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HYDROCARBONS IN MARINE ORGANISMS AND SEDIMENTS OFF WEST GREENLAND

by

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ABSTRACT

Examination of the hydrocarbons in marine invertebrates, fish, and sediments from West Greenland has been performed by means of gaschromatography and gaschromatography/mass spectrometry.

Isolation and identification of the hydrocarbons showed that pristane (2, 6, 10, 14-tetramethyl pentadecane) and/or squalene (a non-cyclic dihydro-triterpene, $C_{30}H_{50}$) were the main components of the analytical material. Three other hydrocarbons were isolated in smaller quantities, one of which was identified as a n-alkene with the formula $C_{19}H_{38}$. The position of the double bond is probably between C_4 and C_5. Another hydrocarbon had the formula $C_{20}H_{38}$ and a branched and unsaturated structure. Presumably, the component could be phytadiene (2, 6, 10, 14-tetramethylhecadecadiene), which has previously been found in zooplankton. The last component isolated had a branched and highly unsaturated structure, which probably caused an unstable character as in the case with squalene.

In general the hydrocarbon concentration in sediments off West Greenland is extremely low compared to other areas. Considerable variation of the concentration of single biogenic hydrocarbons in organisms is apparent.

It is concluded that at present the marine environment off West Greenland does not seem to be loaded with petroleum hydrocarbons but that the hydrocarbons found here are biogenic.

INTRODUCTION

The occurrence of hydrocarbons in marine organisms and sediments off West Greenland is being investigated in order to obtain baseline data for the area. The investigations started in 1975, the same year that petroleum exploration licences were issued for an area between 63° and 68° N lat. (Figure 1).

The studies were initiated especially because of the large vulnerability of the arctic environment to petroleum pollution. This is a result of the effect of the low temperature on the physical nature of petroleum and on biological processes. For example biodegradation is known to be a slow-acting process in the arctic compared to biodegradation in temperate areas. Also more petroleum may be dissolved/dispersed at lower than at higher temperatures, and evaporation is less at lower than at higher temperatures. Further, arctic marine organisms grow slower than the same species in more southern latitudes. Finally the biological production, especially the plankton production, is concentrated in a short period of the year, compared to temperate areas. All facts mentioned here indicate that pollution by petroleum will affect the marine environment more severely in arctic than in temperate areas, as more petroleum remain in the environment for longer periods, and as populations will regenerate slower, once affected.

In addition to the concern expressed above, which is general for the arcti a specific concern exists for the concession area off West Greenland, namely that an important commercial fishery takes place within the concession area. A large oil spill would probably affect the fishery. Finally the concession area hosts important populations of sea birds (guillemots and others), which may be affected by a spill.

The general and the specific concern expressed here points to the need for thorough control of the effect of oil spills, and the study reported here aims at obtaining information on existing hydrocarbon concentrations in marine organisms and sediments and to develop methods that will delineate the impact on the environment of a spill, should it occur.

Only the main results will be presented in this paper. It is expected that all results will be published as a Technical Report of Fisheries and Marine Service, Canada.

MATERIALS AND METHODS

Sampling and preservation

Samples of invertebrates, fish and sediments were obtained during a cruise with the Danish research vessel DANA in the period 28 July to 13 August 1975. Sampling was done over a considerable depth range, from approx. 20 m to approx. 600 m, and in a relatively large area (Figure 2). Various gear was used: dredges, grabs, trawls, plankton-nets, and handlines.

Contamination of samples by fuel oil, lubricants etc. on board a ship causes considerable difficulties. Attempts were made to avoid contamination, for example by solvent-rinsing equipment such as grabs and knives before use, and by shutting off the discharge of water from the engine room (cooling water and bilge water) during sampling, as this discharge obviously was the source of an oil film spreading around the vessel.

Most samples were stored in glass jars, and aluminium foil was put between

the edge of the jar and the plastic lid, to avoid contamination from the lid. Some samples, i.e. whole fish, were stored in plastic bags. Contamination was not expected to arise from the bags, since the tissue actually used for analysis had not been in contact with the bag. Samples were frozen within few hours of collection and kept frozen until analyses were made.

Lipid analysis

Total lipid of the samples was determined by soxhlet-extraction overnight of dried material (Na_2SO_4). The pentane phase was evaporated on until dryness, and the residue was estimated by weighing.

Dry-weight analysis

Dry-weight of the samples was determined by drying the material at 105°C until constant weight.

Hydrocarbon analysis

In general the procedure of Farrington et al. was applied for extraction and isolation of the hydrocarbons (C_{14}-C_{36}) (1.2). All solvents were destilled before use. Solid reagents were pre-extracted with destilled solvents and all glassware was solvent-rinsed. Blanks were routinely run through the entire procedure to check for contamination from reagents or handling.

Clean-up procedure

Approximately 20 g (including liquids) of biological material (liver tissue only 2.5 g) or 50 g of a sediment sample was used for analysis. After homogenization in a blender, the sample was refluxed for two hours with 67 g KOH/l in 80% methanol. There must be at least 25% of water in the saponification mixture. After cooling, the mixture was filtered with suction, if solid materials were found (e.g. sediments and shells). The residue was washed on the filter with a small volume of pentane. The saponification mixture, if filtration was unnecessary, or the whole filtrate, was extracted three times with pentane. The extract was evaporated on a rotary evaporator until reduced to 1-2 ml. Column chromatography of the extract was performed by using a column of equal amounts of aluminia (Al_2O_3) packed on top of silica (SiO_2). The Al_2O_3 and SiO_2 were activated overnight at 250°C and 150°C respectively, and then both were de-activated with 5% of water. The ratio of column material to non-saponifiable lipid had to be 100:1 or more. The extract was eluted with 1.5 column volumes (from 15 to 75 ml) of pentane + benzene (80+20). The eluate was evaporated nearly to dryness on a rotary evaporator and then redissolved in a small volume of CCl_4. A few microlitres were injected into the gaschromatographic column.

