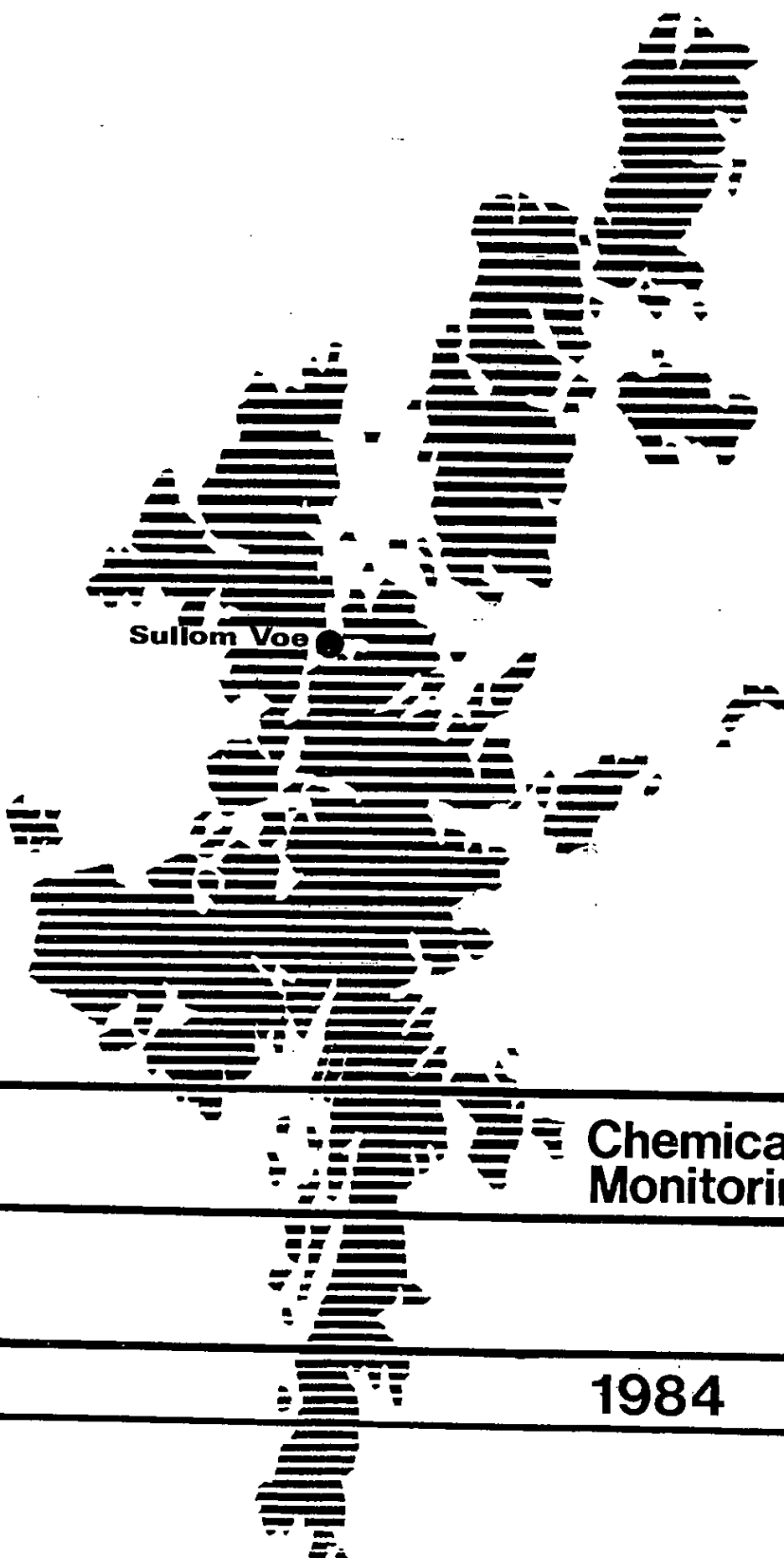


DB 11/03

SOTEAG Original,
return to SOTEAG
office

691



Sullom Voe

**Chemical and Biological
Monitoring Report**

1984

Scottish Marine Biological Association

SMBA

Dunstaffnage Marine Research Laboratory

SCOTTISH MARINE BIOLOGICAL ASSOCIATION

CHEMICAL AND BIOLOGICAL MONITORING REPORT FOR
SULLOM VOE, ORKA VOE AND CAT FIRTH

1984

Dunstaffnage Marine Research Laboratory,
P.O. Box No. 3, OBAN, Argyll PA34 4AD

T.H. PEARSON
J. BLACKSTOCK
A. DOUGLAS

25th May 1985

This report is the property of the Sullom Voe Association Limited and its agent the Shetland Oil Terminal Environmental Advisory Group (SOTEAG) and is not to be cited without prior agreement of SOTEAG.

Copyright 1984. The Shetland Oil Terminal Environmental Advisory Group.

CONTENTS

SUMMARY	Page	1
1. INTRODUCTION		5
2. WATER COLUMN MEASUREMENTS		6
3. ORGANIC CARBON AND NITROGEN IN SEDIMENTS		13
4. HYDROCARBONS IN SEDIMENTS		15
5. METALS IN SEDIMENTS		57
6. MACROBENTHIC FAUNA AT REFERENCE STATION IN CAT FIRTH AND ORKA VOE		70
7. CONCLUSIONS AND GENERAL COMMENTS		82
8. REFERENCES		83

SUMMARY

1. Water column

Surface temperatures varied between 9.5 and 11.7°C and bottom temperatures between 6.7° (deep inner basin of Sullom Voe) and 10.9°C (shallow embayment of Garth's Voe). Salinities varied little, but a pycnocline was evident between 30 and 35m depth in the inner basin of Sullom Voe. The bottom water was fully oxygenated, and in general the water column appeared to be well mixed throughout the area.

2. Organic carbon and nitrogen in the sediments.

In general, carbon values were similar to those recorded in 1983. An exception was at station I19 (4) where the 1984 values were lower. This is attributed to sediment patchiness in that area. In Orka Voe carbon values at the two inner stations were slightly lower than those recorded in 1983.

3. Hydrocarbons in the sediments.

The sediments all contained saturated hydrocarbons ranging in amounts from 4 ppm to 545 ppm (measured with respect to dry sediment weight). The amounts of hydrocarbons in most of the sediments are comparable to those in previous years, but at stations S39 (11) and 50VI there were large increases (more than 2½ times) compared to the average values for the past four and three years respectively. Note should be taken of the steady increase in the hydrocarbon content at station 50VI since monitoring began in 1982.

Gas chromatographic analyses of all the saturated hydrocarbon fractions and combined gas chromatographic-mass spectrometric analyses of selected samples allowed the following conclusions to be drawn. There is no contamination of the sediment at control station CT1. At four stations there is evidence of very mild contamination, while at the remaining 14 stations, half contained < 50 ppm /

< 50 ppm of petrogenic hydrocarbons, while the other half contained between 60-160 ppm. At the former 7 stations we estimate the maximum contribution of petrogenic hydrocarbons to be 29 ppm; at the latter 7 stations the sediments which appear to be most highly contaminated are at four of the Orka Voe stations: these contain 95-159 ppm of petrogenic hydrocarbons, representing 81% to 95% of their hydrocarbon content. At the stations containing significantly more hydrocarbons than in previous years, station S39 (11) is estimated to contain 60% and station 50VI 80% of petrogenic hydrocarbons. Replicate samples should be taken at these two sites in summer 1985. At three beach sites, sampled at low and high tide, there are petrogenic hydrocarbons present at Houb of Scatsta, but in very small amounts indeed: at the other two beaches there appears to be no petrogenic input.

