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INVESTIGATIONS MADE DURING THE EKOFISK BLOW-OUT

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SUMMARY

Following the Ekofisk 'Bravo' blow-out samples of fish, sediments and sea water from the area around the oil-field were collected and analysed for petroleum hydrocarbons using a computerized GC-MS system. The compounds quantified for each sample were the n-alkanes of carbon numbers 12 to 17 and pristane; and naphthalene, phenanthrene, dibenzothiophene and some of their alkylated derivatives.

Considerable variation was observed between the hydrocarbon concentrations found at adjacent stations, and between the two samples (at 1 and 5 m below the surface) taken at each station. The higher levels found, however, were generally in the area of the oil-slick.

Both from the alkane pattern and from the low levels of aromatic hydrocarbons present, it was apparent that at the time of sampling (up to one week after the blow-out began) little or no contribution had been made to the hydrocarbon content of either the fish or sediments by the 'Bravo' blow-out.

Lack of comparative data prevents any further interpretation of the results at this time, but this should be possible when the results of the Norwegian survey are available.

INTRODUCTION

On 23 April 1977 a blow-out occurred during maintenance operations on the 'Bravo' platform of the North Sea Ekofisk oil-field and oil began to escape from the well at a rate of approximately 3 000 tonnes per day. Following an approach by Norwegian scientists, the MAFF Research Vessel CORELLA began a co-ordinated work programme with the Norwegian Research Ships G. O. SARS and JOHAN HJORT on 28 April. This involved the collection of sediment, fish and water samples for hydrocarbon analysis on a grid system as in Figure 1. The Norwegian vessels operated to the same system but between them also worked stations closer to and further from the 'Bravo' rig.

SAMPLE COLLECTION

Seawater samples were collected from 1 and 5 m below the sea surface by a method similar to that used for the IGOSS project (1), except that the bottle was sealed with a rubber bung wrapped in solvent-rinsed aluminium foil which was removed at depth by means of a cord. Ten ml of dichloromethane was added to each sample bottle before collection to prevent biological activity in the sample prior to extraction. The top half-inch of the sample was removed after recovery by quickly shaking the bottle, and an aluminium foil-lined cap was then screwed on to it. Finally the sample bottle was stored in the dark prior to transport back to the laboratory.

Surface sediments were sampled using a 0.1 m^2 Day grab. Sub-samples of the sediment were transferred to pre-cleaned glass jars with aluminium foil-lined lids and preserved at -20°C.

Samples of fish were obtained from two sites by bottom-trawling. One trawl haul was carried out within the reported boundaries of the oil-slick, and one outside. The fish caught were wrapped in aluminium foil and kept frozen at -20°C until extracted as soon as possible after returning to the laboratory.

EXTRACTION OF SAMPLES

Following a visit to the Institute of Marine Research, Bergen shortly before the 'Bravo' blow-out, the procedures used by the Norwegian workers at the Institute had been adopted as routine and measures are in hand to intercalibrate methods with these workers.

Water samples were extracted with 1 x 50 ml and 2 x 25 ml dichloromethane. The extracts were combined and concentrated to $<$ 1 ml on a rotary evaporator. The solution was transferred to a 1 ml glass vial and the solvent removed with a stream of nitrogen. Pentane (20 μl) was then added and a septum cap crimped on to seal the vial. The extracts were stored in a freezer at -20°C prior to GC-MS analysis.

Alkaline digestion of tissue has been shown to be an efficient and relatively rapid method for the extraction of hydrocarbons (2,3). Fish muscle samples (20 g) and liver samples (6 g) were digested under reflux with methanolic KOH for 1½ hours, and the mixture was allowed to cool to room temperature. The non-saponifiable lipids were then extracted with 2 x 25 ml pentane, the extracts being combined and the treatment thereafter being exactly as for the water samples above. Sediment samples (70 g) were digested and extracted using a similar technique. In all cases an internal standard containing a known amount of fluorene and anthracene was added to the sample prior to the extraction.

ANALYSIS

Analyses were carried out on a Finnigan 3200-6110 computerized GC-MS system, with a splitless injection on to a 20 m OV-1 glass capillary column. The carrier-gas (helium) flowrate was 1.5 ml per minute and the column was connected directly to the ion source of the mass spectrometer by a platinum capillary.

