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UK AREA HYDROCARBON BASELINE SURVEY: MAIN FINDINGS, PRELIMINARY CONCLUSIONS AND IMPLICATIONS FOR FUTURE SURVEY AND MONITORING PROGRAMMES

K J Whittle*, P R Mackie*, R Hardy*, A D McIntyre[/] and R A A Blackman[x]

Abstract

Analyses for alkanes in the environment of the seas and coast around the UK are summarised, conclusions drawn and comments made on the possible future need for programmes of similar type.

Introduction

The Department of Agriculture and Fisheries for Scotland, Aberdeen, and the Ministry of Agriculture, Fisheries and Food, Aberdeen and Burnham-on-Crouch, have co-operated in the UK area hydrocarbon baseline survey of the marine environment. Some of the preliminary results have been reported previously to ICES (Whittle et al, 1973 and 1974).

At the start of the programme in 1971 little systematic data existed to determine accurately the extent and detail of a sampling programme which would provide sufficient information to establish a realistic baseline. Suitable and tested analytical methods were not available to determine unequivocally the presence of petroleum derived hydrocarbons in samples perhaps contaminated with very low levels of petroleum. In addition, little information was available on the biochemical role of hydrocarbons, or on their biosynthesis and metabolism in marine organisms so that inevitably difficulties would arise in determining the significance of the baseline data obtained.

The constraints outlined above were important factors in the type and objectives of the programme undertaken. Attention was directed mainly to the problem of continuous low level input of, or contamination by, petroleum hydrocarbons. A fairly extensive sampling programme was undertaken to cover both the physical environment and representative marine organisms. Where possible, surface-film, sub-surface water (1 metre, mid-depth and bottom), sediment, mixed plankton, benthos and pelagic and demersal fish were collected on a routine basis. The species analysed to date are summarised in Table 1. The sampling stations (Figure 1) were selected to include relatively unpolluted sites as control or reference points, sites receiving heavy industrial and urban inputs with or without refinery complexes, and areas of potential oil and gas production. To simplify the analytical problem the

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*Torry Research Station, Aberdeen, Scotland
[/] Marine Laboratory, Aberdeen, Scotland
[x] Fisheries Laboratory, Burnham-on-Crouch, England

relatively simple approach of alkane, particularly n-alkane analysis was adopted; alkanes being the major constituent class of compounds in most crude oils. In addition, complementary studies were initiated on the biosynthesis, uptake, transfer and metabolism of hydrocarbons at different trophic levels.

Methods

The manner of collection, solvent extraction and analysis for alkanes (by capillary gas-liquid chromatography) of the various types of sample and the regard to the problems of contamination have been described in detail elsewhere (Mackie et al, 1974). However, it is worth emphasising that the routine water analyses were made on a 20/um filtrate.

Results and Conclusions

Table 2 lists average n-alkane values in both inshore and open sea environments for some of the routine samples taken and for a selection of species. Tables 3 and 4 provide for comparison of data from the stations, which are numbered 1 to 16 in Figure 1 and which represent both inshore waters (1 to 8, Tables 3a and b) and open sea sites (9 to 16, Tables 4a and 6). It is inappropriate to reproduce the results from the entire survey but it is considered that the 16 stations presented provide an adequate range from the survey. Both groups, inshore and open sea, include two control or reference sites for comparison, stations 1 and 8, 9 and 16 respectively. A more detailed comparison between three stations of actual n-alkane profiles for routine samples, including a reference site and one near a refinery complex, is shown in Figure 2.

Physical environment

The entire survey is characterised by low n- alkane values although a few 'wild' figures can be identified, eg the Wash sub-surface (1 metre) water value which may be explained by the high level of suspended material in the sample and/or faulty filtration. The similarity of the n- alkane profiles, except for sediments and a few other isolated cases is quite striking. The ratio of pristane to n-alkanes varies by a factor of about 10 in surface film and sub-surface water samples but in sediments by a factor of about 100. Some of the isolated cases show an increase in the proportion of lower molecular weight components (eg Mersey surface film, Figure 2) such as might arise from petroleum hydrocarbon contamination.

Surface film contents vary considerably and may well reflect patchiness of the microlayer in area, thickness and composition. There is no simple relationship between expected input and amount found over the range of values measured. These results represent a real concentration of hydrocarbons at the surface as might be expected for hydrophobic compounds.

