days. From the findings by Clark and Finley⁶⁾ and the results of the present study, it is suggested

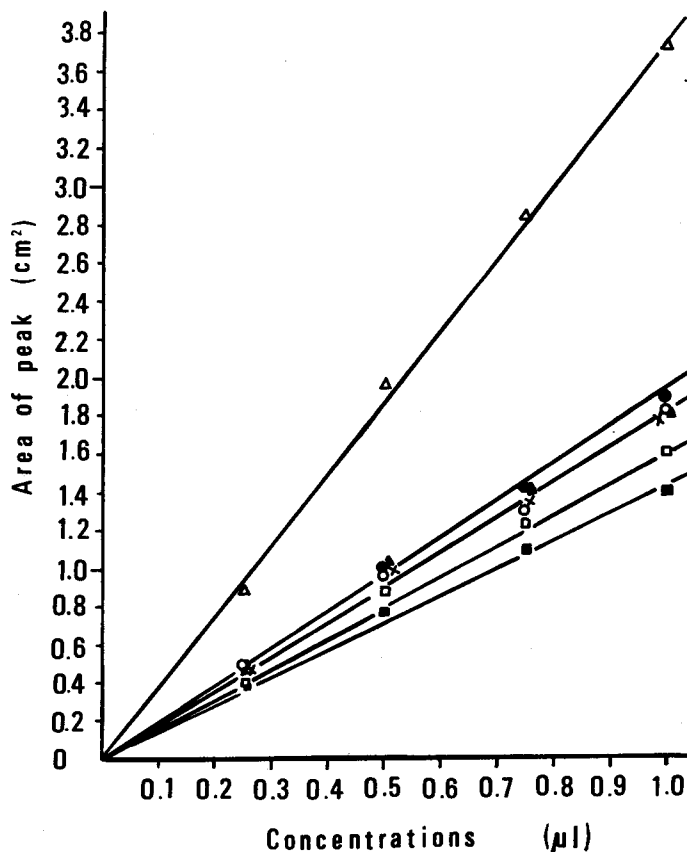


Fig. 1. Relation between the area of chromatogram of n-paraffins from C_{14} to C_{24} and the concentrations.

—○— C_{14} , —●— C_{16} , —△— C_{17} , —▲— C_{18} , —□— C_{20} , —■— C_{22} , —×— C_{24}

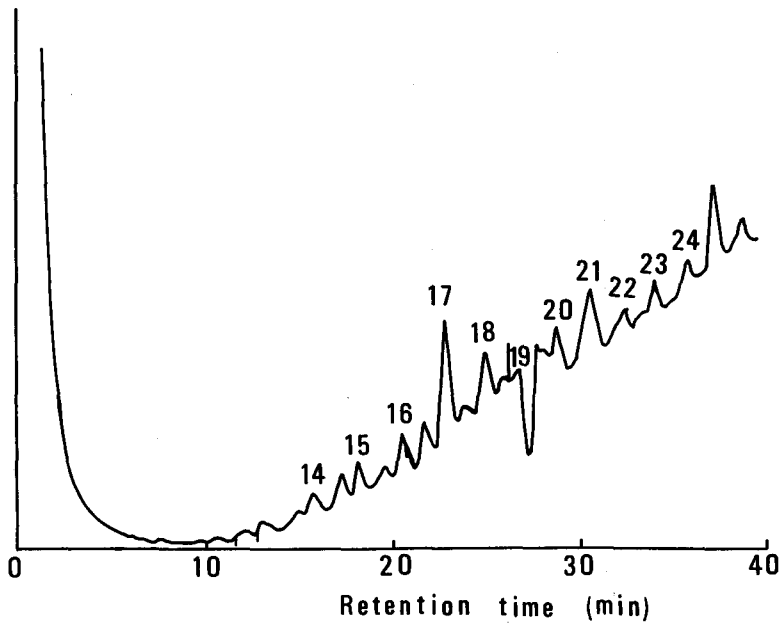


Fig. 2. n-paraffins in marine sediments detected by gas chromatography.