Gaschromatography (GC)

The equipment used was a Hewlett Packard Model 5830 A with a flame ionisation detector (FID). The oven was programmed from 85°C to 275°C at 4°C/min.

One glass column of 1.8 m in length packed with 3% OV-1 was used. Nitrogen (N_2) was used as carrier-gas at a flow rate of about 30 ml/min.

A standard n-alkane mixture of known concentration was used to measure detector response per unit weight of alkane. C_{22} was used as an internal standard.

Gaschromatography/mass spectrometry (GC/MS)

The GC/MS analyses were made by using glass columns packed with either 3% Dexsil 300 or 3% OV-17. The oven was programmed from 150°C to 320°C at 10°C or 15°C/min. The column was coupled to a Varian Mat 311 mass spectrometer through a Biermann-Watson separator kept at 250°C. With the ion source temperature at 200°C, mass spectra of the eluted components were recorded at an accelerating voltage of 3 KV and an electron energy of 70eV.

RESULTS

Main results from the analytical estimation of the hydrocarbons, lipid analyses and dry weight analyses are presented in Tables 1-8. A list of the marine species analysed is given in Table 11. "Position" in the tables refers to the number given in Figure 2. The hydrocarbons estimated in each case are indicated by the retention time relative to C_{22}, obtained on an OV-1 column. The mean values and the sum (total) of the identifiable hydrocarbons are calculated and mentioned in the tables. A list of the relative retention times for n-alkane standards (C_{14}-C_{36}, C_{33} is lacking) is given in Table 9. The figures are mean values of several determinations. Normally the retention times alone were used to determine unknown hydrocarbons. In few cases, hydrocarbons were identified by gaschromatography/mass spectrometry (see below).

At the beginning of the analytical work attention was focussed on the range of concentration of hydrocarbons higher than 0.05 µg/g in samples of low lipid content and higher than 0.5 µg/g in samples of high lipid content. Later an attempt was made to reduce the detection limits by a factor of five. This has been taken into account in the tables under "detection limit".

Squalene is very unstable and the quantitative estimates are therefore doubtful because of degradation of the hydrocarbons during the analytical procedure. Presumably, this is also the case for other hydrocarbons of an unsaturated structure. This fact reduces the accuracy of the analytical results of some of the hydrocarbons. Also analytical estimates of concentrations near the detection limits are subject to a relatively high degree of uncertainty. Several of the unidentified hydrocarbons found in the sample material are probably the same components (i.e. have the same or nearly the same retention time). Through gaschromatography it is only possible to distinguish between hydrocarbons which have a difference in the relative retention time of more than 0.03.

Gaschromatography/mass spectrometry analysis

A list of results from the GC/MS analysis is given in Table 10. Isolation and identification of the hydrocarbons showed that pristane (2, 6, 10, 14-tetramethylpentadecane) and/or squalene (a non-cyclic dihydrotriterpene, $C_{30}H_{50}$) were the major components in the analytical material. Identification of pristane and squalene was based on spectra of standard solutions. Therefore, the detection of those two hydrocarbons is unequivocal.

Three more hydrocarbons were isolated in small quantities. One of those hydrocarbons was found in redfish (Sebastes marinus). Figure 3 shows the mass spectrum of the component (retention time relative to C_{22}:0.76). The peak m/e = 278 a.m.w. (probably the molecular peak) gives the molecular weight corresponding to the formula $C_{20}H_{38}$. The pattern of the spectrum indicates that the component is a branched unsaturated hydrocarbon, presumably with two double bonds instead of one triple bond. The spectrum suggests the following formula:

$$C_7H_{11} - C_2H_4 - C_{11}H_{23}$$

The C_7H_{11}-part contains the two double bonds and is possibly of a branched structure. The C_2H_4-part may have a methyl-substitute, and the $C_{11}H_{23}$-part has at least two branching points.

The peaks of the mass spectrum at m/e = 179 and 193 a.m.w. indicate the following possibilities for the $C_{11}H_{23}$-part:

The isolated component might be phytadiene (2, 6, 10, 14-tetramethyl-hexadecadiene), which has previously been detected in zooplankton (3).

Figure 4 shows the mass spectrum of one of the components (retention time relative to C_{22}:0.77) isolated from capelin (Mallotus villosus). The peak m/e = 266 a.m.w. (probably the molecular peak) indicates the formula $C_{19}H_{38}$. The pattern of the spectrum indicates that the component is an alkene without branching. The position of the double bond is difficult to estimate, but the peak m/e = 238 a.m.w. may be explained by a double bond between C_4 and C_5.

A component (retention time relative to C_{22}:1.24) was isolated from capelin (Mallotus villosus) and seems to be of an unstable structure similar to that of squalene. This is based on a reduction in the concentration of the components from the GC analysis until GC/MS analysis was made. The mass spectrum shows no molecular peak, for which reason it is impossible to give a formula of the component. The spectrum seems to indicate a polyunsaturated structure with conjugated double bonds. Presumably the molecule is branched.

Sediments and invertebrates

The result of the sediment analyses are presented in Table 1.

A summary of the content of pristane, squalene and the total amount of hydrocarbons in sediments and invertebrates is presented in Table 7.

On a wet weight basis the hydrocarbon levels are low in all sediment samples and invertebrates, except in shrimp (Pandalus borealis) and zooplankton. Pristane is found in a considerable amount in shrimp. It is notable that the pristane concentration in shrimp varies considerably, depending on the position of sample collection (Table 3). The variation of the pristane concentration in shrimp collected at the same position indicates a considerable difference between the concentration of pristane in the individual shrimp. In zooplankton pristane is found in a relatively high concentration in one sample from Position 42 (Table 2). The total concentration of hydrocarbons in all other invertebrates analysed are below 1.5 µg/g wet weight.

As dry weight and lipid content of most invertebrates are very low, the total amount of hydrocarbons on dry weight and lipid basis can be considerable, in spite of the low level on wet weight basis.

The mean value of the total amount of hydrocarbons in sediments is 0.40 (range 0.06-1.30) µg/g dry weight. Pristane and squalene are frequently found in both invertebrates and sediments.

