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The Drupa oil spill, investigation concerning oil, water and fish

by

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1. INTRODUCTION

February 14, 1976 between 0700 and 0800 the tanker "Drupa" touched the ground at Klakken when approaching the oil - refinery near Stavanger in southwestern Norway. Two thousand tons of Iranian crude were spilt. In calm weather conditions the oil spread northwest-wards during the first days after the accident and contaminated the shoreline from Kjør to Røvær and also two seine-nets with saithe Gadus virens, one with 150 tons at Kvitsøy and one with 50 tons at Røvær. Later some oil contaminated the shoreline further north.

In removal of the oil from the sea booms and skimming was used to some extent. The oil was cleaned from parts of the contaminated shoreline by physical methods, some dispersants were also used.

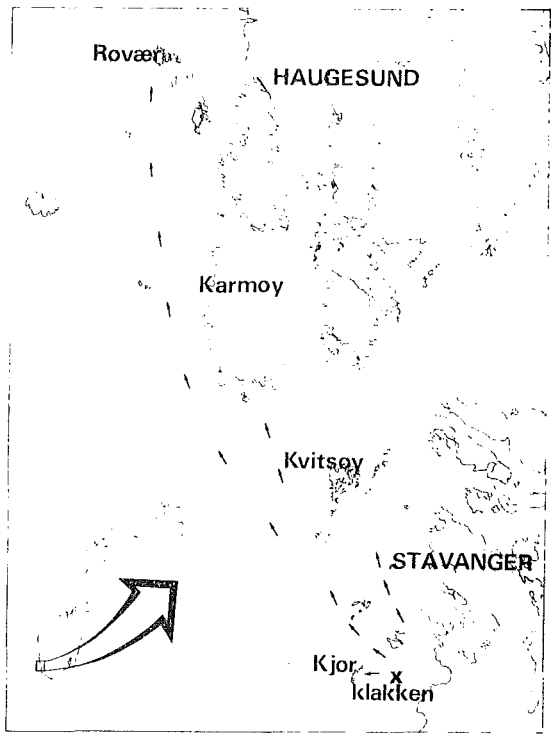

Fig. 1. X near klakken shows where "Drupa" touched the ground and the crosshatched area indicates where the oil was spilt. The small arrows show the spreading of the oil during the first days after the spill.

February 20. samples of the oil and water were collected at Kjør, Kvitsøy and Røvær, and samples of the saithe, both dead and alive, were collected from the seine-nets at Kvitsøy and Røvær.

The purpose of the investigation was to study: 1. the qualitative and quantitative changes if the oil resulting from the exposure to the environment, 2. the amount of petroleum hydrocarbons in the water in the vicinity of the oil on the surface and 3. the uptake of hydrocarbons in saithe from the contaminated seine-nets.

2. OIL

2.1 Experimental. Subsamples of the oil were dissolved in pentane and chromatographed on a 20 m x 0.3 mm glass capillary column with SE-54 as liquid phase (from JAEGGI, CH-9043, Trogen, Switzerland). Helium was used as carrier gas at a rate of 2 ml per minute. The oven was programmed from 100 °C to 230 °C with 6 °C per minute. The column was connected

by a platinum capillary without any separator directly to the ion chamber of a Finnigan 3200 mass spectrometer. The mass fragmentographic analysis was achieved by setting the quadrupole analyser at the ions 128, 142 and 156 the first 4.7 minutes after injection and thereafter on 170, 178, 184 and 192. These mass units represent respectively 128 : naphthalene, 142 : methylnaphthalene, 156 : dimethylnaphthalene, 170 : trimethylnaphthalene, 178 phenanthrene, 184 : tetramethylnaphthalene and dibenzothiophene and 192 : methylphenanthrene. The mass fragmentograms were stored for further treatment in Finnigan 6100 datasystem.