The samples were analysed by mass fragmentography, a technique which is particularly good for the investigation of aromatic hydrocarbons (4), owing to their very stable molecular ions. Any alkylated aromatics detected in the samples would be expected to indicate hydrocarbons of fossil fuel origin, as these compounds have not been found to be produced biogenically (5).

During a GC run mass fragmentograms were recorded using the MS-data system for five groups of ions, a switch being made from one group to the next at a pre-set time. The ions used and the compounds which they represent were as follows:

57: alkanes 128: naphthalene 141: methyl naphthalenes
57: 141: di-methyl naphthalenes 166: fluorene 170: tri-methyl naphthalenes
57: 184: dibenzo-thiophene
178: phenanthrene and anthracene 192: methyl phenanthrene 198: methyl dibenzo-thiophene
206: di-methyl phenanthrene 212: di-methyl + 226: tri-methyl dibenzo-thiophene

Quantification of these aromatic compounds, and of the n-alkanes of carbon numbers 12 to 17 and the isoprenoid pristane, were obtained by comparison of the areas obtained from mass fragmentograms with those obtained for the known weights of the internal standards.

RESULTS AND DISCUSSION

The results of the analyses of water, fish and sediments are given in Tables 1, 2 and 3 respectively. The concentrations of pristane are listed separately where this is a large proportion of the ΣAL values (sum of concentrations of n-alkanes C12-17 and pristane), i.e. in the fish and sediments.

Aromatic hydrocarbons are rapidly taken up from sea water by fish (6) and shellfish (7,8), and the sediments provide a sink for the removal of hydrocarbons from the water column. The alkane pattern in the fish was predominantly natural, being made up mainly of pristane, n-heptadecane and n-pentadecane. In most of the sediments also these same aliphatic hydrocarbons were predominant. It was apparent, therefore, that by 30 April, when the fish and sediment samples were collected, very little contribution had been made by the 'Bravo' blow-out to the hydrocarbon load of either fish or sediments.

The results of the water analyses show the highest values for the aromatic hydrocarbons within the reported boundaries of the oil-slick, but the sampling grid was very widely spaced and there was considerable variation between adjacent stations as well as between the two samples at each station. Although these differences are not systematic, it is noticeable that, although in the surface water sample (1 m) the ΣAR level (see Table 1) is usually less than ΣAL by a factor of 2-4, the concentration of aromatics in some of the 5 m samples is either very similar to, or in several cases greater than, the ΣAL values. This is perhaps a reflection of the greater volatility of the aliphatic hydrocarbons and the greater solubility of the aromatics. There does not seem to be any tendency for high levels in both 1 and 5 m water samples, and as the water column was not stratified at the time this is at first sight surprising. However, the samples were taken while oil was still being released, and dissolution and total mixing must be expected to be a gradual process.

As this was the first practical survey we had been involved in, we have little data with which to compare our results. However, as no oil was reported in the north-eastern sector of the grid during the period of time following the blow-out, the levels at station 10 probably represent true background. In this case the highest elevation above background was less than 100-fold.

Time has not allowed for a formal exchange of data with Norwegian laboratories and it will be interesting to see how their results match those reported here. As mentioned earlier, the techniques used are identical but, although measures are in hand to intercalibrate methods, this has not yet been done. However, it is understood by informal contact that the results are of the same order.

During the period of sampling, 28-30 April, CORELLA encountered no sizable quantities of floating oil, only thin films on the sea surface. The generally low concentrations of hydrocarbons found in the water may therefore have been exceeded in waters below patches of thick oil.

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Table 1 Hydrocarbon concentrations in sea water (ng/l)

Station	1 m		5 m	
	ΣAL	ΣAR	ΣAL	ΣAR
1	282	97	181	37
2	137	67	378	80
3	283	183	222	139
4	188	71	163	33
5	581	65	315	101
6	127	86	NO SAMPLE	
7	360	111	282	19
8	523	246	164	28
9	250	47	NO SAMPLE	
10	54	35	NO SAMPLE	
11	218	111	137	49
12	98	57	92	58
13	2141	301	2349	1119
14	140	65	NO SAMPLE	
15	144	94	1107	565
16	349	169	1510	718
17	393	143	18	45
18	205	74	20	32
19	736	273	68	47
20	490	192	831	667
21	877	273	1547	1144
22	859	252	106	214
23	553	306	132	469
24	3867	1696	246	221
25	506	318	1387	1121
26	308	59	726	364