Fish

A summary of the content of pristane, squalene and the total amount of hydrocarbons in liver and muscle samples from fish is presented in Table 8.

In most cases squalene is the dominating hydrocarbon especially in Greenland halibut (Reinhardtius hippoglossoides) (Table 4). Pristane is also frequently found in fish. In redfish (Sebastes marinus) and capelin (Mallotus villosus) pristane is the most prominent hydrocarbon (Tables 5 and 6). The bulk of the pristane and squalene is found in the liver tissue, but muscle tissue of high lipid content may also contain a considerable amount. It has only been possible to detect hydrocarbons other than pristane and squalene in smaller quantities. Therefore practically the total amount of hydrocarbons in many of the samples is the sum of the squalene and the pristane concentration. As is the case with shrimp, the concentrations of the single hydrocarbons vary considerably from fish to fish of the same species.

DISCUSSION

Hydrocarbon sources

Hydrocarbons in the marine environment are derived from different sources such as biosynthesis (by living organisms in the water, on the sea floor and in sediments), advection (through land run-off), precipitation (from the atmosphere), and accidental or intentional release of fossil fuels during production, transportation and use (4.5.6).

Biogenic hydrocarbons

Marine organisms make their own hydrocarbons (4.7-13).

The organisms synthesize n-alkanes, predominantly with odd-numbered carbon chains. In many instances, one or two odd numbered n-alkanes are predominant. Branched alkanes, including pristane, have been found in several organisms. In some species of fish pristane is the most abundant hydrocarbon. Alkanes often make up a major proportion of the hydrocarbons found in marine organisms. An example is squalene, which is found in livers of some species of fish. Isoprenoid C_{19} and C_{20}, mono, di, and tri-olefins are present in copepods and some species of fish. Straight-chain, mono- to hexaolefins have been found in considerable quantities in many organisms. It has been suggested that polynuclear, aromatic hydrocarbons may be synthesized by marine microorganisms. Until now aromatic hydrocarbons have been found in extremely low concentrations, generally less than 1% of the total hydrocarbons of marine organisms.

Only a limited number of marine species from a few geographic locations have been analysed for their native hydrocarbons, and many investigators have limited their analytical techniques to searching for only one or two classes of hydrocarbons, usually alkanes and alkenes. Thus other classes of hydrocarbons might be more prevalent in nature than the limited analyses suggest.

Petroleum hydrocarbons

Petroleum and biogenic hydrocarbons may be distinguished in several ways: (4.6.9.10)

- Petroleum contains a much more complex mixture of hydrocarbons with much greater ranges of molecular structure and weight.
- Petroleum contains several homologous series of hydrocarbons.
- Petroleum contains more kinds of cycloalkanes and aromatic hydrocarbons; also alkylsubstituted aromatic and naphteno-aromatic hydrocarbons. The last mentioned compounds have not been reported as biogenic.

A criterion of gaschromatographic screening for identifying petroleum contamination in marine samples is the presence or absence of an unresolved complex mixture signal "boiling envelope", due to overlapping series of homologous and isomeric hydrocarbons. Petroleum normally shows little or no predominance of n-alkanes with an odd number of carbon atoms.

Uptake and fate of hydrocarbons in marine organisms

Marine organisms receive hydrocarbons from their food source and the water, or convert precursor compounds obtained with their food or the water (4.12-33). Much attention has been given to the concentrations of petroleum hydrocarbons in marine organisms, especially filter-feeding marine bivalves. Uptake of petroleum hydrocarbons in mulluscs has been identified as a result of acute and chronic inputs in natural waters. Experimental studies on the uptake of petroleum hydrocarbons have also been undertaken.

Among other factors that influence the uptake of hydrocarbons from seawater is the lipid content of the organism, as well as the concentration of hydrocarbons in the water (31). The effect of dissolved organic matter in seawater on the uptake of mixed individual hydrocarbons is discussed in a paper by Boehm and Quinn (33). Feeding experiments show that the dietary route of entry is more important quantitatively than direct uptake from solution (20).

Recent reports have discussed the fate of hydrocarbons in a variety of marine animals (22-32). Several studies demonstrate that fish and some crustaceans (crabs and shrimps) may metabilize hydrocarbons. The evidence to date suggests that mussels are unable to metabolize hydrocarbons (25). Although some bivalves store hydrocarbons, most of those taken up are excreted during depuration experiments.

Hydrocarbons in sediments

Aquatic sediments receive small amounts of organic matter originating from a variety of sources, e.g. hydrocarbons can be released during metabolism and decomposition of organisms (17-19. 34-39). Field studies have shown that petroleum hydrocarbons from oil spills are able to persist in sediments for a long period of time due to a very slow biodegradation (17). The most readily degraded compounds, and hence those lost first from the sediments, are the n-alkanes, while the cyclic branched and aromatic compounds are left behind. Hydrocarbons incorporated in the sediment may enter the food web through deposit-feeding organisms.

Evaluation of the analytical results

The absence of homologous series of resolved peaks of n-alkanes above an unresolved complex mixture signal in the gaschromatograms indicates the absence of petroleum contamination in all the analysed samples collected off Greenland 1975. Isolation and identification of some of the hydrocarbons present in the samples in all cases show typical biogenic hydrocarbons.

Total hydrocarbon concentration, including biogenic compounds in surface sediment samples determined by a variety of techniques, covers the range 100-1200 µg/g in highly polluted coastal areas; usually 70 µg/g in unpolluted coastal areas and deep marginal seas or basins; and 1-4 µg/g (including about 90% biogenic) in deep sea areas (2). Compared with those data the level of hydrocarbons in sediment samples from West Greenland seems to be extremely low. This supports the assumption that the area at present is uncontaminated by petroleum hydrocarbons, and thus all the existing hydrocarbons in the sediments are of biogenic origin.