2.2 DISCUSSION

2.2.1 Identification of oil spills. One of the problems concerning oil pollution of the marine environment is to find the sources of oil spills. A number of analytical methods have been used for such identification purposes (BENTZ 1976). Gas chromatography has proved to be one of the most versatile. The method was introduced by RAMSDALE and WILKINSON (1968) and further developed by EHRHARDT and BLUMER (1972) and several other analysts. It is based on visual observation of the gas chromatograms of oil samples, taking into consideration the relative heights of the single peaks, specially the normal alkanes and the branched alkanes pristane and phytane, and the size and shape of the unresolved background signal. The American Society for Testing and Materials has now standardized the method (1975). Furthermore, the method has been computerized by using pattern recognition techniques (CLARK and JURS, 1975). ADLARD et al. have extended the method to sulfur compounds by the use of a sulfur sensitive flamephotometric detector.

The aromatic hydrocarbons have attracted increasing attention during the last years because they are more soluble, more toxic and more persistent in the marine environment than the saturated hydrocarbons with corresponding molecular weight.

Crude oils contain a wide spektrum of aromatics and the amounts of the different aromatics varies from crude oil to crude oil. With a proper analytical method the relative composition of selected aromatics could therefore be used in the identification of oils and oil spills.

By gas chromatography of an oil with a non-selective flame ionization detector the aromatics will be hidden in the unresolved background signal which also contains branched aliphatics and cyclic aliphatics (naphthenes). Gas chromatographic analysis of the aromatics must therefore either be based on a preseparation of the aromatics from the other hydrocarbons in the sample (ANON, 1975 a, GRUENFELD 1973, WARNER 1973), or on a selective detector.

A mass spectrometer coupled to the gas chromatograph is very well suited for the application as a selective detector, especially for the aromatic hydrocarbons (BIERI et al. 1974), since they give stable molecular ions. With the spectrometer tuned to detect the molecular ions of the aromatics as described above the characteristic patterns as shown in Fig. 2 was obtained. Here the pattern of Iranian crude from "Drupa" is shown together with the collected samples of the spilt oil. The fragmentograms were adjusted in a manner so that the most intense peak within each of the three groups: 1. trimethylnaphthalene, 2. tetramethylnaphthalene and 3. dibenzothiophene, phenanthrene and methylphenanthrene attain the same height. The figure gives a correct picture of the relative composition within each group, but the relation between the groups is incorrect.

The fragmentograms appear to be identical: the samples can still after one month of exposure to the environment be identified with their source.

The same method was applied to an oil spill which appeared in January 1976 at Hitra in western Norway. A sample of the spilt oil was compared with a sample of oil from a suspected ship as shown in Fig. 3. The difference in the fragmentograms means that the two oils were different.