4. Metals in the sediments.

Metal concentrations in Sullom Voe sediments remained generally similar to those found in previous years. At station Z24 (6) a significant decrease in copper and increase in chromium was recorded, and at D4 (1) a slight increase in copper and zinc concentrations was recorded. These fluctuations may represent some natural patchiness in metal distributions.

There were no significant changes in metal concentrations in Cat Firth since 1983. In all shore samples, metal levels were relatively low and the minor changes noted between 1983 and 1984 are considered to have little environmental significance.

In Orka Voe, metal concentrations at the three inner stations on the transect remained higher than those recorded at the outer stations. AT 20VI levels had increased somewhat over 1982-83 levels, and at 30VI mean levels were a little lower, but replicated, these showed considerable variability. It is suggested that further replication of the estimates of metal concentrations is required for the sediments from Orka Voe, to allow a valid statistical assessment of temporal changes in metal concentrations at the most affected location (20VI).

5. /

5. Macrobenthic fauna at reference station in Cat Firth and in Orka Voe.

Voe
In Cat Firth abundances were lower than in many previous years but biomass levels were relatively high. The bivalves Tellina fabula and Abra nitida dominated the populations, which were predominantly composed of large mature organisms.

In Orka Voe a species succession is described, apparently responding to a gradient of organic enrichment from the outer area of the Voe to the inner area near the bund. Species commonly associated with highly enriched sediments predominated in the inner area, where visible oil globules were found in the sediment residues. In these areas a recently settled population of bivalve molluscs was found, in addition to a more mature population of annelid worms.

6. Conclusions

It is suggested that a detailed examination of the benthic fauna at station S39 (11) be made, to assess the possible effects of the higher hydrocarbon levels measured at that station.

In Orka Voe a marked succession of benthic fauna from the outer to the inner parts of the Voe was observed, relating to increasing organic enrichment of the sediment. It is considered that hydrocarbon contamination has contributed to this enrichment, which in the inner area, has resulted in a population dominated by small opportunist annelids. In 1984 there was some evidence of recolonisation of this area by a more varied fauna.

Table 1.1. Summary of stations worked and samples taken in 1984.

Station	Area	Position		Water and Sediment		
		Latitude	Longitude	Samples		
D4 (1)	Sullom Voe	60° 24.13'N	1° 22.00'W	TSO	HM*	HY
H13 (3)	Sullom Voe	60° 25.37'N	1° 21.00'W	TSO	HM	HY
I19 (4)	Sullom Voe	60° 26.17'N	1° 20.64'W	TSO	HM*	HY
O23 (5)	Sullom Voe	60° 26.70'N	1° 19.00'W	TSO	HM	HY
T27 (8)	Sullom Voe	60° 27.23'N	1° 17.62'W	TSO	HM*	HY
W27 (7)	Sullom Voe	60° 27.34'N	1° 16.82'W	TSO	HM	HY
Z24 (6)	Sullom Voe	60° 27.19'N	1° 16.00'W	TSO	HM*	HY
P31 (9)	Sullom Voe	60° 27.77'N	1° 18.70'W	TSO	HM	HY
S39 (11)	Sullom Voe	60° 28.84'N	1° 17.91'W	TSO	HM	HY
V45 (14)	Outer Sullom Voe	60° 29.68'N	1° 17.17'W	TSO	HM*	HY
T44 (13)	Sullom Voe	60° 25.55'N	1° 17.60'W	TSO	HM	HY
AA44 (15)	Outer Orka Voe	60° 29.51 'N	1° 15.70'W	TSO	HM*	HY
CC45 (16)	Outer Orka Voe	60° 29.65'N	1° 15.03'W	TSO	HM	HY
FF48 (17)	Yell Sound (Off Mioness)	60° 30.07'N	1° 14.35'W	TSO		
10VI	Orka Voe	60° 28.63'N	1° 15.92'W	TSO	HM	HY
20VI	Orka Voe	60° 28.67'N	1° 15.85'W	TSO	HM	HY
30VI	Orka Voe	60° 28.73'N	1° 15.80'W	TSO	HM*	HY
40VI	Orka Voe	60° 28.86'N	1° 15.73'W	TSO	HM	HY
50VI	Orka Voe	60° 28.98 N	1° 15.66'W	TSO	HM	HY
CT1	Cat Firth	60° 15.90'N	1° 11.82'W	TSO	HM*	HY

Key to symbols:

TSO - Temperature, salinity and dissolved oxygen in the water column using submersible probe;

HM - Sediment samples for metals

HY - Sediment samples for hydrocarbons

* - Replicate samples

1. INTRODUCTION

This report provides the results of the survey carried out between 18th and 23rd June 1984. The survey was carried out in conjunction with the staff of the Oil Pollution Research Unit, using the local vessel 'Stanes Moor'. Samples for biological and chemical analysis at each station were taken at the same time.

The stations worked and a list of samples collected are shown in Table 1.1. All the designated stations were sampled with the exception of FF48 (17)* where the ground proved to be too hard for either grab or cores to penetrate. The positions of the sampling stations are shown in Figs 1.1, 1.2 and 1.3.

* Station numbering.

In this report stations in Sullom Voe are designated by their original SMBA numbering. The OPRU numbering appears in brackets.