The higher values in the open sea as compared with inshore sub-surface waters (1 metre) are contrary to what was anticipated. Sampling extended over a long period and it has not been possible thus far to determine the contribution of seasonal effects to the data or provide any other factual explanation at this stage for the effect. However, further work is in progress to compare more closely inshore and open sea sampling. Where sampling was possible at different depths, mainly in estuarine areas, the range of values for each depth overlaps quite closely, suggesting that the hydrocarbon load in these waters does not vary significantly with depth. The unfiltered samples (station 8) are close to the range of the remaining values. Analysis of the residue remaining on a 20/um filter suggests that the filtrate value accounts for approximately half the total extractable alkanes in the original sample, the remainder being held on the filter. This residue also shows a somewhat different alkane profile to the filtrate.

The sediment analyses are characterised by the high odd-carbon predominance which generally is considered to be indicative of alkanes originating primarily from land plant sources (Mackie et al, 1974). The carbon preference index (CPI) which is a measure of the predominance of odd carbon number abundance compared with even carbon numbers is lower for open sea samples. It tends to approach unity for these and shows the reducing influence of the land input. These sediments also tend to have a lower load of alkanes. Phytane is readily identified in the sediments.

Organisms

On a comparative weight basis the plankton generally have the highest load of n-alkanes and pristane and the range of values is extremely large. In some, but not all cases, pristane is more abundant than the n-alkanes. However, the very nature of a mixed plankton sample introduces enormous variation in terms of composition to which may be added seasonal fluctuations within species. Judging from the analyses some samples are heavily contaminated with sedimentary material (eg Burghead, Figure 2) presumably particles in suspension and stirred up locally from the bottom. In the higher organisms the plankton pristane levels, and to a much lesser extent those of the alkanes, are approached generally only in the muscle of pelagic species such as herring, mackerel and horse mackerel. Again, there is considerable scatter among the results. For the great majority of the remaining species analysed the n-alkanes and pristane are present in the muscle at considerably lower concentrations, sometimes close to the limits of analysis. However, concentrations in the livers of these species are generally about an order of magnitude higher. It has been suggested (Whittle et al, 1974) that the distribution of alkanes in the muscle and liver tissues of fish is related quite closely to the distribution of neutral lipids in these tissues. Comparison of the profiles of n-alkanes in fish muscle and liver tissues provides a striking contrast (Mackie et al, 1974). The former tissues usually show a smooth distribution curve peaking at about carbon number C27 whilst the latter invariably exhibit a marked odd carbon predominance especially in the higher molecular weight range. This difference remains unaccounted for as yet, but Hardy et al (1974) have shown that the normal liver profiles can be masked in cod by adding small amounts of alkanes (as crude oil) to the diet. However, the new profile cannot be explained in terms simply of direct uptake of the dietary crude oil alkanes. With cod no significant deposition of alkanes was observed in the muscle tissue though this has been demonstrated in plaice (Blackman and Mackie, 1973) and, more recently in herring (Whittle, Murray and Farmer, unpublished). In herring the uptake was rapid and the percentage incorporation high. Thus, we can expect to find some alkanes that have been ingested with the diet in the tissues of fish although the turnover rate of dietary alkanes in the muscle of fatty fish appears to be quite high (Whittle et al, 1974; Barner et al, 1975). The invertebrates show a similar difference in n-alkane profiles between the smooth distribution curve for muscle and the odd carbon number predominance for digestive gland or hepatopancreas. Comparison of the species examined suggests that there is no evidence of accumulation of n-alkanes at higher levels of the food chain. It is of interest as a general comment that phytane has been tentatively identified throughout this survey at levels less than those of pristane and often close to the limits of detection.

Preliminary results (Murray, unpublished) from the biochemical work on hydrocarbons in marine organisms suggest that certain phytoplankton at least in culture have very limited ability to synthesis n-alkanes and are characterised by a very specific and narrow range of components including olefins. Again, mixed zooplankton studied experimentally in non-bacteria-free conditions do not seem markedly to modify their dietary hydrocarbons or rapidly to synthesise alkanes de novo but do produce significant amounts of pristane as previously shown by Avigan and Blumer (1968). However in contrast, wild plankton samples show a varied range of alkanes suggesting that some of these may be exogenous in origin.