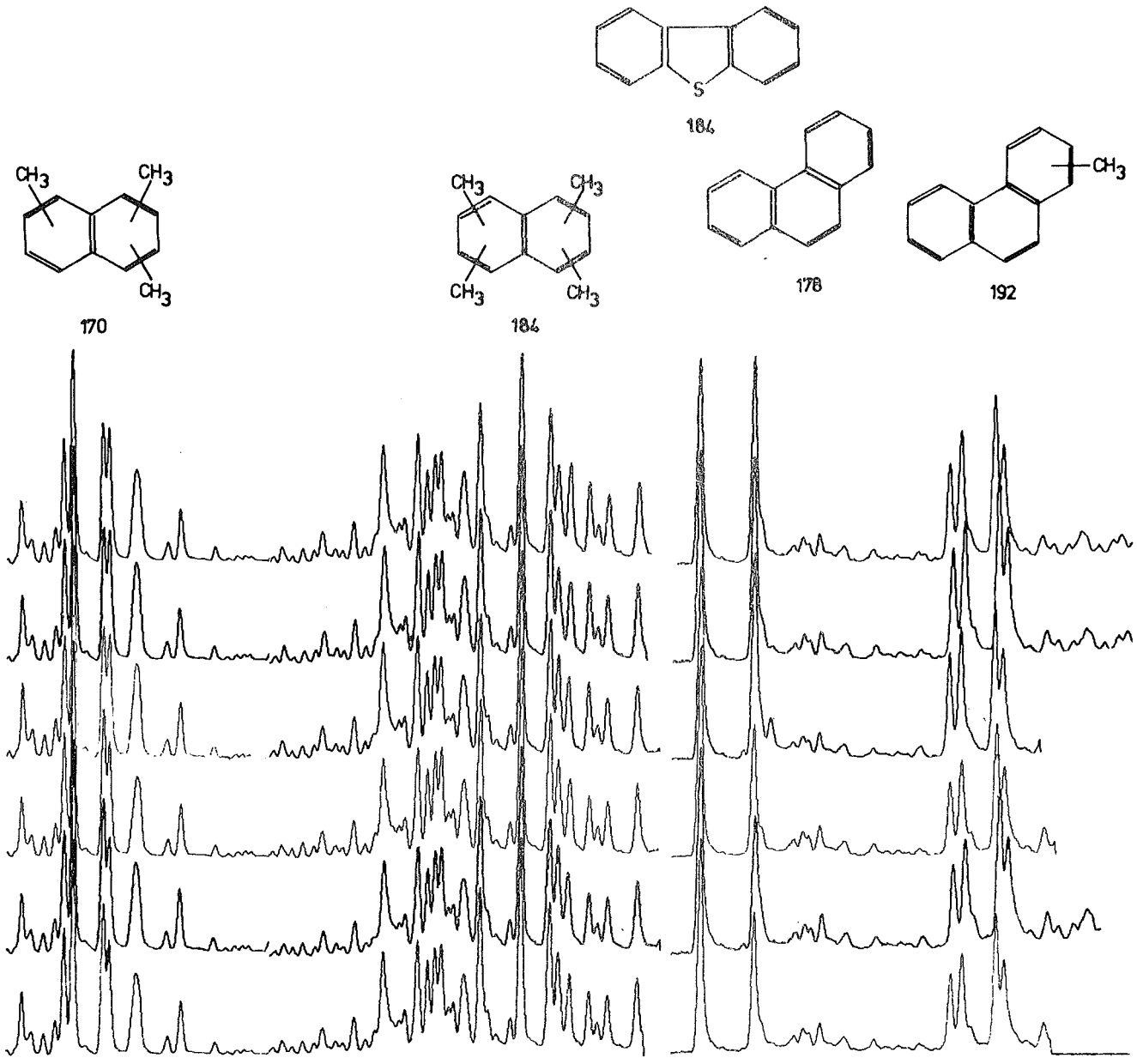

Fig. 2. Mass fragmentogram of the molecular ions of trimethylnaphthalenes, tetramethylnaphthalenes, dibenzothiophene, phenanthrene and methylphenanthrenes. The fragmentograms represent from below: Iranian crude, oil sample from Kjør - 6 days old, oil sample from Røvær - 6 days old, oil sample from Bømlo - 12 days old, oil sample from Stolmen - 25 days old and oil sample from Karmøy - 27 days old.

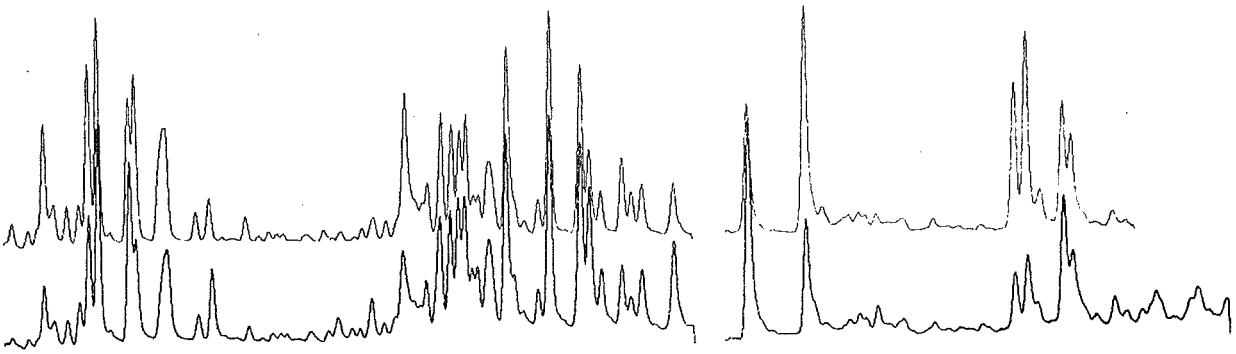

Fig. 3. Mass fragmentogram of an oil spill from Hitra, on top, and of oil from a suspected ship, below.