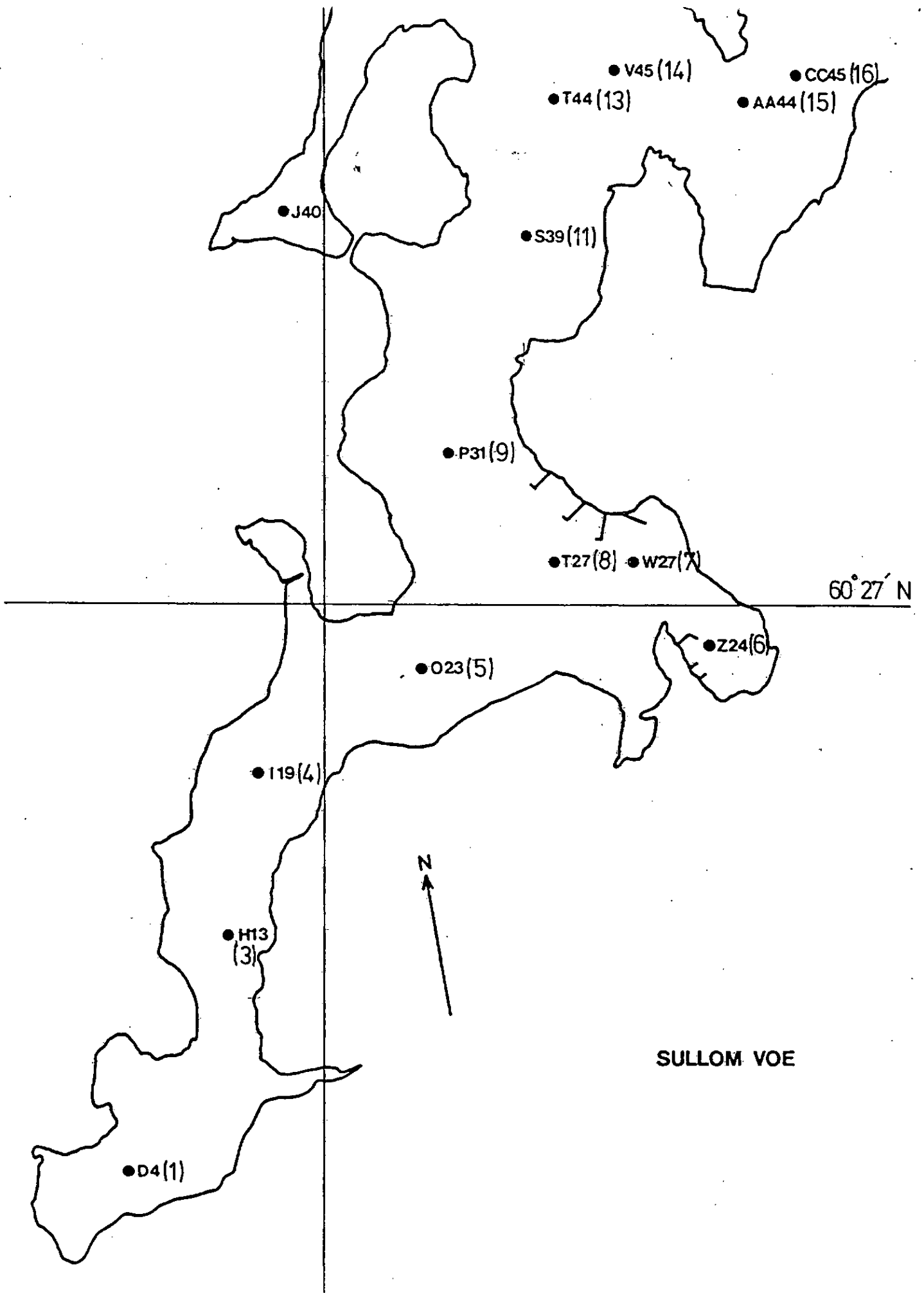


Fig. 1.1 Sampling stations in Sullom Voe

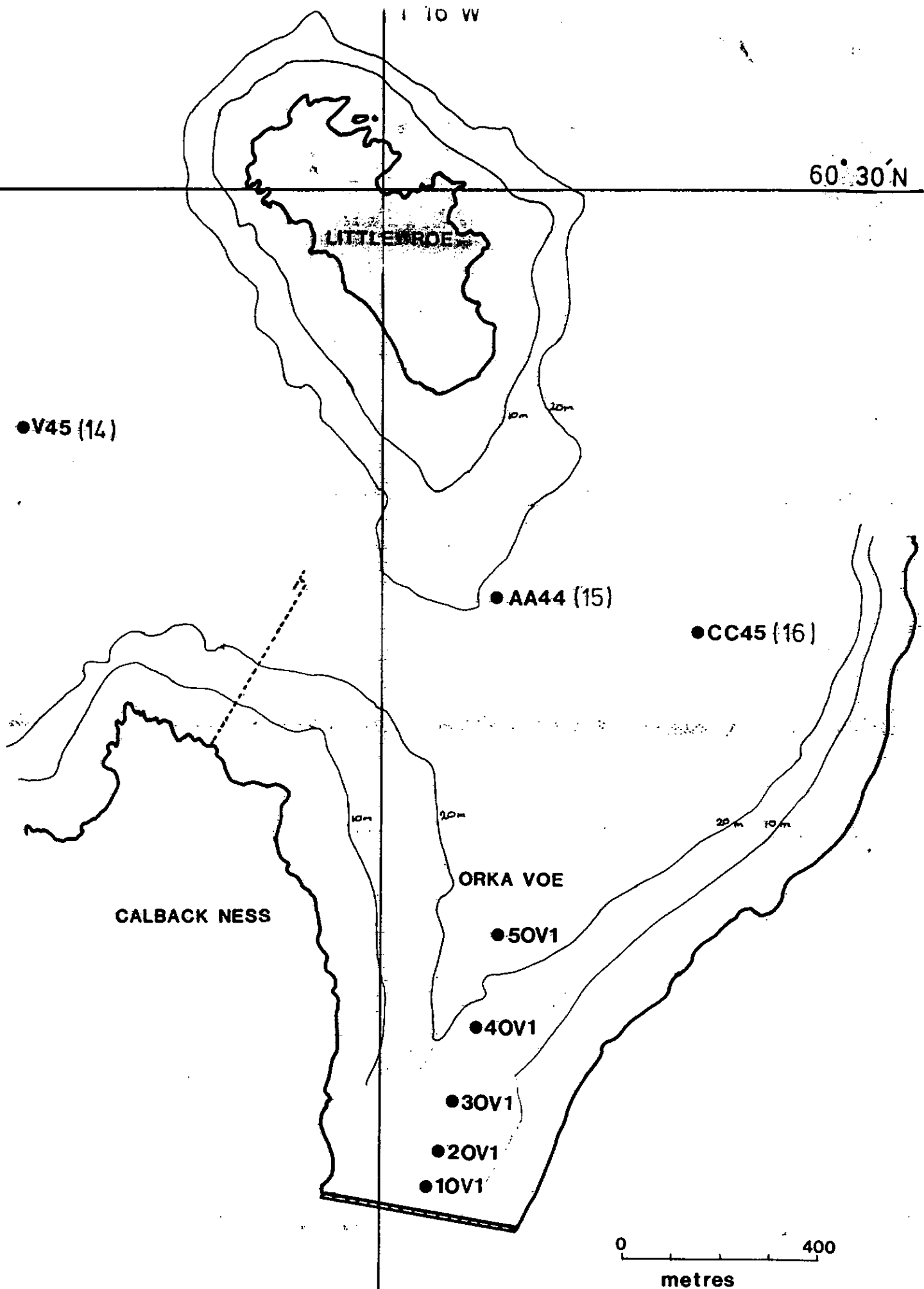
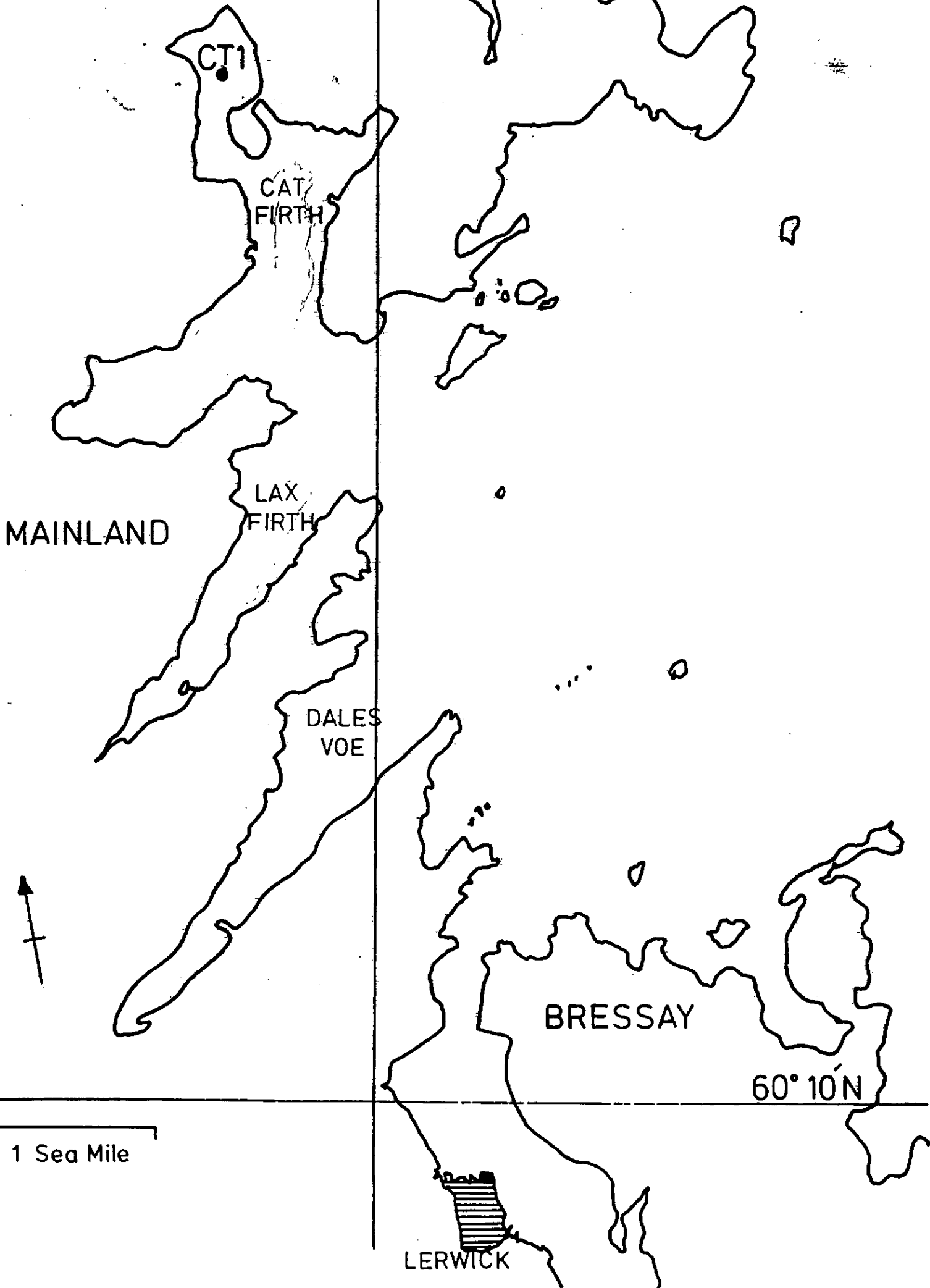