As mentioned earlier marine organisms are in a state of continuous interchange of hydrocarbons with their environment. Hydrocarbons found in organisms may originate from their food sources. The supply of hydrocarbons may vary considerably if the majority is derived from the food. In "selective"

predators the intake is based on the actual hydrocarbon level in a single species, whereas in omnivorous (e.g. some shrimp and starfish) the hydrocarbons are derived from several species. Hydrocarbon synthesis of the organism may be influenced by several conditions (season, sexual maturity stage and age of the organisms among others). The actual hydrocarbon level in the individual organisms seems very much to depend on the ability of metabolizing hydrocarbons.

These factors may explain the considerable variation in the concentration of single hydrocarbons found in the organisms.

Evaluation of the sample material

The most important objective of the analytical work on the sample material from West Greenland is to control the inputs (and fate) of petroleum in this area.

Certain investigations indicate that some marine organisms are well suited as indicator organisms for evaluation of pollution by petroleum hydrocarbons (16.30). Especially the blue mussel (Mytilus edulis), because of its widespread distribution and easy accessibility, has been used as an indicator organism in several investigations. Among the criteria which must be fulfilled by organisms used ad indicators of petroleum pollution are that they are abundant in the area and that the organisms retain hydrocarbons due to a very slow or complete ebsence of hydrocarbon metabolism and excretion. At present, however, our knowledge is insufficient as to the rate of uptake, metabolism and excretion of petroleum hydrocarbons by marine organisms. This in particular is the case for the species living off West Greenland. It thus seems reasonable that, for the time being, the interest is focussed on sediment analyses, in spite of the difficulty in obtaining a homogeneous mixture of the wet sediment and reproducable subsampling. The analytical results have, however, also given valuable baseline information on the hydrocarbon concentrations in marine organisms that may be used for monitoring purposes in case of oil pollution.

Evaluation of the analytical method

A number of analytical techniques are available for measuring low and high molecular weight and total hydrocarbons in samples of sediments and marine organisms. Gaschromatography seems to be superior to other analytical techniques in differentiating hydrocarbons. In order to identify individual hydrocarbons it is however necessary to supplement gaschromatography with other methods, and mass spectrometry seems to serve this purpose.

These methods could advantageously, especially when oil pollution occurs and the number of samples may be large, be supplemented with a simple routine method (e.g. fluorescence spectroscopy) to estimate e.g. the toxic aromatic hydrocarbons specific for petroleum.

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Advice received from John W.Farrington, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA.

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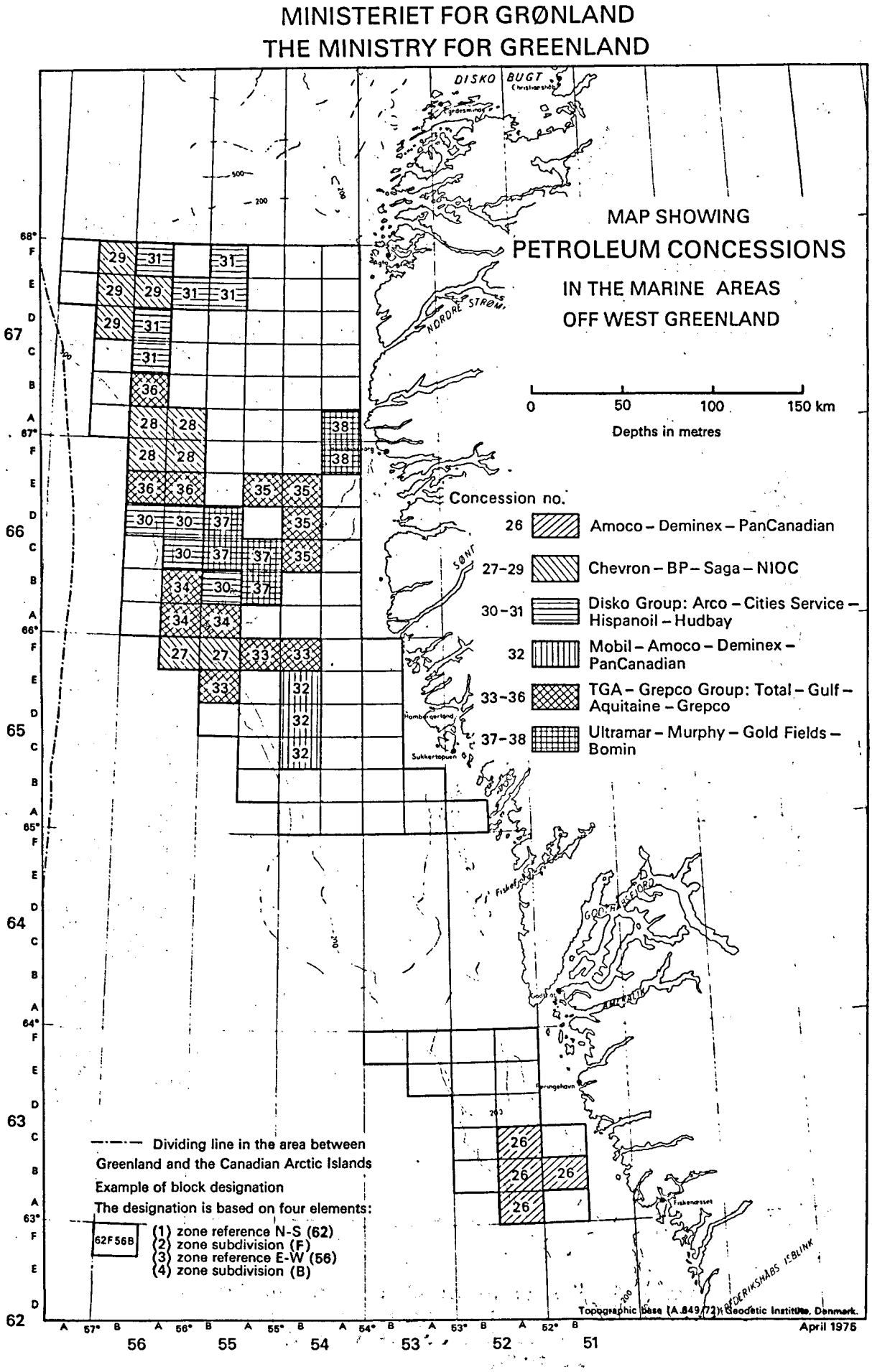

Figure 1. Greenland offshore concessions.