2.2.2 Weathering of spilt oil. The environment affects the oil in different ways, e.g. evaporation, solution/emulsification/ sorption to particulate matter, microbial degradation and photochemical degradation. Evaporation and solution/emulsification/ sorption are most important in the first stages after an oil spill, and will during the first days lead to a substantial loss of weight. This is shown in the gas chromatogams in Fig. 4.

The chromatograms of samples from the oil spill show a reduction in the first part relative to the crude oil during the 6 first days: All components more volatile than C_{11} have disappeared and those eluted between C_{11} and C_{16} are reduced relative to the less volatile. This is even more obvious on the chromatogram of the 25 days old sample.

On the basis of the chromatograms the percentage reduction of the oil was estimated: The total area of the chromatogram, which is equivalentto the remaining oil, was determined relatively to the amount of the C_{23} alkane, which is assumed not to disappear from the oil. By comparison of this ratio,

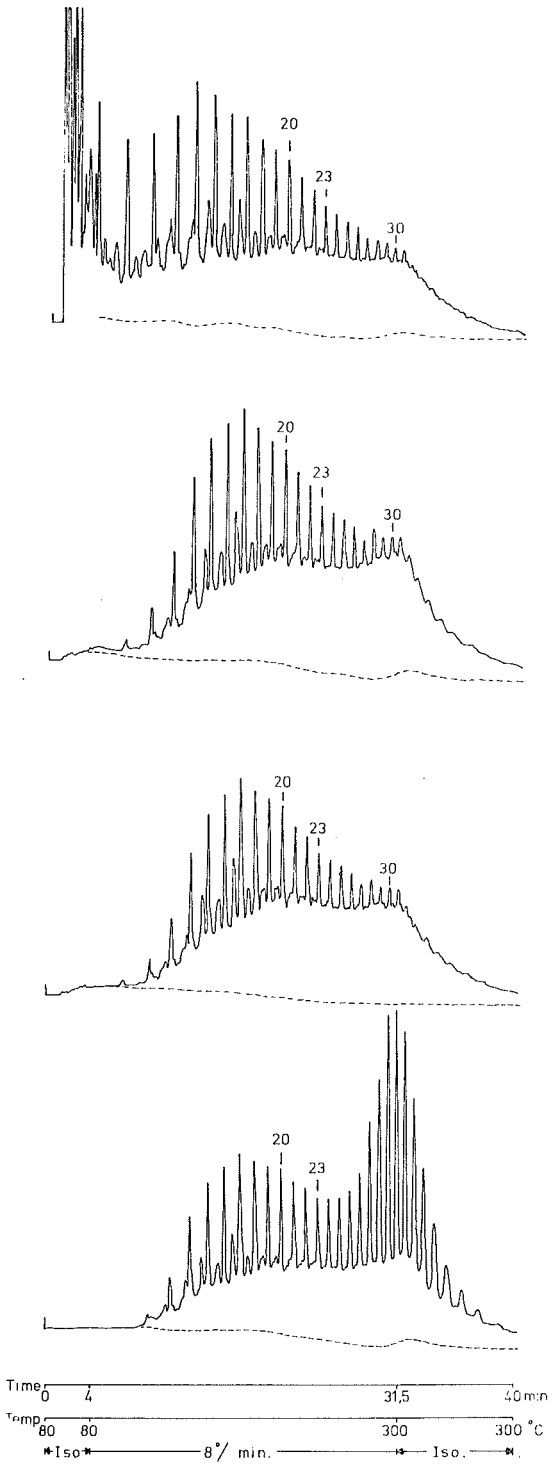

Fig. 4. Gas chromatograms of, from top; Iranian crude, oil sample from Røvær - 6 days old, extract of a water sample taken 1 m outside an oil boom at Røvær, and oil sample from Stolmen - 25 days old. The chromatograms were obtained on a Perkin-Elmer 900 gas chromatograph equipped with flame ionisation detector. A glass column, 3 m x 3 mm packed with 3% OV-1 on 80/100 mesh gas-chrom Q. Nitrogen, 15 ml per minute, was used as carrier gas. The broken line is the baseline of the chromatograms found by chromatography of pure solvent under identical conditions.

total area versus C_{23}, for the samples of the spilt oil with the same ratio for the crude oil, the percentage reduction was calculated. The results are given in Table 1.