Fig. 1.2; SMBA Sampling stations in Orka Voe

1 10 W

FIG 1.3

Sampling stations in Cat Firth



2. WATER COLUMN MEASUREMENTS

2.1 Methods.

Temperature and salinity were measured at each station using a Braystoke Model STM-500 Temperature/Salinity submersible probe. Salinities were checked and calibrated with measurements of bottom water salinities made with an Autosal Model 8400A Salinometer. The temperature was checked at each station against a reversing thermometer. Dissolved oxygen was measured from bottom water samples taken with an N10 sampler, using a YSI Model 81 oxygen meter with a submersible stirrer. Data on temperature, salinity and dissolved oxygen at all stations sampled are shown in Table 2.1.

2.2 Dissolved Oxygen

The bottom water at all the stations sampled was fully oxygenated. There was no evidence of oxygen depletion at the station in the inner basin of Sullom Voe Station D4 (1) as had been found in some previous years (Fig. 2.1).

2.3 Temperature/Salinity

A fairly sharp pycnocline was established at 35m depth in the inner basin of Sullom Voe (Station D4 (1)). This was probably a recently established feature as there was no evidence of oxygen depletion in the bottom water (see above). This would have been expected if the discontinuity inhibiting exchange of the bottom water had persisted long enough for the biological oxygen demand of the bottom sediments to exert a significant effect on the stagnant water column.

Elsewhere typical surface to bottom gradients of temperature were found. Slightly higher surface temperatures and slightly lower bottom salinities were /

were recorded at stations in the centre of the Voe in the Garths' Voe and jetty areas, but in general the water column appeared to be well mixed throughout the area.

Temperatures and salinities in Orka Voe and Cat Firth differed little from those recorded in Sullom Voe.

Table 2:1. Dissolved oxygen, temperature and salinity at each sampling station.

Station	Sampling date	Depth (m)	Temperature	Salinity	Dissolved Oxygen (mg l ⁻¹)
D4 (1)	18.6.84	45	6.7	35.1	8.5
		40	6.8	35.1	
		35	7.4	35.3	
		30	9.0	35.2	
		25	9.2	34.9	
		20	9.2	35.0	
		15	9.4	35.0	
		10	9.6	35.1	
		5	9.6	35.0	
		0	9.6	35.1	
H13 (3)	18.6.84	20	9.4	36.2	9.5
		15	9.5	35.4	
		10	9.8	35.3	
		5	10.0	35.2	
		0	10.0	35.2	
I19 (4)	19.6.84	20	8.4	35.7	9.5
		15	9.8	35.3	
		10	9.9	35.2	
		5	9.9	35.2	
		0	10.5	35.1	
O23 (5)	19.6.84	20	9.4	36.1	9.6
		15	9.9	35.3	
		10	10.0	35.4	
		5	10.1	35.2	
		0	10.5	35.2	
Z24 (6)	19.6.84	5	10.9	35.7	9.1
		0	11.3	35.4	

W27 /

Table 2:1a contd. Dissolved oxygen, temperature and salinity at each sampling station

Station	Sampling date	Depth (m)	Temperature	Salinity	Dissolved Oxygen (mg l ⁻¹)
W27 (7)	19.6.84	17	9.4	35.7	9.8
		15	9.4	35.9	
		10	10.0	35.6	
		5	10.4	35.3	
		0	11.7	35.0	
T27 (8)	19.6.84	22	9.6	36.6	9.9
		20	9.4	36.0	
		15	9.5	35.7	
		10	9.8	35.4	
		5	10.0	35.3	
P31 (9)	20.6.84	25	9.5	35.5	9.7
		20	9.2	35.5	
		15	9.4	35.4	
		10	9.4	35.4	
		5	9.9	35.4	
S39 (11)	20.6.84	0	10.3	35.2	9.4
		45	9.2	35.6	
		40	9.2	35.4	
		35	9.2	35.4	
		30	9.2	35.4	
		25	9.2	35.4	
		20	9.2	35.3	
		15	9.4	35.3	
		10	9.6	35.3	
		5	10.2	35.1	
0	10.4	35.2			

Table 2:1 contd. Dissolved oxygen, temperature and salinity at each sampling station.

Station	Sampling date	Depth (m)	Temperature	Salinity	Dissolved Oxygen (mg l ⁻¹)
V45 (14)	20.6.84	52	9.2	35.3	9.9
		50	9.2	35.3	
		45	9.2	35.3	
		40	9.2	35.3	
		35	9.2	35.3	
		30	9.2	35.3	
		25	9.3	35.3	
		20	9.3	35.3	
		15	9.4	35.3	
		10	9.6	35.3	
		5	9.8	35.3	
	0	10.0	35.2		
T44 (13)	21.6.84	50	9.4	35.2	9.7
		45	9.5	35.3	
		40	9.5	35.4	
		35	9.5	35.4	
		30	9.5	35.4	
		25	9.5	35.4	
		20	9.5	35.4	
		15	9.5	35.5	
		10	9.5	35.5	
		5	9.5	35.6	
	0	9.6	35.0		
AA44 (15)	21.6.84	18	9.4	35.4	9.8
		15	9.4	35.4	
		10	9.5	35.6	
		5	9.5	35.4	
		0	9.6	34.4	
CC45 (16)	21.6.84	30	9.4	35.3	
		25	9.4	35.3	
		20	9.5	35.3	
		15	9.5	35.3	
		10	9.5	35.3	
		5	9.5	35.3	
		0	9.6	35.3	

Table 2:1 contd. Dissolved oxygen, temperature and salinity at each sampling station