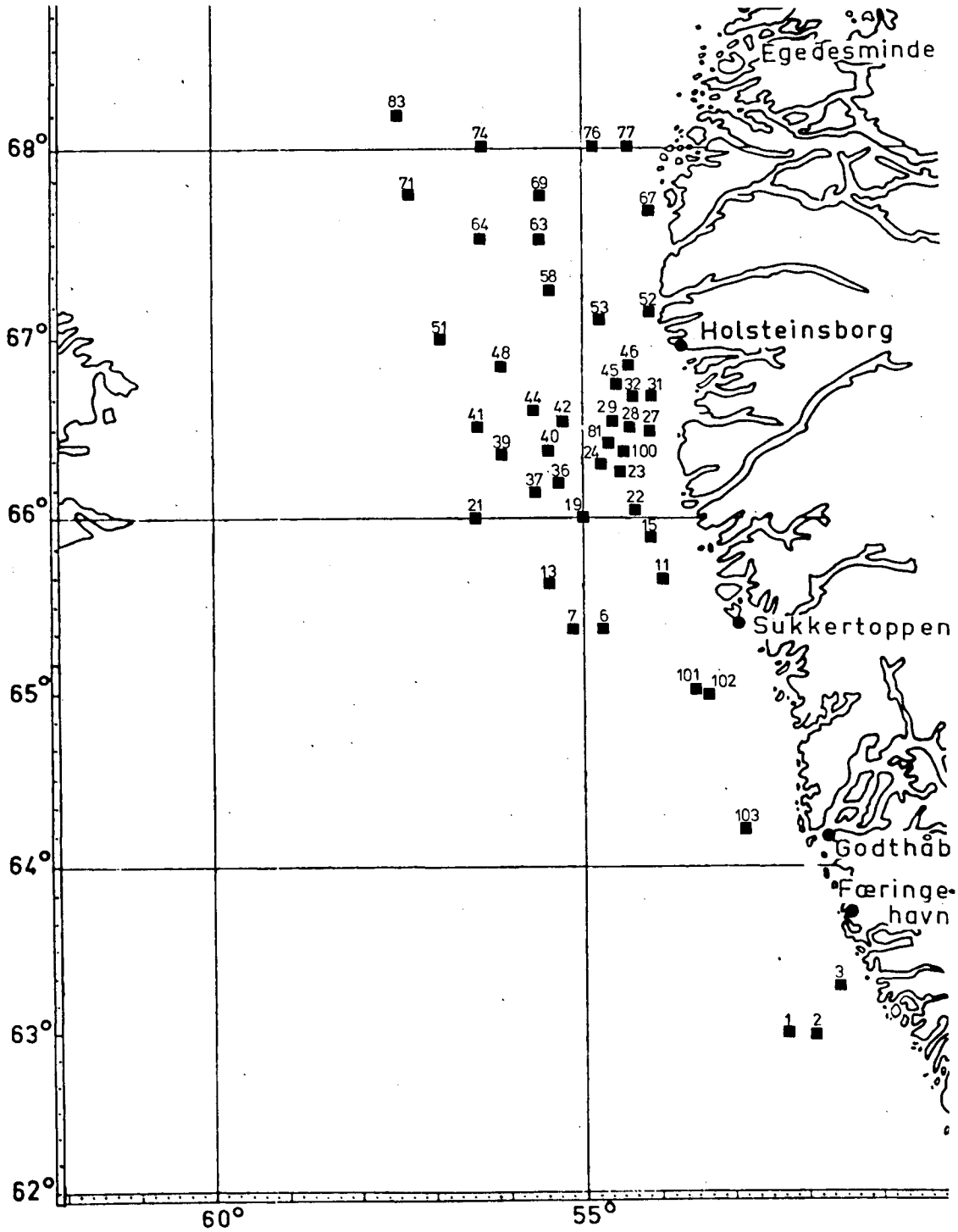

Figure 2. Positions at which samples for chemical analyses were taken during the cruise with R/V DANA in 1975.

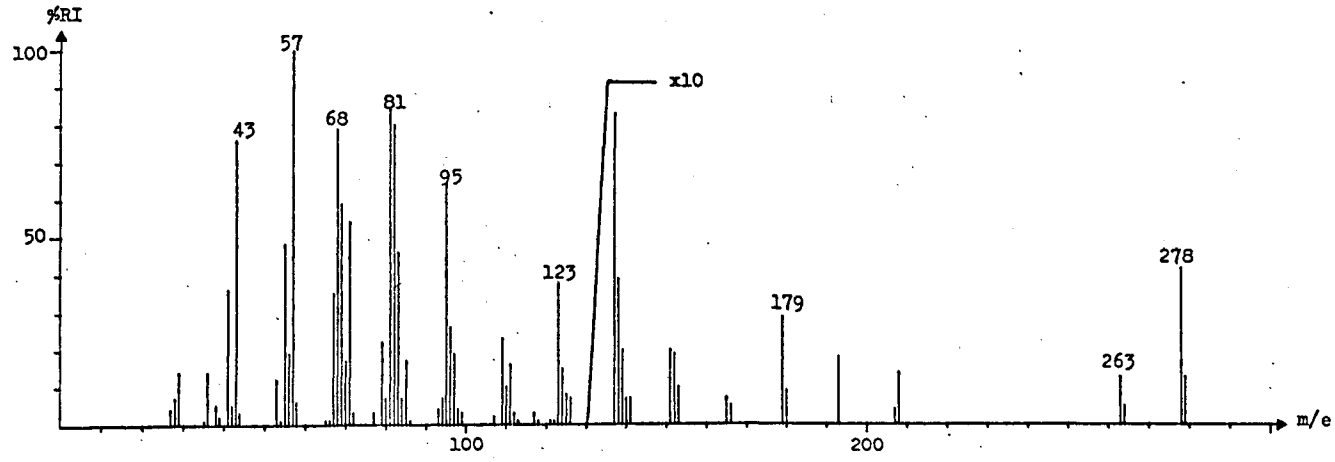

Figure 3. Mass spectrum of a hydrocarbon (retention time relative to C_{22}:0.76) isolated from redfish (Sebastes marinus).