Table 1. The disappearance of oil from the surface/shore, calculated with C_{23} as reference, see text.

Locality	Days after spill	% disappeared
Iranian crude	0	0
Kjør	6	28
Kjør	6	31
Røvær	6	32
Bømlo	12	50
Bømlo	15	48
Stolmen	25	49
Karmøy	65	50

Thirty percent of the oil had disappeared after 6 days and after one month only about one half was left. This part appears to be pretty stable; further reduction could not be observed during the next month.

These results correspond with those found in controlled experiments in other laboratories. In the Continental Shelf Division of the Royal Norwegian Council for Scientific and Industrial Research it was found that at an air temperature of 3 - 6 °C 25% of Ekofisk crude disappeared after 24 hours and approximately 43% after 30 days, while at 15 - 20 °C approximately 40% disappeared after 24 hours and about 55% after 30 days (HÆGH et al.). C_{19} was used as reference and compared with the remaining alkanes and the proportion of alkanes in different distillation cuts.

In an English paper concerning oil pollution of the North Sea is indicated, without experimental details, that up to 40% of North Sea crude will disappear from the surface during the first 24 hours after a spill (ANON 1975 b).

A Swedish laboratory test states that 56% Nigerian crude disappeared during 30 days on water. Fortyfive per cent had evaporated, 9.5% were dissolved/emulsified and 1,5% were degraded microbially or chemically. No experimental method was given (NOTINI 1976).

However important the knowledge of the disappearance of the oil from the surface might be, the most important question is how much oil is transported down in the water column. There is general agreement that this is a small portion of the total. The Swedish investigation (NOTINI 1976) suggests that 9.5% are dissolved in the water after 30 days. This appears to be rather much, i.e. McAULIFFE et al. (1975) have estimated that less than 1% of a crude oil spilt from a platform in the Mississippi delta in 1970 was dissolved in the water after 24 hours.

The portion that is transported down in the water will be enriched in the components which are most soluble, the aromatics (ANDERSON et al. 1974). These are also the most toxic and most persistent hydrocarbons.

3. WATER

3.1 Experimental. Water was collected on 2.8 litre bottles. Exept from one case when the sample was taken from the surface layer, the others were taken about 20 cm below the surface. Approximately 30 ml dichloromethane was added to the bottles to prevent biological activity.

In the laboratory the water was transferred to a separatory funnel together with the dichloromethane, the bottle was rinsed with another 30 ml dichloromethane which afterwards

was poured into the funnel which thereafter was thoroughly shaken for 1 minute. After removal of the dichloromethane the extraction was repeated twice, with 30 ml which were first used in rinsing the bottle. The combined extracts was dried with sodium sulfate and a measured portion depending on the contents of hydrocarbons, was withdrawn and evaporated to about 0.3 ml on a rotary evaporator under reduced pressure at approximately 20°. The residue was quantitatively transferred to a vial with conical bottom and further evaporated in a stream of nitrogen gas to about 10 µl and this was quantitatively transferred to a capsule for automatic injection on a glass column packed with OV-1 in a Perkin Elmer 900 gas chromatograph equipped with a flameionisation detector.

A chromatogram of a water sample extract is shown in Fig. 4 together with chromatograms of Iranian crude and samples of the spilt oil. The chromatograms consist of a series of peaks, which represent the normal alkanes, on top of an unresolved background signal, which consists of the thousands of components present in crude oil not resolvable by a packed column.

Integration of the total area of a chromatogram, background plus peaks, of a known amount of Iranian crude it was found that 1 µg oil was equivalent to 0.05 area units. This response factor was applied in quantification of the oil in the water extracts. The found values are given in Table 2.