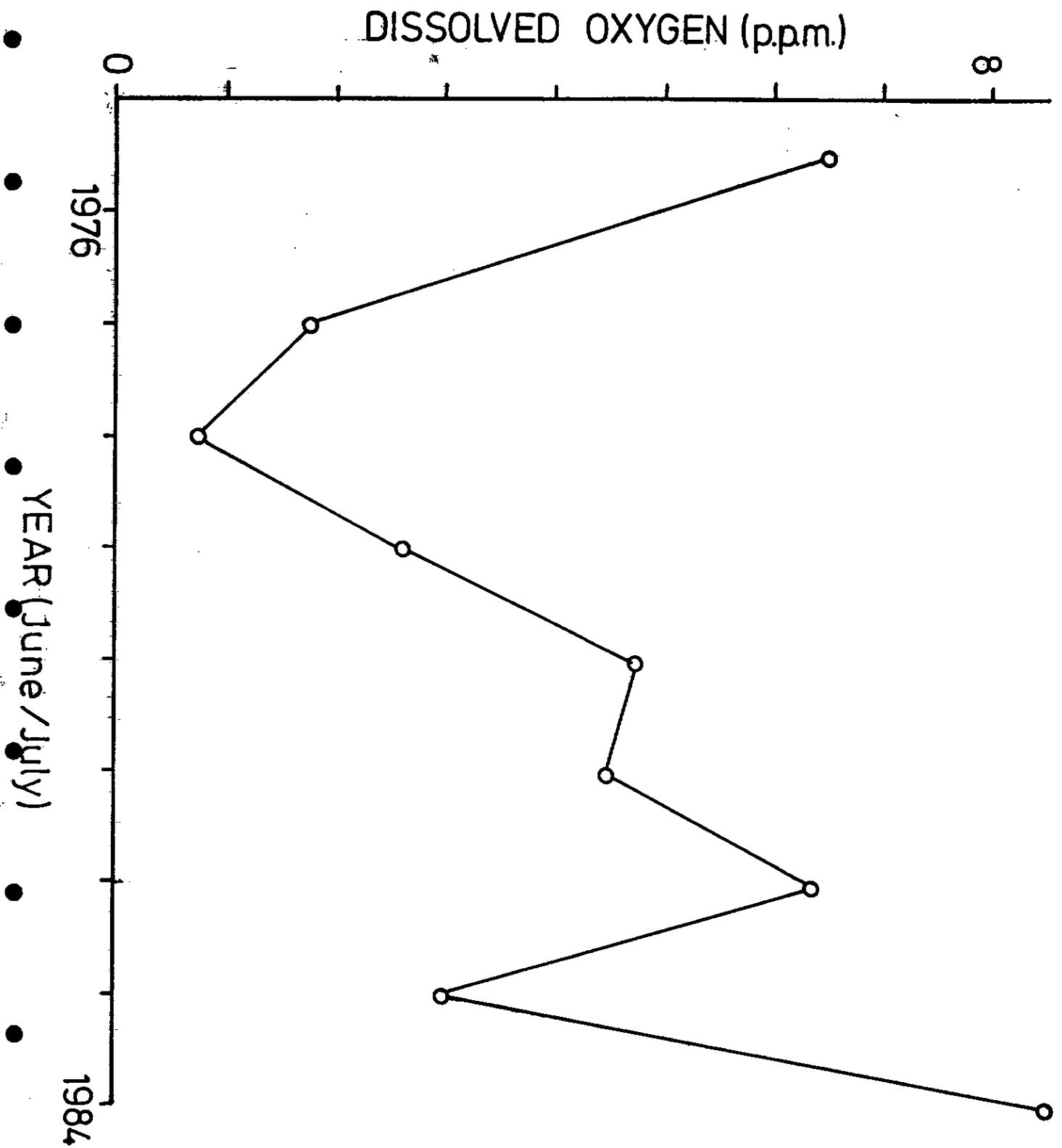
Station	Sampling date	Depth (m)	Temperature	Salinity	Dissolved oxygen (mg l ⁻¹)
FF48 (17)	21.6.84	25	9.5	35.3	-
		20	9.5	35.3	
		15	9.5	35.3	
		10	9.5	35.3	
		5	9.6	35.3	
		0	9.7	35.3	
10VI	21.6.84	13	9.5	35.4	9.9
		10	9.6	35.4	
		5	9.6	35.4	
		0	9.8	35.4	
20VI	21.6.84	18	9.4	35.4	-
		15	9.6	35.4	
		10	9.6	35.4	
		5	9.6	35.4	
		0	9.8	35.5	
30VI	21.6.84	18	9.6	35.4	10.0
		15	9.7	35.4	
		10	9.7	35.4	
		5	9.7	35.3	
		0	9.8	35.4	
40VI	21.6.84	20	9.7	35.7	-
		15	9.8	35.6	
		10	9.8	35.5	
		5	9.8	35.5	
		0	10.0	35.3	
50VI	23.6.84	25	9.6	35.2	10.1
		20	9.6	35.2	
		15	9.6	35.2	
		10	9.6	35.2	
		5	9.6	35.2	
		0	9.5	35.2	

Table 2:1 contd. Dissolved oxygen, temperature and salinity at each sampling station.

Station	Sampling date	Depth (m)	Temperature	Salinity	Dissolved oxygen (mg l ⁻¹)
CT1	23.6.84	8	9.8	35.5	9.7
		5	9.6	35.5	
		0	9.7	35.3	

Oxygen levels in bottom water at station D4 (1) in the inner basin of Sullom Voe.

FIG 2.1



3. ORGANIC CARBON AND NITROGEN IN SEDIMENTS

Sediment samples for organic carbon and nitrogen analysis were taken using the Craib Corer at most stations. At those stations where the sediment was too coarse to allow adequate corer penetration, samples were taken from a Day grab sample. Samples were dried, ground and then acid treated to remove carbonates prior to determination of organic carbon and nitrogen using a Perkin Elmer Model 240 Elemental Analyser. Data from all stations is shown in Table 3.1, together with the 1983 data from the same stations. A comparison over the two years suggests that there has been little change in the carbon values at most stations. Only at Station 119 (4), where the 1984 value was half that recorded in 1983, was there a large difference. However, the C:N ratio remained much the same over the two years, suggesting that the variation was caused by sedimentary patchiness rather than by an overall decrease in carbon content. This supposition is reinforced by a comparison of the values recorded at this station over a seven year period (Fig.3.1). This shows considerable variation in this area from year to year, with the 1984 values being comparable to those recorded in 1978-81.

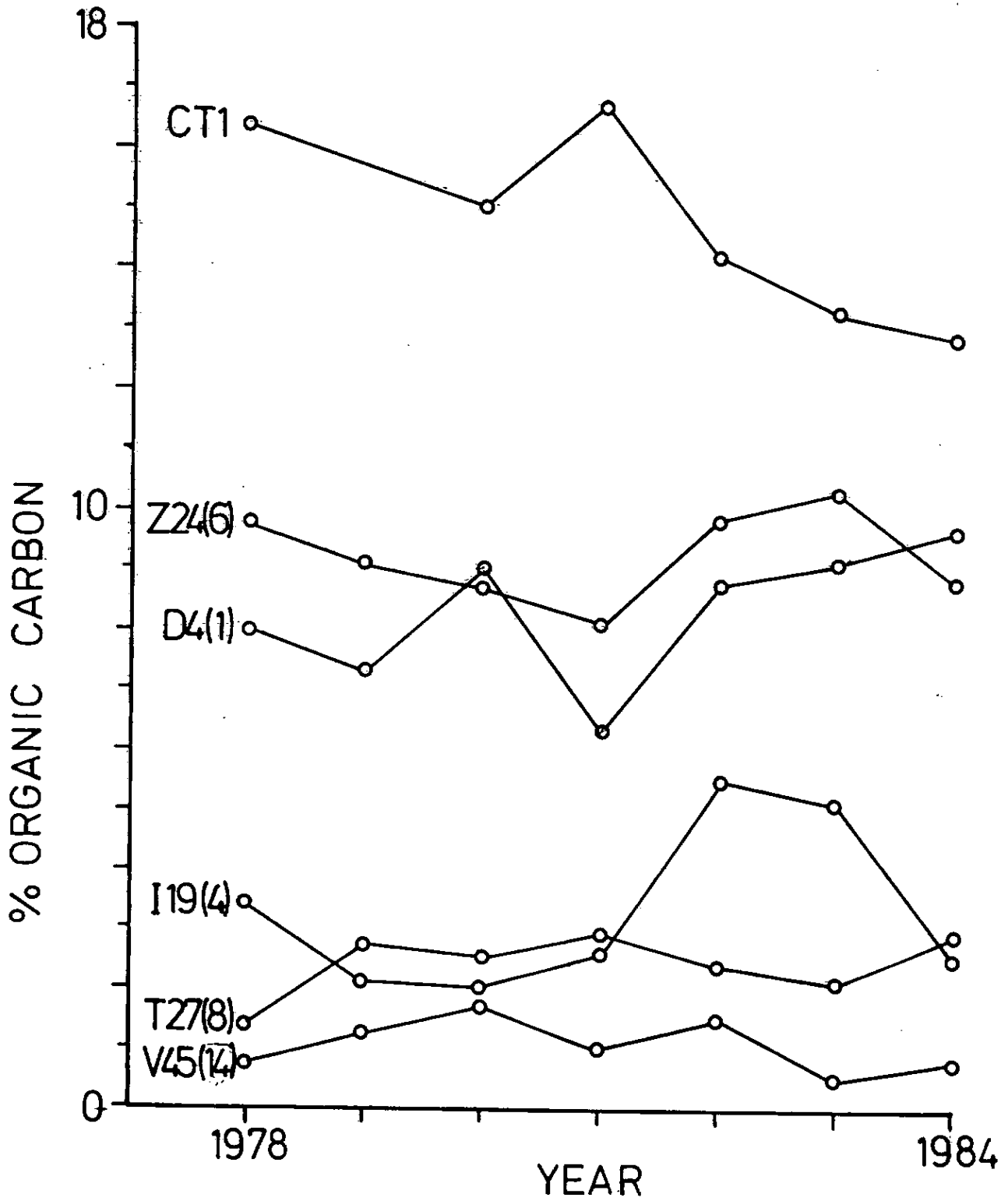
In Orka Voe the carbon values at the two inner stations were slightly lower than those recorded in 1983.