Discussion

The quantities of alkanes and the n-alkane distributions are insufficient to determine unequivocally the degree of petroleum contamination in the marine environment under these conditions of low level contamination. The occurrence of phytane and the use of pristane/phytane ratios as additional aids have been questioned previously (Whittle et al, 1973; Corner et al, 1975). The survey data will stand considerably more analysis and interpretation, and further information on differentiating the source of the hydrocarbons identified will no doubt be forthcoming. In addition, the detailed chromatographic information can be examined more closely. Unfortunately no analyses were available on refinery effluents at those stations where this input was probably of major importance.

Analyses of water samples is complicated by problems associated with filtration and by the complex relationship between hydrocarbon content, productivity and particulate suspension, particularly in coastal waters. The data suggest that the hydrocarbon levels are fairly uniform. 72% of the results in Tables 3a and 4a fall within the range 0.2 to 2.0 µg/l and there is little evidence of differentiation between areas on the basis of expected input. The mean value is about 10 times lower than that measured beneath oil slicks (Flowers, 1974) and the inference is that the hydrocarbon content of a water sample is not a sensitive indicator of the extent of contamination but should record a very recent introduction, as from an oil slick. On the other hand, one might surmise that measurements of the surface film where hydrophobic materials are concentrated would be sensitive. This may well be so, but the effect is probably transient and indicative only of recent phenomena (Whittle et al, 1973).

In terms of assessing the extent of petroleum hydrocarbons in the environment the survey suffered from a major gap in sampling, namely the lack of routine quantitative or qualitative measurements on tar-balls either in the surface layer or suspended in the water column. However, a rather crude survey in the Western Approaches, the Celtic Sea, the Irish Sea and the North Channel suggests that levels are very much lower than those quoted for the Sargasso Sea (Butler and Morris, 1974). This was confirmed recently by some studies in the North Sea (G E J Gassmann, personal communication).

It has not been possible, so far, to mount any extensive inter-calibration of methods of sampling and analysis to determine the extent to which our data may be compared with those of other workers. Before any further major monitoring is undertaken such studies should be completed.

The selection of sites and of species for analysis is a difficult problem and we tended to use a multiple approach, sampling as many parameters as possible within the bounds of practicability, at least to provide some rationale for defining any future programme. Supply of material in the right place at the right time is difficult and is compounded by the uneven distribution of species around the coast hence the gaps in Tables 3b and 4b.

Inevitably, it is necessary to collect enough sufficiently similar species to ensure that a particular type of organism, eg a fatty, planktonivorous fish, is represented throughout the entire region surveyed and that sufficient overlap occurs between the representatives to make valid comparisons. The importance of examining different tissues was demonstrated by both the survey and the experimental work since the lipid metabolism of different organisms differs in important respects such as deposition.

In opting for the simpler approach of alkane analysis as an indication of petroleum contamination the problem of suitable aromatic hydrocarbon analysis has not been ignored and development of methods is proceeding in what is a more difficult analytical field. In view of the lack of evidence of accumulation of alkanes, the

relatively low concentration of these compounds found, and the wide scatter in the data with no clear concentration profiles present preclude differentiation between areas on the basis of expected input. It is considered, that an appropriate interval is advisable for assessment of sampling and analytical problems before any further similar exercise or a fullscale monitoring programme is mounted. This interval could be well employed in testing practical, widely acceptable methods of sampling and analysis to cover, aromatic components and, other minor constituents of petroleum such as sulphur components which may be better indicators. Further experimental work will of course be necessary to test the hypotheses developed.

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Table 1

Organisms Analysed during the Hydrocarbon Baseline Survey

Skate	Raja sp.
Sandeel	Ammodytes sp.
Sprat	Sprattus sprattus
Herring	Clupea harengus
Mackerel	Scomber scombrus
Horse mackerel	Trachurus trachurus
Cod	Gadus morhua
Saithe	Pollachius virens
Haddock	Melanogrammus aeglefinus
Whiting	Merlangius merlangus
Pout	Trisopterus luscus
Hake	Merluccius merluccius
Plaice	Pleuronectes platessa
Lemon sole	Microstomus kitt
Megrim	Lepidorhombus whiffiagonis
Sole	Solea solea
Witch	Glyptocephalus cynoglossus
Flounder	Platichthys flesus
Dab	Limanda limanda
Gurnard	Trigla sp.
John Dory	Zeus faber
Bass	Morone labrax
Monk	Lophius piscatorius
Welk	Buccinum undatum
Hermit crab	Pagurus sp.
Shore crab	Carcinus maenus
Swimming crab	Macropupus sp.
Pink shrimp	Pandalus sp.
Brown shrimp	Crangon sp.
Starfish	Asterias rubens

Table 2

Range and average n-alkane values C15-C33 for routine samples in both inshore and open-sea sites with the number of sites averaged.