Table 2. Concentrations, µg per litre, of petroleum hydrocarbons in the water.

Kjør	
Outside (sample taken from a boat)	90
Inside (sample taken from land)	130
Tidepool	230
Kvitsøy	
Seine-net	18
Røvær	
1 m outside boom	20 000
5 m outside boom	9 000
Seine-net surface	60
Seine-net 20 - 30 cm depth	20
Alongside quay	6-13

3.2 Discussion - water. The chromatogram shown in Fig. 4 of the extract of the water sampled 1 outside the boom at Røvær, is very similar to the chromatogram of the oil from inside the boom This can also explain the rather high concentration, 20 mg per litre. The chromatograms of the extracts of the water which contained less hydrocarbons were different from the oil chromatograms. In these cases hydrocarbons are selectively extracted into the water form the oil on the surface depending on the solubility.

The overall picture is that the water contained only small amounts of hydrocarbons. In a small tidepool with oil on the surface the concentration was only 0.2 mg per litre. Even without a visible oil film on the water a difference between the surface sample and the sample taken from 20 cm below the surface was observed. The samples from the two seine-nets gave about the same results. In both cases there was oil on the equipment but no oil visible on the water surface The two paralell samples taken alongside the quay at Røvær showed 6 and 13 µg per litre, respectively. These are values close to what is normally considered to be unpolluted water. Here also, oil was observed along nearby shoreline.

Only the most volatile hydrocarbons, espesially the aromatics, and compounds which contain the elements oxygen, nitrogen or sulfur, have some solubility in water. After 6 days on the water most of these either have evaporated or have been washed out of the oil. Any oil in the water phase at this stage should therefore be expected either to be emulsified or sorbed to particulate matter. Therefore, under the conditions: calm weather and clear and clean water it was reasonable that only small amounts of oil was found in the water phase even in fairly close proximity to the remaining oil on the water surface and on the shoreline. These results correspond with those found by DODDS (1970): 8 - 9 hours after an arranged oil spill the water 1 m under the oilslick contained 450 µg per litre, and after 24 hours the oil content was below the detection limit of 10 µg per litre. Simular values were found by FREEGARDE et al. (1971).

4. FISH

After 2 days on the sea oilslicks contaminated two seine-nets with saithe, one with 150 tons at Kvitsøy and one with 50 tons at

Røvær. The oil remained for two days at the surface of the seine-nets, heavely clogging to the upper parts of the equipment. The oil later drifted away, but more oil remained at the nearby shoreline at Røvær than at Kvitsøy.

Due to the pollution nobody wanted the fish, neither for human nor animal consumption. On this basis it was of interest to have the fish analysed for hydrocarbons, both by organoleptic and chemical methods. The samples from the seine-nets were both of fish in apparently good condition and of dead fish. No oil could be observed on any of the fish.

4.1 Organoleptic analysis. The fish were cooked separately and subjected together with control fish from an uncontaminated catch to a taste panel of 10 selected persons who gave their individual judgements. The result was clearcut: the fish was not tainted.

4.2 Chemical analysis. The analytical method was based on saponification followed by extraction (FARRINGTON and MEDEIROS 1975). Samples of liver and muscle was boiled for 1.5 hours under refeux in 50 ml methanol containing 3 g potassium hydroxide. The tissue was hereby destroyed and the fat was saponified. A known amount of fluoren was added as internal standard before the saponification. The resulting suspension was divided in two portions. One was extracted with pentane, the extract was poured through a 20 x 5 mm column filled with SiO_2. The total eluate was evaporated and the residue was dissolved in carbondisulfide and 0.1 µl of this solution was analysed by gas chromatography coupled to a mass spectrometry as described above, with the difference that complete mass spectra between 30 and 350 mass units were recorded automatically every second and stored in the computer. In this manner it was possible to conduct a search for hydrocarbons after the sample had been chromatographed. The search was concentrated on aromatic hydrocarbons and it turned out that characteristic patterns of naphthalene, mono-, di- and trimethyl-naphthalenes, phenanthrene, methylphenanthrene, fluoranthene

and pyrene were present. These aromatics were quantified in the computer by help of the internal standard fluorene. No correction was made for possible differences in the intensities of the molecular ions of the various aromatics. The values are shown in Table 3.