Table 3.1 Organic carbon and nitrogen in sediment samples from Sullom Voe, Orka Voe and Cat Firth.

Station	1983			1984		
	%C	%N	C:N	%C	%N	C:N
D4 (1)	9.2	1.0	9.4	9.7	1.0	9.4
H13 (3)	3.6	1.4	9.3	5.0	0.5	5.4
II9 (4)	5.1	0.6	8.7	2.5	0.3	9.1
O23 (5)	2.9	0.3	8.9	2.8	0.4	7.5
Z24 (6)	10.4	0.6	17.3	8.8	0.5	18.0
W27 (7)	3.5	0.3	11.6	4.4	0.4	11.5
T27 (8)	1.9	0.2	9.8	2.9	0.2	12.7
P31 (9)	1.5	0.1	11.6	1.2	0.2	7.6
S39 (11)	1.7	0.2	7.3	1.6	0.2	7.5
T44 (13)	1.3	0.3	5.1	1.4	0.3	4.7
V45 (14)	0.5	0.2	2.8	0.8	0.1	7.5
AA44 (15)	0.6	0.1	5.8	0.3	0.1	4.4
CC45 (16)	0.4	0.1	4.0	0.6	0.1	4.3
10VI			.	1.6	0.2	9.0
20VI	2.9	0.4	7.4	0.9	0.2	5.4
30VI	1.1	0.2	5.3	0.6	0.1	4.6
40VI	0.6	0.1	5.0	0.6	0.1	4.7
50VI	0.9	0.04	23.2	0.4	0.1	4.5
CT1	13.6	0.8	17.0	12.9	0.8	16.4

variation in the organic carbon values of the sediments at various stations over a seven year period.

FIG 3.1



4. HYDROCARBON ANALYSES OF SEDIMENTS

A. DOUGLAS

4.1 Introduction

Baseline studies begun in 1976, aimed at monitoring the hydrocarbon content of sediments (and in some years molluscs, and beach sands) collected from Sullom Voe and nearby stations, are continued in this report: the data reported are for samples collected between 18th and 23rd June, 1984.

Previous reports have provided values for the hydrocarbon content of sediments at a large number of sampling stations, some of which have been changed in certain years. In 1981, five stations at Orka Voe were included for annual sampling and were again analysed this year. In 1983, a suite of sites designated X13 - X32 (which were set out in a grid pattern around the Jetty area) were included for analysis, but were not sampled in 1984.

The analytical methods used were set out in some detail in the 1978 report, as was the rationale of the interpretation of results. In brief, the samples are examined microscopically, extracted in a mixed solvent system, the extract is separated by column and thin-layer chromatography and the recovered aliphatic hydrocarbons are analysed by capillary column gas chromatography and combined gas chromatography-mass spectrometry.

4.2 Materials

A total of 25 samples were collected for analysis; these included beach sands collected at low and high tide at three sites, and also samples from the 5 stations at Orka Voe.

4.3 Results and Discussion

A lithological description of the samples is provided in Table 4.1 This indicates that while some of the sediments are composed largely of mud, others are very sandy: comparisons with last year's (and previous) descriptions show that, on the basis of the subjective quantitative evidence available, the lithologies do not differ greatly from year to year.

The amount of sediment used, and the total amount of extractable organic matter recovered (reported in ppm dry sediment weight) using dichloromethane and methanol (separately and mixed) is shown in Table 4.2. The range of values is from about 60 ppm to 14,000 ppm; lower values (600 ppm) are, as before, for sites AA44 (15), CC45 (16) and V45 (14) and for all of the shore sands (except Gluss Voe at low tide). High values (10,000 ppm) were recorded at stations CT1 and Z24 (6), again the two stations with the highest values in previous years. Comparative figures have been tabulated for the extractable organic matter in the five years 1980-1984 (columns 1-5 in Table 4.4). The low and high values noted above stand out clearly. At most other sites, values given for 1984 are generally near the range of values recorded from 1980-1983. The most noticeable exception is at station S39 (11) where 80% more material was extracted this year, compared to last, and which shows a steady increase from 1980: at stations P31 (9) and 10VI (for which we have data only for 1982) increases are 37% and 60% respectively. Note that the shore sands at Houb of Scatsa have by far the lowest amount of extractable organic matter (Table 4.2).

The content of saturated hydrocarbons (total alkanes) in these sediments ranges from very low values (2 ppm dry weight of sediment) to less than 250 ppm for all stations except reference station CT1. At the latter station, the high value of 545 ppm (.0.04 of extract) is very similar to the /

the 1980 and 1982 values (cf. Table 4.4 but, as will be seen later, consists of non-petrogenic (i.e. biogenic) hydrocarbons. All of the other values fall within those recorded in previous years with four exceptions. There is an increase of 37% at station H13 (3) over the average for the previous 3 years; Table 4.4 and at station S39 (11) the saturated hydrocarbon content this year is more than double that recorded last year and is nearly 80% greater than the previous highest value (1981:cf Table 4.4). In Orka Voe, values recorded this year are identical to last years at stations 30VI and 40VI and about half of last years at 20VI. At station 10VI the saturated hydrocarbon content is somewhat greater (16%) than the only previous value we have (1981 - Table 4.4) and, interestingly, at station 50VI the figure this year (145 ppm) is double last years value and shows a steady increase since 1982.

In the shore sands, hydrocarbon contents are very low at Houb of Scatsta and, although surprisingly high in one sample each from Dales Voe and Gluss Voe, these two sites, as indicated later, are free of petrogenic * hydrocarbons.

* Footnote: The terms petrogenic hydrocarbons and petroleum-like hydrocarbons are used synonymously, and mainly refer in this report to the complex mixture of hydrocarbons (so-called UCM) that remains unresolved into separate constituents when analysed by high resolution gas chromatography. There is no known biogenic source of such a complex mixture of hydrocarbons; indeed there is no biosynthetic rationale for such and the presence of a UCM in saturated hydrocarbon mixtures is taken, today, by petroleum and environmental scientists to indicate the presence of petrogenic hydrocarbons. The most usual origin of petrogenic hydrocarbons in recent sediments is contaminated by petroleum and, where the boiling range is wide (indicated by a UCM covering a wide molecular weight range), it is generally considered that crude oil is the source. Narrower boiling ranges, derived from crude oil fractions, may also appear as contaminants typically from marine diesel fuels, sewage outlets and other industrial outlets. Finally, erosion of sediments that contain organic matter that has undergone previous burial (and geothermal maturation) may contribute reworked detritus that contains petroleum-like hydrocarbons. It is not possible, currently, from hydrocarbon analyses to distinguish between petroleum hydrocarbons sensu stricto, and hydrocarbons deposited in sediments by reworking and redeposition.