	Surface film µg/m²				Water, 1 metre µg/l				Sediment µg/g dry wt				Mixed Plankton µg/g dry wt			
	n	min	max	X̄	n	min	max	X̄	n	min	max	X̄	n	min	max	X̄
Inshore	22	13.7	145.4	37.0	22	0.4	5.2	1.7	22	0.1	22.0	3.0	22	5.7	1585.7	262.0
Open Sea	29	4.3	84.2	31.3	24	0.2	11.8	2.8	34	0.1	4.7	1.0	21	3.2	263.0	30.0

		Mackerel µg/g wet wt				Cod µg/g wet wt				Plaice µg/g wet wt			
		n	min	max	X̄	n	min	max	X̄	n	min	max	X̄
Inshore	Muscle	4	0.4	2.8	1.4	5	0.005	0.3	0.1	8	0.005	1.8	0.6
	Liver	5	0.4	17.3	5.3	4	0.9	3.1	1.6	7	1.1	118.0	19.0
Open Sea	Muscle	4	0.6	1.4	1.0	4	0.1	0.3	0.2	1	-	-	1.5
	Liver	4	1.3	47.6	15.0	4	1.4	4.6	3.0	1	-	-	8.9

n is the number of samples taken and X̄ is the arithmetic mean.

TABLE 3(a)

ALKANE LEVELS IN THE MARINE ENVIRONMENT - INSHORE WATERS

Site		1	2	3					4	5					6	7	8
		Sullom Voe	Burghead	Firth of Forth (inner) (i)	(ii)	(iii)	(iv)	(outer) (v)	Wash	Southampton Water/ Solent/Spithead (inner) (i)	(ii)	(iii)	(iv)	(outer) (v)	Milford Haven	Mersey	Loch Ewe*
Surface Film	Σ	16.9	25.9	17.4	14.1	23.8	16.1	40.5	36.5	20.6	69.3	13.7	21.1	25.5	48.3	148.6	30.0
ug/m²	p	0.3	0.1	0.1	0.1	0.1	0.2	0.5	0.2	0.3	0.2	0.3	0.1	0.5	0.4	24.6	0.1
Water 1 metre	Σ	5.9	5.2	2.7	1.6	1.4	1.6	1.6	24.0	0.4	1.4	0.6	0.4	0.5	1.7	1.3	2.2
ug/l	p	0.05	0.05	0.1	0.05	0.03	0.04	0.02	0.06	0.03	0.03	0.02	0.03	0.02	0.06	0.07	0.01
	Σ		1.6			2.4		2.3	1.0	1.2	0.4	0.3	0.4	0.4	1.7	1.2	3.1
mid depth		nc		nc	nc		nc										
	p		0.01			0.03		0.01	0.02	0.03	0.02	0.02	0.02	0.01	0.02	0.08	0.04
	Σ	3.6	1.9	1.8		1.0		1.5	1.0	0.9	0.5	0.7	0.4	1.0	0.2	0.6	3.7
bottom					nc		nc										
	p	0.06	0.07	nd		0.02		0.03	0.03	0.02	0.03	0.03	0.02	0.01	0.01	0.08	0.04
Sediment	Σ	30.7	0.1	22.0	4.4	5.3	11.8	0.3	1.4	0.9	0.9	4.8	4.1	0.8	1.4	0.5	0.3
ug/g dry wt	p	.05	0.002	1.0	0.1	0.1	1.7	0.01	0.1	0.08	0.04	0.1	0.03	0.03	0.06	0.05	0.02
	CPI	8.54	1.17	3.79	2.64	3.07	1.67	1.40	1.80	2.03	2.53	2.27	1.07	2.32	1.55	2.01	1.54
Mixed Plankton	Σ	52.3	133.2	279.2	134.9	354.4	767.4	173.6	5.7	139.3	182.9	124.5	1585.7	94.9	12.8	531.4	1.4
ug/g dry wt	p	9.8	2.9	21.4	36.0	18.8	79.5	21.9	0.5	25.4	5.2	1.4	69.4	20.4	2.3	284.4	512.2
Benthos	Σ	0.5					3.7	0.1	0.3	0.2	0.5	0.8		15.6	1.2	0.7	0.2
Ast. (A)		(A)	nc	nc	nc	nc	(A)	(A)	(C)	(B)	(C)	(B)	nc	(B)	(A)	(C)	(B)
Bucc. (B)	p	nd					nd	nd	nd	0.03	nd	nd		0.1	nd	0.08	0.06
Crang. tail(C) ug/g wet wt																	