Table 3. Concentrations of aromatic hydrocarbons, mg per kilo, found in oilcontaminated saithe.

		Based on fat	Based on wet weight
Kvitsøy			
Dead*	- liver	-	-
Dead	liver	0.3	0.09
	muscle	-	-
Alive	- liver	0.5	0.11
Røvær			
Dead*	- liver	3.4 - 3.9	1.5 - 1.9
Dead	liver	9.5	1.6
	muscle	(22)	
Alive	- liver	2.8	1.2

* Muscles from these fishes were also used for taste samples.

The amount of fat in the sample was determined from the other half of the saponified suspension. This was acidified by concentrated sulfuric acid, the fatty acids were then extracted with petrol ether which thereafter was dried with sodium sulfate and evaporated. The amount of fatty acids was then found by weighing.

4.3 Discussion - fish. Oil pollution is a smaller threat against adult fish than against eggs and larvae. The adult fish has greater resistance and also the possibility to avoid the polluting oil. Lethal effects of oil on adult fish is therefore rarely reported even if it is known that infection of the gills by oil emulsion may lead to suffocation (NELSON - SMITH 1972). Fish in seine-nets will be extra exposed.

Nevertheless, the few dead fish in the seine-nets at Kvitsøy and Røvær had probably died of other reasons. No traces of oil was observed on the fish nor on their gills. The contents of hydrocarbons found by chemical analysis, Table 3, was not large enough to kill them. Laboratory tests carried out at a later stage showed that saithe can live in an aquarium with oil on the surface for weeks without increase in the natural mortality.

Another effect of oil pollution which may have consequences for commercial fishing and aquaculture is oil tainting of fish. This has been reported in connection with several oil spills (SIDHU et al. 1972, BLACKMAN et al. 1973, PALMORK and WILHELMSEN 1974, WHITMAN 1975).

In the present case the organoleptic analysis revealed no tainting. On the other hand, chemical analysis showed aromatic hydrocarbons, especially in the liver of the fish, but also in the muscles Table 3. These hydrocarbons are expected to originate from the oil spill, because aromatics, in particular the alkylated, are not biogene (FARRINGTON and MEYER 1975). Accordingly, control analysis of unpolluted fish did not show any of these compounds.

The significant difference between the samples from Kvitsøy and Røvær is probably due to the more closed waters and heavier pollution along the shores at Røvær.

These findings show that hydrocarbons may be present in the fish even if no tainting can be detected. The relatively low level of aromatics would probably be of no health hasard if the fish was used for consumption. However, there is a need for treshold levels.

Several investigations have shown that fish will take up petroleum hydrocarbons, both aliphatic and aromatic, from polluted waters and assimilate them in the tissue. A review

is given by McINTYRE et al. (1975). It remains to be disclosed which hydrocarbons are responsible for the tainting. The aromatics found in the fish in this investigation will not necessarily give tainting even if present in higher concentration.

The quantitated aromatics, naphthalene, mono-, di- and trimethylnaphthalenes, phenanthrene, methylphenanthrene, fluoranthene and pyrene, were found to amount to only 0.35% of the total hydrocarbons in a sample of the oil from the surface at Røvær. This means that they are significantly enriched in the fish tissue relatively to the other hydrocarbons in the spilt oil.

Since the aromatics are among the most water soluble components of crude oil they will be enriched in the water phase. Depending on the type of oil an enrichmentfactor of up to 125 for the aromatics versus the normal alkanes have been found (ANDERSON et al. 1974). In this manner the aromatics are made more available for the fish. ANDERSON (1975) has also shown that the naphthalenes are accumulated at the most and are most persistent in the tissue of marine organisms. In accordance with this the naphthalenes were responsible for the bulk of the quantitated aromatics in the saithe from Kvitsøy and Røvær.

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