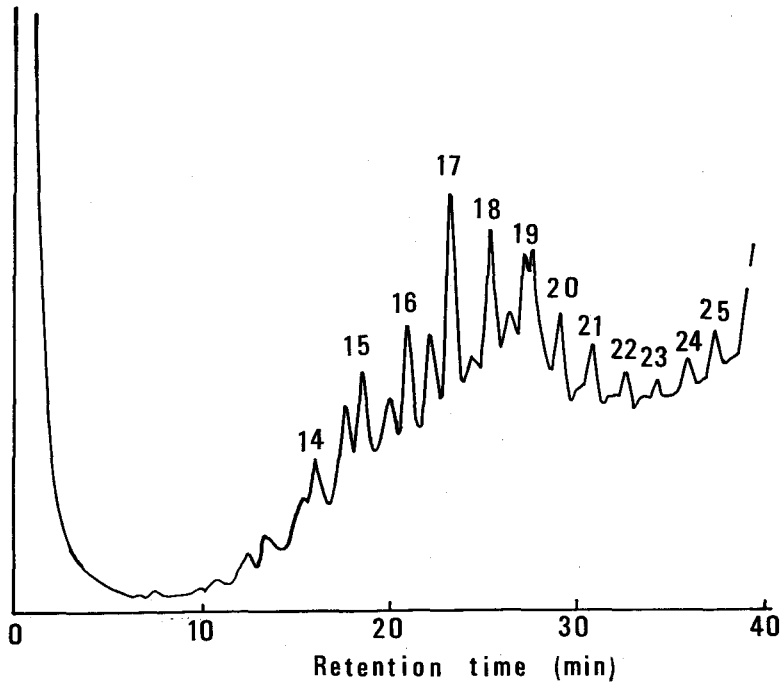


Fig. 3. n-paraffins in scallop detected by gas chromatography.

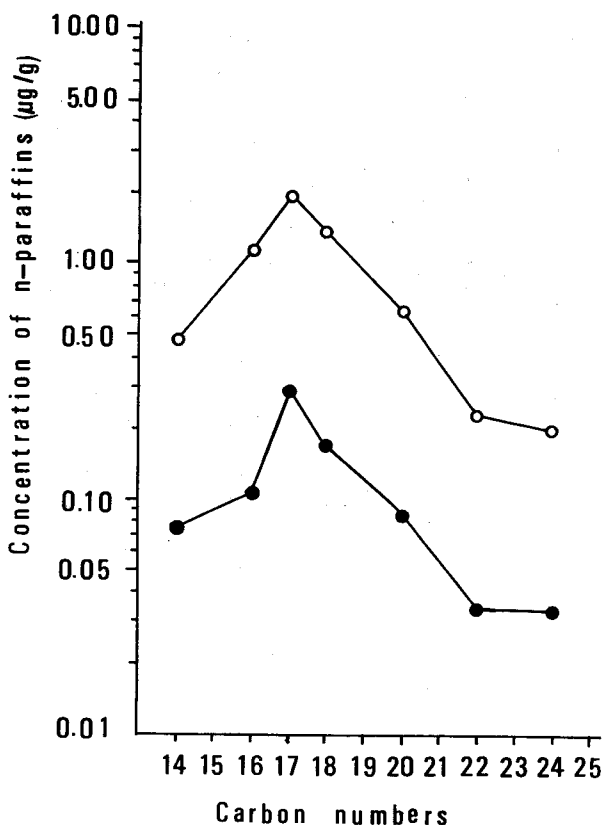


Fig. 4. Concentrations of n-paraffins in marine sediments and scallop.
 —○— Scallop, —●— Marine sediments.

that the n-paraffins contained in the scallop were accumulated through the marine sediments being polluted by oil.

The concentrations of n-paraffins from C_{14} to C_{24} both in marine sediments and scallops are shown in Fig. 4. There is considered to be a similarity in the patterns of n-paraffin concentrations in the marine sediments and in the scallops. C_{14} n-paraffin level was the highest among those of other n-paraffin constituents in marine sediments and scallop, and was 0.29 and 2.0 $\mu\text{g/g}$ dried material, respectively.

The concentrations of total n-paraffins from C_{14} to C_{24} in marine sediments and scallop were 6.2 and 0.55 $\mu\text{g/g}$ dried material, respectively. This fact indicates that the n-paraffins in marine sediments were taken and condensed in the scallop body; the concentration in scallop is higher than that previously reported in oyster, 0.2 $\mu\text{g/g}$ ⁴.

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