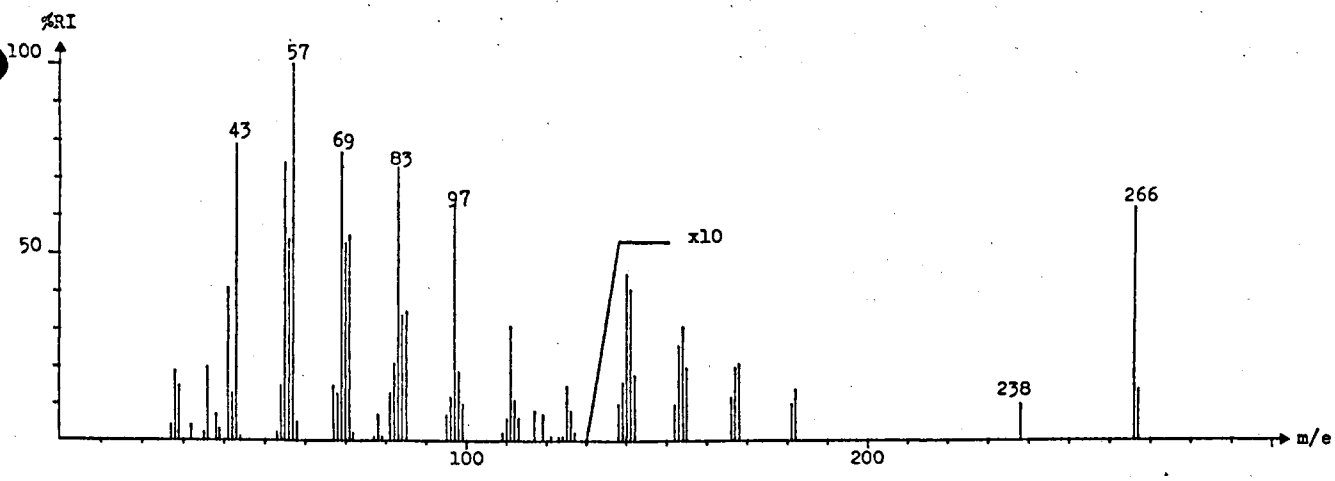

Figure 4. Mass spectrum of a hydrocarbon (retention time relative to C_{22}:0.77) isolated from capelin (Mallotus villosus).

TABLE 1: HYDROCARBON COMPOSITION (DRY WEIGHT BASIS) OF SEDIMENTS

POSITION	3	3	6	6	15	31	32	37	37	40	41	51	58	64	71	74	76	MEAN
SAMPLE No.	F1	F2	B1	B2	B2	C1	A1	A1	A2	A1	A1	A1	B1	B1	B1	A1	A1	
DRY WEIGHT mg/g	481	538	847	812	793	435	762	730	603	650	867	846	837	810	765	805	887	733
RETENTION TIME RELATIVE TO C_{22}	µg/g DRY WEIGHT																	µg/g DRY WEIGHT
0.64 PRISTANE	-	-	-	-	-	-	0.04	0.08	0.08	-	0.02	-	-	0.02	-	-	-	0.014
0.73	0.08	0.11	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.012
0.88	0.18	0.35	-	-	-	-	0.01	0.99	0.86	-	-	0.20	-	0.05	-	-	-	0.155
0.91	0.06	0.21	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.016
0.94	0.04	0.17	-	-	-	-	0.04	-	-	-	-	-	-	-	-	-	-	0.015
1.14	-	-	-	-	0.05	-	-	-	-	-	0.10	-	-	-	-	-	-	0.009
1.24	-	-	-	-	-	-	-	0.05	0.05	-	-	-	-	-	0.03	0.01	-	0.008
1.30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.01	-	0.001
1.35 SQUALENE	0.10	-	0.30	0.12	0.04	1.13	0.04	0.10	0.10	0.14	0.08	-	0.19	0.07	0.03	0.12	0.10	0.156
1.44	-	-	-	-	-	-	-	0.08	0.08	-	-	0.05	-	-	-	-	-	0.012
1.53	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.01	-	-
TOTAL	0.46	0.84	0.30	0.12	0.09	1.13	0.13	1.30	1.17	0.14	0.20	0.25	0.19	0.14	0.06	0.15	0.10	0.40
DETECTION LIMIT	0.01	0.01	0.05	0.05	0.01	0.05	0.01	0.01	0.01	0.05	0.01	0.01	0.01	0.01	0.01	0.01	0.05	

Table 2.

HYDROCARBON COMPOSITION (WET WEIGHT AND DRY WEIGHT BASIS) OF ZOO-PLANKTON.

POSITION	11		13		42		42		MEAN	
SAMPLE NO.	D1		C1		C1		C2			
DRY WEIGHT mg/g	41		56		56		56		56	
LIPID mg/g	-		< 1		< 1		-			
RETENTION TIME RELATIVE TO C_{22}	µg/g wet weight	µg/g dry weight	µg/g wet weight	µg/g dry weight	µg/g wet weight	µg/g dry weight	µg/g wet weight	µg/g dry weight	µg/g wet weight	µg/g dry weight
0.64 PRISTANE	0.90	22	1.00[a]	17.8	9.85[a]	175	0.68	12.1	3.11	56.7
0.88	-	-	-	-	-	-	0.08	1.4	0.02	0.35
1.35 SQUALENE	0.01	0.24	0.19	3.4	0.06	1.1	0.02	0.35	0.07	1.26
TOTAL	0.91	22.2	1.19	21.2	9.91	176	0.78	13.9	3.2	58
DETECTION LIMIT	0.01		0.05		0.05		0.01			

a) IDENTIFIED BY MASS SPECTROMETRY

Table 3.