As far as the authors are aware from the limited microscopical analyses of the sediments under discussion, and from hydrocarbon data arising from analyses at reference station CT1, there is no evidence of any substantial amount of reworked sediments containing petroleum-like distributions of hydrocarbons onshore near Sullom Voe.

The percentage of saturated hydrocarbons making up the total extractable organic matter is less than ca. 7% except at stations 10V1, 20V1, 30V1, 50V1 (9.6%, 8.3%, 11.1% and 21.6% respectively): a value of more than 20% has been recorded previously only at sites 20V1 (1983) and 10V1 (1981). This years value of 21.6% saturated hydrocarbon in the organic matter extracted from sediment at site 50V1 is nearly three times last years value.

The total organic extract of the sediments, after subdivision by column chromatography, gave the data provided in Table 4.3. The dichloromethane (DCM) eluate is considered to contain mainly aromatic hydrocarbons and the methanol eluate mostly the more polar oxygen-, nitrogen- and sulphur-containing compounds. The losses shown in the last column of Table 4.3 represent the highly polar molecules that are irreversibly adsorbed by the silica gel column packing. All of the saturated hydrocarbon fractions (discussed above) were obtained from the pentane eluates (Table 4.3) using silver ion thin-layer chromatography to remove free sulphur and unsaturated hydrocarbons.

All of these separated saturated hydrocarbon fractions were analysed by capillary column gas chromatography (gc) and after examination of all the chromatograms nine samples were chosen for analysis by computer-aided combined gas chromatography-mass spectrometry (gc-ms). The capillary gc analyses for all of the samples were repeated in two different laboratories but since the results were similar only chromatograms originating from one laboratory are reproduced in this report. The mass spectral data attached contains only mass chromatograms of the hopane fragment ion m/z 191, although fragment ions of the steranes (m/z 217) were recorded as well as mass spectra of selected peaks: the latter data are omitted largely to keep

the report within reasonable bulk and also because the mass spectra are well documented in the literature.

The samples that were analysed are discussed below under the headings (i) clean sediment, (ii) very mildly contaminated sediments, (iii) contaminated sediments containing less than 50 ppm petrogenic hydrocarbons, (iv) contaminated sediments containing 60 - 160 ppm of petrogenic hydrocarbons and (v) shore sands.

4.3.1. Clean sediment (CT1).

Gas chromatographic analyses of the hydrocarbons isolated from the sediment at station CT1 (reference station) indicate that it is free of petrogenic hydrocarbons (Fig. 4.3). Methods for interpretation of the data are discussed more fully in a previous report (1978) but essentially the chromatogram shows the presence of predominantly odd-numbered normal alkanes, typical of those distributed in the cuticular waxes of higher plants (e.g. nC_{27} , nC_{29} , nC_{31} , nC_{33}) with smaller amounts of nC_{21} and nC_{23} (which may be derived from Sphagnum sp.). The absence, in any part of the chromatogram, of normal hydrocarbons with a smooth distribution, the absence of a suite of acyclic isoprenoid hydrocarbons, particularly in the C_{16} - C_{20} range, and the absence of a baseline "hump" of hydrocarbons (the so-called unresolved complex mixture, or UCM) provides prima facie evidence that this sediment is clean.

Reference to all previous reports will show that chromatograms of saturated hydrocarbons isolated from sediments at reference station CT1 have not markedly changed over the baseline study period.

Confirmation of the cleanliness of the CT1 sediment was obtained by examining the reconstructed ion chromatogram for hopanes (m/z 191:

cf. Fig. 4.26). This hopanogram is typical of that of a sediment free from petrogenic hydrocarbons since it shows hopanes with $\beta\beta$ and $\beta\alpha$ stereochemistry and C_{31} $\alpha\beta$ homohopane with 22R stereochemistry but not the epimeric 22S compound. Further, there are no hopane doublets with $\alpha\beta$ stereochemistry in the $C_{32} - C_{35}$ range which are normally present in petroleum (cf. with Fig. 4.33). This mass chromatogram (Fig. 26) is very similar to those obtained for CT1 hydrocarbons in previous years.

A more sensitive test, which confirmed that this sediment is clean, was made by establishing (from the m/z 217 mass chromatogram - not shown) that the C_{27} , C_{28} and C_{29} 20R and 20S $\alpha\alpha$ and $\alpha\beta\beta$ steranes are absent. These compounds are ubiquitous in petroleum and also in mildly-contaminated sediments (cf. Jones et. al. Marine Poll. Bull. 1985, in prep.).

4.3.2. Very mildly contaminated sediments (D4 (1), H13 (3), T27 (8) and Z24 (6))

Hydrocarbons isolated from the sediments at stations D4 (1), H13 (3), T27(8) and Z24(6) appear from their gas chromatograms (Figs 4.4, 4.5, 4.10, 4.14) to be substantially free of petrogenic hydrocarbons. However, integration** of the original chromatographic traces suggested that there was a small percentage (< 10%, Table 4.5) of non-biogenic hydrocarbons present, and this was confirmed for three of the samples by inspection of their hopanograms. Thus, for sample D4 (1) (Fig. 4.27) although the biogenic hopanes evident in clean sample CT1 are still predominant (peaks 3, 7, 9, 12) they are accompanied by other hopanes with $\alpha\beta$ stereochemistry, including the $C_{32} - C_{35}$ extended C_{22} S and R hopane doublets (peaks 10, 11; 13, 14; 15, 16; 17, 18) which are used inter alia to indicate the presence of petrogenic hydrocarbons.

**Footnote: This percentage should be taken as a guide: it was obtained from the original gc traces using a Hewlett-Packard 85B P.C., a Summagraphics Bit Pad One digitising table and a H.P. Imagan programme. (We thank Dr. I. Pazaris, Geotechnical Engineering, for advice and for the use of this instrument.)

A similar argument can be advanced for samples T27 (8) (Fig. 4.30) and Z24 (6) (Fig 4.32). Also, the sterane fragmentograms (not shown) of these samples contain the C₂₇, C₂₈ and C₂₉ ~~αα~~ and ~~αα~~ multiplets: this confirms that traces of petroleum-like hydrocarbons are present (cf Jones et al loc.cit.).

The amount of petrogenic hydrocarbons present in these sediments is low (<10ppm) as computed from Tables 4.2, 4.4 and 4.5: these data together justify the conclusion that at these four stations the sediments are only very mildly contaminated.

4.3.3. Contaminated sediments (50ppm of petrogenic hydrocarbon; AA44 (15), CC45 (16), O23 (5), P31 (9), T44 (13), V45 (14), 40VI)

The remainder of the sediments can be equally divided into those (a) with less than 50ppm and (b) those containing 60-160ppm of petrogenic hydrocarbons.

(a) In this group the total amount of alkanes and petrogenic hydrocarbons (in ppm, dry sediment weight) and the percentage of the latter, are shown in Table 4.5. As indicated, the amount of saturated hydrocarbons in these sediments varies from 4-65 ppm of which the petrogenic content varies from 3-29 ppm (44% to 69%). From the gas chromatograms of these seven hydrocarbon fractions (Figs 4.1, 4.2, 4.7, 4.8, 4.11, 4.12, 4.18) the rise in the baseline giving the unresolved complex "hump" can be seen (better in some gc's than others) but the proportion attributable to this can only be estimated using the HP integration method of the original traces as outlined previously.

A mass chromatogram of the hopanes (m/z 191) for sample P31 (9) is shown in Fig. 4.28 in which it is clear that dilution of the biogenic by petrogenic hopanes is more pronounced than in the very mildly contaminated sediments, discussed earlier, which contained 10% of petrogenic hydrocarbons.