ΣAL - sum of concentrations of n-alkanes C12-17 and pristane

ΣAR - sum of concentrations of naphthalene, phenanthrene and dibenzo-thiophene, and their methylated derivatives

Table 2 Hydrocarbon concentrations in fish (ng/g wet weight)

Species	Section	Station	ΣAL	Pristane	ΣAR
Plaice	Liver	30	1301	1199	0.2
"	"	32	1616	1256	31
"	Muscle	30	111	39	1.7
"	"	30	343	317	0.5
"	"	32	332	253	1
"	"	32	923	851	2
Haddock	"	32	200	68	2
"	"	32	48	28	0.4
Whelks		32	168	131	16
Horse mussels		32	311	98	14

Table 3 Hydrocarbon concentrations in surface sediments (ng/g wet weight)

Station	ΣAL	Pristane	ΣAR
2	57	40	18
26	17	4	3
27	45	24	11
28	82	46	10
29	43	20	14

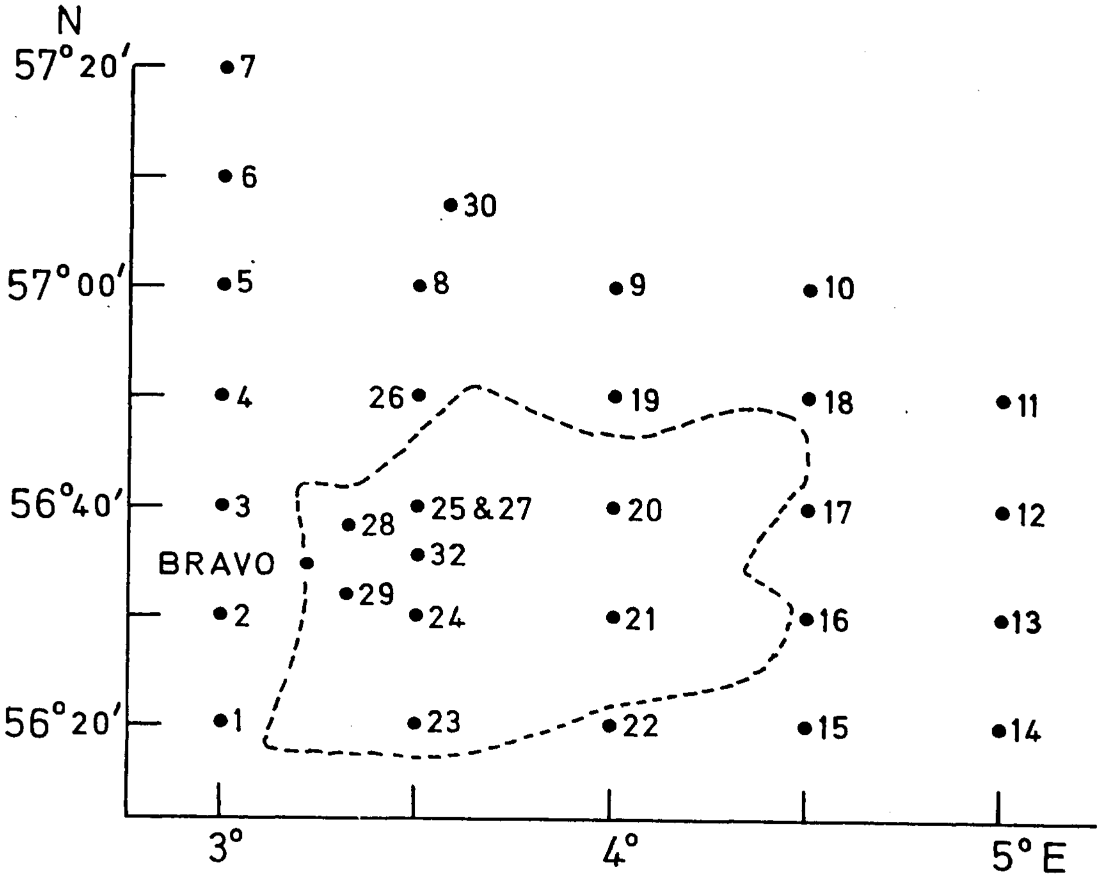

Figure 1. Sampling grid worked by R.V. Corella, with station numbers and showing the approximate position of the oil slick.