HYDROCARBON COMPOSITION (WET WEIGHT, DRY WEIGHT AND LIPID BASIS) OF SHRIMP (PANDALUS BOREALIS)

POSITION	81			83		MEAN	
DRY WEIGHT mg/g	238						
LIPID mg/g	18			25		22	
RETENTION TIME RELATIVE TO C_{22}	µg/g wet weight	µg/g dry weight	µg/g lipid	µg/g wet weight	µg/g lipid	µg/g wet weight	µg/g lipid
0.56	0.04	0.15	2.0	-	-	0.02	1.0
0.64 PRISTANE	0,93	3.9	52	37[a]	1480	25.5	766
0.72	0.02	0.07	0.9	-	-	0.01	0.5
1.18	0.38	1.59	21	-	-	0.19	10.5
1.35 SQUALENE	0.23	0.98	12.9	0.68	27	0.46	20.0
1.39	0.03	0.12	1.56	-	-	-	-
TOTAL	1.65	6.8	91.7	37.7	1507	27	798
DETECTION LIMIT	0.01			0.01			

a) SEVERAL ANALYSES ARE MADE. THE RESULTS ARE 24,36 AND 50 µg/g WET WEIGHT. THE MEAN VALUE IS ENTERED IN THE TABLE. IDENTIFIED BY MASS SPECTROMETRY.

Table 4.

HYDROCARBON COMPOSITION (WET WEIGHT AND LIPID BASIS) OF GREENLAND HALIBUT (REINHARDTIUS HIPPOGLOSSOIDES)

TISSUE	LIVER									
POSITION	81		81		83		83		83	MEAN
SAMPLE NO.	K 11		K 12		A 4		A 5		A 7	
LENGTH cm	40		51		48		48		43	46
DRY WEIGHT mg/g										
LIPID mg/g	93		317		163		236		-	
RETENTION TIME RELATIVE TO C_{22}	µg/g wet weight	µg/g lipid	µg/g wet weight	µg/g lipid	µg/g wet weight	µg/g lipid	µg/g wet weight	µg/g lipid	µg/g wet weight	µg/g wet weight
0.64 PRISTANE	0.82	8.8	0.15	0.46	3.2	19.6	203	660	50[a]	51.4
0.77	-	-	-	-	-	-	3.2	13.5	-	0.64
1.09	-	-	-	-	-	-	-	-	-	-
1.19	-	-	-	-	-	-	2.9	12.3	-	0.58
1.24	-	-	-	-	-	-	0.7	3.0	-	0.14
1.35 SQUALENE	156	1670	696	2190	167	1120	1170	4930	327[a]	503
1.44	-	-	-	-	-	-	1.4	6.1	-	0.28
1.50	-	-	0.25	0.8	-	-	0.49	2.1	-	0.14
1.60	-	-	0.33	1.0	-	-	-	-	-	0.06
TOTAL	157	1679	698	2190	170	1140	1380	5630	377	556
DETECTION LIMIT	0.1		0.1		0.1		0.1		0.5	

a) IDENTIFIED BY MASS SPECTRPMETRY

Table 4 cont.

TISSUE	MUSCLE											
POSITION	81			81			83		83		MEAN	
SAMPLE NO.	K 11			K 12			A 4		A 7			
LENGTH cm	40			51			48		43		46	
DRY WEIGHT mg/g	208			231			-		-		-	
LIPID mg/g	62			88			70		133		88	
RETENTION TIME RELATIVE TO C_{22}	µg/g wet weight	µg/g dry weight	lipid	µg/g wet weight	µg/g dry weight	lipid	µg/g wet weight	lipid	µg/g wet weight	lipid	µg/g wet weight	lipid
0.64 PRISTANE	3.4	16.2	54	3.3	14.5	30	5.6	81	6.5	49	4.7	56
0.77	-	-	-	-	-	-	-	-	-	-	-	-
1.09	0.01	0.05	0.16	-	-	-	0.01	0.14	-	-	0.005	0.07
1.19	-	-	-	-	-	-	-	-	-	-	-	-
1.24	0.01	0.06	0.19	-	-	-	0.03	0.43	-	-	0.010	0.15
1.35 SQUALENE	8.2	39	132	15.9	69	182	9.5	136	20.5	154	13.5	151
1.44	-	-	-	-	-	-	0.01	0.1	-	-	0.003	0.03
1.50	-	-	-	-	-	-	-	-	-	-	-	-
1.60	-	-	-	-	-	-	-	-	-	-	-	-
TOTAL	11.6	55	186	19.2	8.4	220	15.2	218	27	203	18.3	207
DETECTION LIMIT	0.01			0.01			0.01		0.05			

Table 5.

HYDROCARBON COMPOSITION (WET WEIGHT AND LIPID BASIS) OF REDFISH (SEBASTES MARINUS)

TISSUE	LIVER		MUSCLE						
POSITION	83		83		83			MEAN	
SAMPLE NO.	A 16		A 15		A 16				
DRY WEIGHT mg/g	-		-		217				
LIPID mg/g	201		43		34			39	
RETENTION TIME RELATIVE TO C_{22}	µg/g wet weight	lipid	µg/g wet weight	lipid	µg/g wet weight	dry weight	lipid	µg/g wet weight	lipid
0.64 PRISTANE	99	494	36[a]	830	5.0	23	145	20.5	488
0.76	-	-	0.01[a]	0.32	-	-	-	0.005	0.16
0.78	0.09	0.44	-	-	-	-	-	-	-
0.89	2.9	14.8	0.06	1.4	0.03	0.14	0.92	0.045	1.16
1.24	0.11	0.56	-	-	-	-	-	-	-
1.35 SQUALENE	30	150	1.6[a]	37	0.86	4.0	25	1.23	31.0
1.44	0.06	0.27	-	-	-	-	-	-	-
1.48	0.06	0.31	-	-	0.13	0.61	3.8	0.065	1.90
TOTAL	132	660	38	870	6.0	28	175	22	522
DETECTION LIMIT	0.05		0.01		0.01				

[a] IDENTIFIED BY MASS SPECTROMETRY

Table 6. HYDROCARBON COMPOSITION (WET WEIGHT BASIS) OF CAPELIN (MALLOTUS VILLOSUS) (WHOLE FISHES)

POSITION	81
RETENTION TIME RELATIVE TO C_{22}	µg/g wet weight
0.64 PRISTANE	8.9[a]
0.77	1.5[a]
1.24	1.3[a]
1.35 SQUALENE	5.2[a]
TOTAL	16.9
DETECTION LIMIT	0.05

[a] IDENTIFIED BY MASS SPECTROMETRY

Table 7.