nc = not collected

nd = not detected

CPI = carbon preference index (a measure of the odd carbon atom predominance)

Σ = total n-alkanes C15-C33; p = pristane

*unfiltered water samples

TABLE 3(b) - as 3(a)

Site		1	2	3(v)	4	5(v)	7	8
Mackerel (M) Sprat (S)	Σ muscle		0.6	1.6	2.5 (whole)	-	2.8	1.5
	p		14.4 (M)	13.8 (M)	nd (S)	(M)	2.1 (M)	1.8 (M)
µg/g wet wt	Σ liver	nc	6.3	0.4		17.3	1.1	0.4
	p		0.4	nd		0.2	0.5	16.6
Cod	Σ muscle		0.3	trace				0.3
	p	nc	0.02	nd	nc	nc	nc	nd
µg/g wet wt	Σ liver		1.0	0.9				nc
	p		0.08	0.04				
Haddock (H)	Σ muscle				trace (W)		1.1 (W)	
	p	nc	nc	nc	nd	nc	nd	nc
µg/g wet wt	Σ liver				nc		nc	
	p							
Plaice (P) Dabs (D)	Σ muscle		0.5 nd	0.1 nd	0.1 0.03	0.2 nd	trace nd	trace nd
	p	nc	(P)	(P)	(D)	(P)	(P)	(P)
µg/g wet wt	Σ liver		nc	4.3	1.5	1.1	nc	nc
	p			0.1	0.02	0.01		

Table 4(a)

Alkane Levels in the Marine Environment - Open Sea (units as 3(a))

Site		9 NW Shetland	10 E Shetland Basin	11 Beryl	12 Forties	13 Ekofisk	14 Eddystone	15 St George's Channel	16 Gt Sole Bank
Surface Film	Σ	60.4	13.3	75.4	33.6	nc	6.1	5.7	4.7
	P	0.4	0.2	0.8	0.8		0.5	0.2	0.4
Water 1 metre	Σ	1.8	4.2	3.8	2.3	1.4	0.9	2.3	0.6
	P	0.03	0.05	0.05	0.02	0.03	0.01	nd	nd
bottom	Σ	7.4	1.7	1.9	2.9	1.9	nc	nc	nc
	P	0.04	0.05	0.03	0.01	0.04			
Sediment	Σ	0.1	0.2	0.2	0.4	1.6	0.2		
	P	0.01	0.01	0.01	0.02	0.03	0.02	nc	nc
	CPI	1.4	1.9	2.0	1.4	1.0	1.18		
Mixed Plankton	Σ	203.9	<0.3	40.7	nc	22.1	32.5	17.7	42.9
	P	58.2	nd	4.9		2.7	18.0	50.0	310.0

Table 4(b) - as 4(a) (units as 3(a))

Site		9	12	13	14	15	16
Mackerel	Σ Muscle	1.1			0.7	1.4	
	P	27.9	nc	nc	1.9	11.7	nc
	Σ Liver	1.3			2.8	4.7	
	P	1.2			47.6	6.5	
Horse Mackerel	Σ Muscle	0.9			1.0	0.3	3.3
	P	21.1	nc	nc	0.6	0.4	7.1
	Σ Liver	7.5			4.8	6.8	1.7
	P	21.1			1.5	1.1	24.7
Cod	Σ Muscle	0.1	0.2	0.2			
	P	0.03	0.03	0.1	nc	nc	nc
	Σ Liver	2.0	4.6	4.1			
	P	nd	0.05	0.5			
Haddock(H) Whiting(W) Hake(HK)	Σ Muscle	0.3	1.7			0.2	1.6
	P	0.05 (H)	nd (H)	nc	nc	0.01 (W)	0.04 (HK)
	Σ Liver	2.8	3.9			1.6	nc
	P	0.9	0.1			10.7	
Plaice(P) Megrim(M) Lemon Sole(L)	Σ Muscle		0.3	1.5			-
	P		0.03	nd			
		(M)	(L)	(P)	nc	nc	(M)
	Σ Liver	1.4	1.6	8.9			2.4
	P	nd	0.05	-			1.1