PRISTANE, SQUALENE AND TOTAL HYDROCARBON LEVEL IN SEDIMENTS AND INVERTEBRATES

	SEDI-MENTS	BRY-OZOAN	ZOO-PLANK-TON	HOLO-THU-RIAN	BIVALVES ASTARTE	BIVALVES MYTILUS	SHRIMP	STARFISH SOLAS-TER	STARFISH LEP-TASTE-RIAS	HIPPA-STERIA	ASCI-DIAN
PRISTANE											
µg/g wet weight	-	0.02	3.1	-	-	-	26	0.13	0.05	0.01	0.03
µg/g dry weight	0.014	-	57	-	-	-	-	0.44	0.17	0.04	-
µg/g lipid	-	-	-	-	-	-	766	-	1.35	-	-
SQUALENE											
µg/g wet weight	-	0.21	0.07	0.08	0.03	0.02	0.46	0.52	0.09	0.45	0.08
µg/g dry weight	0.16	-	1.26	0.82	-	-	-	1.89	0.30	1.69	-
µg/g lipid	-	-	-	8.0	3.5	1.6	20	-	4.9	-	-
TOTAL											
µg/g wet weight	-	0.23	3.2	0.08	0.22	0.10	27	1.04	0.21	0.48	0.16
µg/g dry weight	0.40	-	58	0.82	-	-	-	5.2	0.71	1.81	-
µg/g lipid	-	-	-	8.0	27	8.0	798	-	8.1	-	-

Table 8.

PRISTANE, SQUALENE AND TOTAL HYDROCARBON LEVEL IN LIVER AND MUSCLE OF FISH

	COD		GREENLAND COD		GREENLAND HALIBUT		AMERICAN PLAICE		WOLF-FISH		REDFISH		CAPELIN WHOLE FISH	HAGFISH
	LIVER	MUSCLE	LIVER	MUSCLE	LIVER	MUSCLE	LIVER	MUSCLE	LIVER	MUSCLE	LIVER	MUSCLE		
PRISTANE														
µg/g wet weight	27	0.08	2.8	-	51	4.7	7.1	0.15	1.86	0.07	99	21	8.9	0.38
µg/g dry weight	-	-	-	-	-	-	-	0.77	-	-	-	-	-	-
µg/g lipid	-	-	-	-	-	56	52	1.83	29	9.1	494	488	-	11.7
SQUALENE														
µg/g wet weight	216	1.20	39	3.3	503	13.5	21	0.89	49	1.60	30	1.23	5.2	9.75
µg/g dry weight	-	-	-	-	-	-	-	5.0	-	-	-	-	-	-
µg/g lipid	-	-	-	800	-	151	168	218	622	146	150	31	-	313
TOTAL														
µg/g wet weight	248	1.3	42	3.3	556	18.3	29	1.1	52	1.8	132	22	16.9	10.1
µg/g dry weight	-	-	-	-	-	-	-	5.9	-	-	-	-	-	-
µg/g lipid	-	-	-	800	-	207	228	239	663	158	660	522	-	324

Table 9. RETENTION TIMES OF n-ALKANES AND SOME BRANCHED HYDROCARBONS RELATIVE TO C_{22}

HYDROCARBONS	RETENTION TIME RELATIVE TO C_{22}
C_{14}	0.38
C_{15}	0.47
C_{16}	0.55
C_{17} & Pristane	0.64
C_{18}	0.72
C_{19}	0.79
C_{20}	0.86
C_{21}	0.93
C_{22}	1.00
C_{23}	1.06
C_{24}	1.13
C_{25}	1.18
C_{26}	1.24
C_{27}	1.29
C_{28} & Squalene	1.35
C_{29}	1.40
C_{30}	1.45
C_{31}	1.50
C_{32}	1.55
C_{33}	-
C_{34}	1.70
C_{35}	1.80
C_{36}	1.93

Table 10. MARINE ORGANISMS INCLUDED IN THE GAS CHROMATOGRAPHIC/MASS SPECTROMETRIC ANALYSES

ORGANISMS, POSITIONS, AND SAMPLE NO.		COMPONENTS IDENTIFIED
Alcyonidium gelatinosum	2	Squalene
Zooplankton	13 C1, 42 C1	Pristane
Pandalus borealis	83	Pristane
Gadus morhua	101 A57	Pristane & Squalene
Reinhardtius hippoglossoides	83 A7	Pristane & Squalene
Sebastes marinus	83 A15	Pristane & Squalene & unknown comp. (see text)
Mallotus villosus	81	Pristane & Squalene & two unknown comp. (see text)

Table 11. Species analysed for hydrocarbons.

Alcyonidium gelatinosum (bryozoan)
Pandalus borealis (shrimp)
Astarte crenata (bivalve)
Mytilus edulis (bivalve)
Cucumaria frondosa (holothurian)
Solaster frondosa (asteroid)
Leptasterias polaris (asteroid)
Hippasteria phrygiana (asteroid)
Boltenia ovifera (ascidian)
Myxine glutinosa (hagfish)
Mallotus villosus (capelin)
Gadus morhua (cod)
Gadus ogac (Greenland cod)
Sebastes marinus (redfish)
Anarrhicas lupus (wolffish)
Anarrhicas minor (wolffish)
Reinhardtius hippoglossoides (Greenland halibut)
Hippoglossoides platessoides (American plaice)