FIGURE 1

UK AREA SAMPLING PROGRAMME

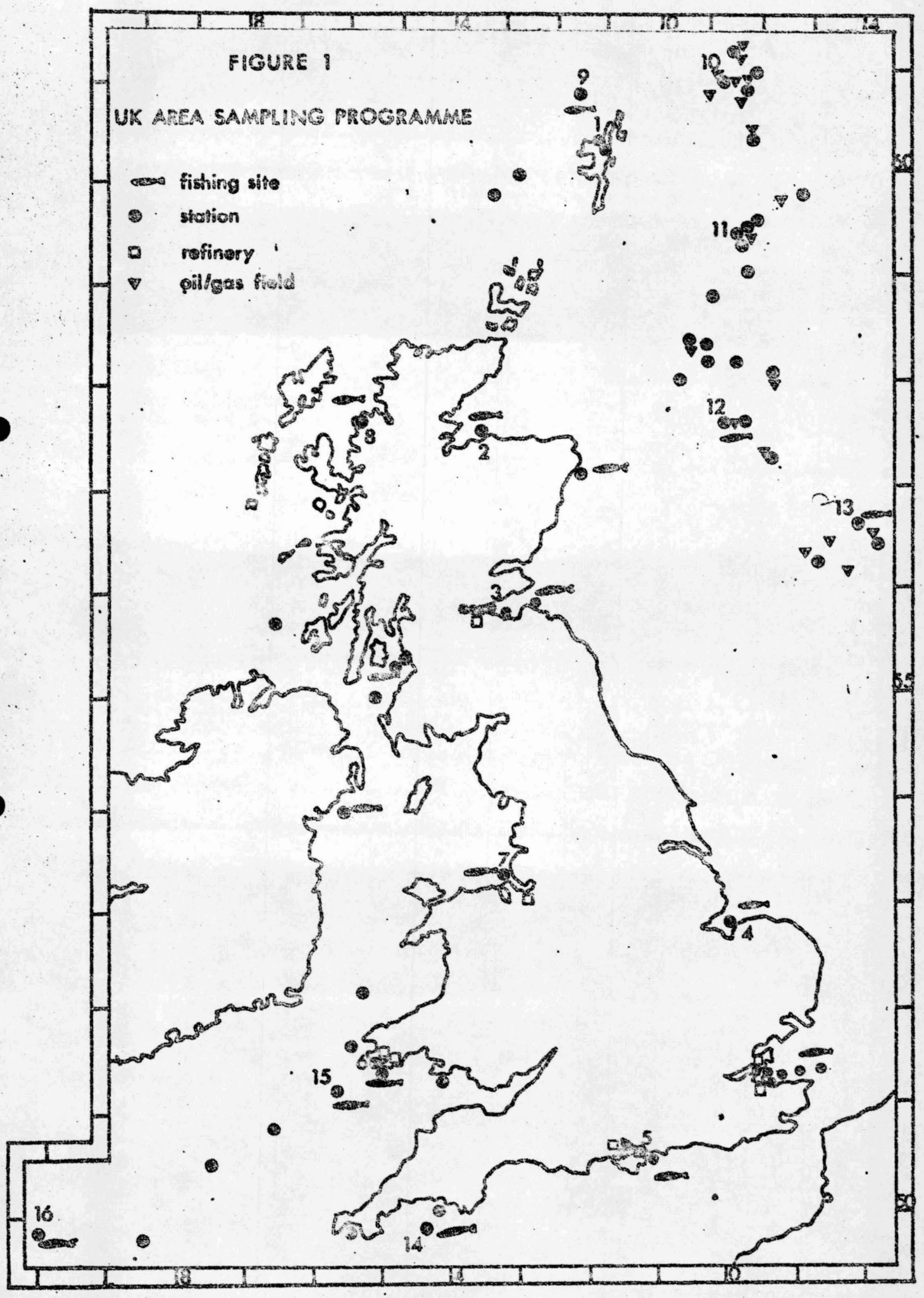
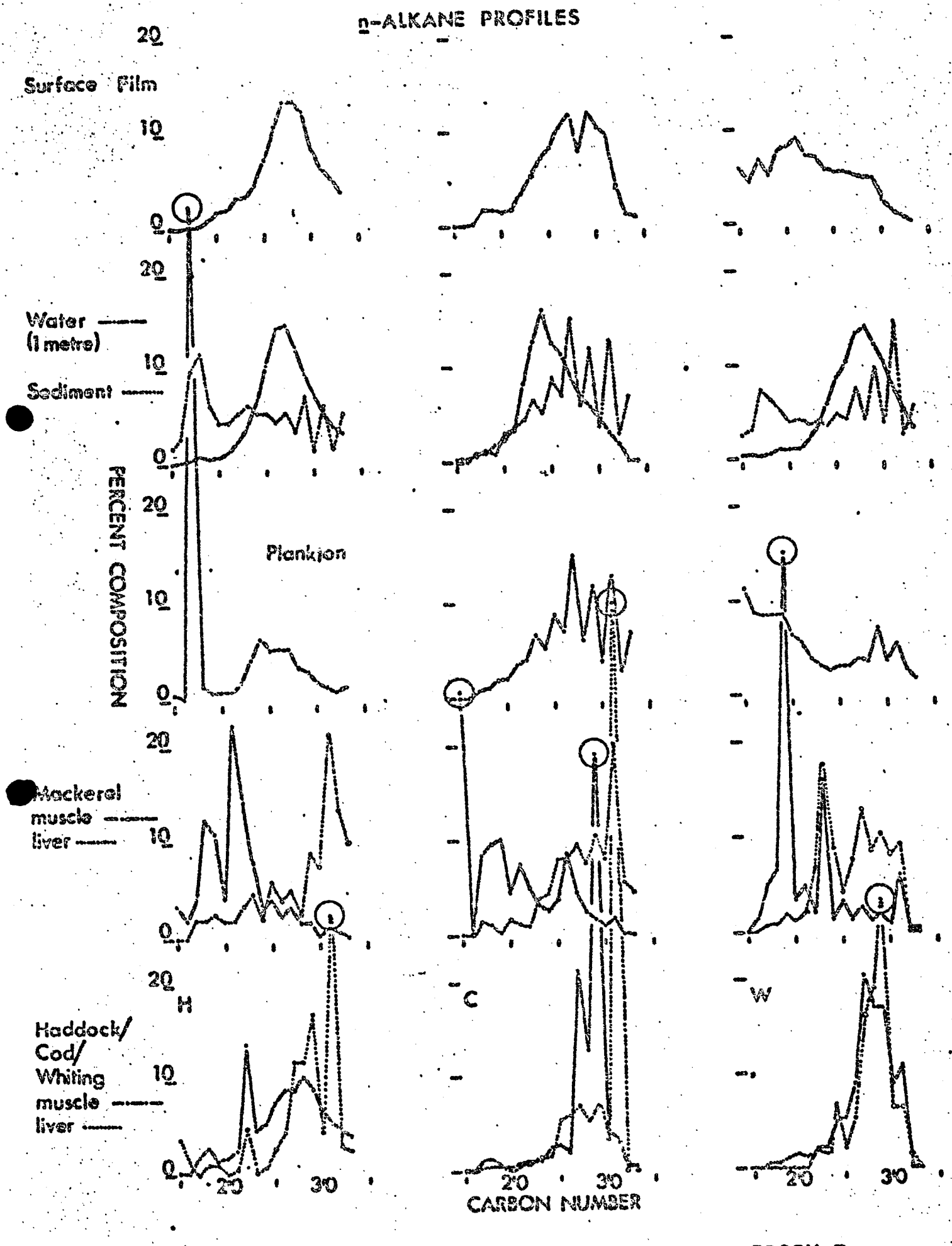


FIGURE 2


n-ALKANE PROFILES
Surface Film
Water (1 metre)
Sediment
Plankton
Mackerel muscle
liver
Haddock/ Cod/ Whiting muscle
liver
PERCENT COMPOSITION
20
10
0
H
C
W
20
30
CARBON NUMBER
N W SHETLAND 9
BURGHEAD 2
MERSEY 7