Also, the mass chromatogram (m/z 217 - not shown) of sample P31 (9) indicated that the C₂₇, C₂₈ and C₂₉ sterane multiplets were present.

4.3.4. Contaminated sediments (60-160 ppm of petrogenic hydrocarbons; I19 (4), S39 (11), W27 (7), 10VI, 20VI, 30VI, 50VI)

(b) in the group of contaminated sediments, the saturated hydrocarbon content varies from 111-219 ppm of which the petrogenic content is in the range 67-159ppm (41% to 95%, Table 4.5). In the gas chromatograms of these seven hydrocarbon fractions (Figs 4.6, 4.9, 4.13, 4.15, 4.16, 4.17, 4.19) it is apparent that there are varying amounts of petrogenic hydrocarbons superimposed on the biological imprint, as evidenced in Figs 4.13 and 4.16 which contain about 41% and 95% of petrogenic hydrocarbons respectively. In the gas chromatogram of the latter (station 20VI) the biological imprint is more fully masked than at other stations, as was noted in last year's report.

Mass chromatograms (m/z 191) of the hopanes of four of these samples (S39 (11), W27 (7), 20VI, 50VI) are shown in figures 4.29, 4.31, 4.33 and 4.34 respectively. The very strong petrogenic signature is evident in samples 20VI and 50VI which have respectively about 95% and 81% contaminant in their total saturated hydrocarbon fractions. Again, mass chromatograms depicting the sterane distributions confirm the presence of petrogenic molecules in these hydrocarbon mixtures.

An attempt was made to show the enhanced dilution of the biogenic by petrogenic hydrocarbons by plotting two ratios namely (A) peaks 13/12+13 and (B) peaks 8/8+12 as percentages: this was done from peak heights in the mass chromatograms. Values obtained are shown in Table 4.8.

4.3.5. Shore sands

Samples of beach sands were collected at low tide (LT) and high tide (HT) at Dales Voe (DV), Gluss Voe (GV) and Houb of Scatsta (HS). The total amount of organic material extractable from these sands varied from 61 ppm to 866 ppm, the lowest figures (<100 ppm) being at Houb of Scatsta. All of the extracts contained saturated hydrocarbons, amounting to only two or three ppm at Houb of Scatsta but from 14-128 ppm at the other two beaches (Table 4.2 and 4.5). Gas chromatograms of the six samples are illustrated (Figs 4.20 - 4.25) from which it appears that the hydrocarbons at Dales Voe and Gluss Voe are principally biogenic whereas those at Houb of Scatsta are contaminated. Confirmation that this is so was obtained by integrating the original chromatograms, as previously explained. From the values shown in Table 4.5, it is clear that there is no measurable content of contaminant hydrocarbons at Dales and Gluss Voe. Table 4.5 also indicates that there is a very small content indeed of hydrocarbons at Houb of Scatsta. Although this is comprised of 73%-88% petrogenic contaminants, the total amounts are so low as to be considered negligible. These results indicate that there would be little further value in analysing these samples by gc-ms this year.

Table 4.1

SEDIMENT DESCRIPTIONS (1984)

AA44 (15)	Shell/Gravel/Sand	Shell fragments and rare gravel granules in dark green clayey sand. Large shell material (gastropod) 3mm to fine sand size, gravel of lithic clasts and pink quartz grains.
CC45 (16)	Shell Sand	Dark green, coarse to fine sand. Coarse fraction composed of fine shell debris the finer fraction quartz. Some pink in colour.
CT1	Mud	Very dark green, almost black, organic rich, slightly silty mud. Occasional 2-3mm shell fragments.
D4 (1)	Mud/Clay	Black clayey mud, fetid smell.
H13 (3)	Mud	Dark green silty mud with very fine shell debris, less than 0.5mm some larger fragments 2-3mm.
I19 (4)	Mud/Sand	Dark green mud with silt, fine sand and skeletal fragments (most less than 1mm), single gravel granule.
O23 (5)	Sand/Mud	Dark green sandy mud. As I19 but larger proportion of sand and shell material.
P31 (9)	Sand/Mud	Dark green, muddy sand. Fine to medium sand size with common small shell fragments, mostly 0.5 to 2mm. Occasional slightly larger fragments.
S39 (11)	Sand/Mud	Dark green, very muddy sand of very finely comminuted skeletal debris. Some large fragments. 1-6mm.
T27 (8)	Shell Sand/Mud	Dark green, very muddy sand of coarse to fine sand sized skeletal debris (5 to 0.5mm) also some fine quartz sand. Recognizable lamellibranchs (cockle?) and echinoid spine. Single gravel granule.
T44 (13)	Sand/Mud	Green, muddy fine sand. Sand composed of finely comminuted skeletal material (less than 0.5mm). Occasional large fragments up to 3mm.
V45 (14)	Sand/Mud	Green, muddy, fine to medium sand. Sand grains mostly shell fragments, also black mica(?) flakes and, less commonly, pink quartz grains.
W27 (7)	Shell/Mud	Dark green, organic-rich clayey mud containing large skeletal fragments (up to 1cm). Three different types of lamellibranch (one entire) and part of a gastropod.
Z24 (6)	Mud	Black, organic-rich (almost peaty), slightly silty mud with filamentous algae. Rare skeletal fragments.

Table 4.1 (contd)

1 OVI	Mud/Sand	Dark green mud with silt and fine sand.
2 OVI	Clay/Mud	Dark green, clayey mud. Very fine filamentous green alga.
3 OVI	Mud/Shell	Very dark green, almost black, clayey mud with fine sand and silt, probably of very fine skeletal material. Rare larger skeletal fragments (0.5-1mm).
4 OVI	Sand/Mud	Yellow/green, slightly muddy, fine to medium sand of skeletal debris, dark grains and quartz grains (some pink). Part of a gastropod and a fine hair-like alga.
5 OVI	Sand/Mud	Dark green, muddy, medium to coarse sand. Sand composed mostly of skeletal debris 0.5-2mm. Larger fragments include echinoid spines, also quartz grains.
Dales Voe (LT)	Sand	All of these six beach samples consist of coarse sand.
Dales Voe (HT)	Sand	
Gluss Voe (LT)	Sand	
Gluss Voe (HT)	Sand	
Houb/Scatsa (LT)	Sand	
Houb/Scatsa (HT)	Sand	

NB LT = low tide; HT = high tide

Table 4.2

Sample Site	Date Collected	Lithology	Sediment Dry Wt (g)	Total Extract (ppm)	Total Alkanes (ppm)*
AA44 (15)	June 1984	Shell/Sand	68	397	7
CC45 (16)	June 1984	Shell/Sand	91	462	4
CT1	June 1984	Mud	22	14,182	545
D4 (1)	June 1984	Mud/Clay	52	2,830	202
H13 (3)	June 1984	Mud	75	2,133	76
I19 (4)	June 1984	Mud/Sand	60	6,250	120
O23 (5)	June 1984	Sand/Mud	80	1,260	65
P31 (9)	June 1984	Sand/Mud	78	1,740	53
S39 (11)	June 1984	Sand/Mud	88	2,364	131
T27 (8)	June 1984	Shell sand/Mud	61	2,690	57
T44 (13)	June 1984	Sand/Mud	63	1,100	25
V45 (14)	June 1984	Sand/Mud	74	580	26
W27 (7)	June 1984	Shell/Mud	75	3,650	219
Z24 (6)	June 1984	Mud	71	11,690	225

Table 4.2 (contd)

Sample Site	Date Collected	Lithology	Sediment Dry Wt (g)	Total Extract (ppm)	Total Alkanes (ppm)*
1 OV1	June 1984	Mud/Sand	51	1,650	159
2 OV1	June 1984	Clay/Mud	55	2,020	167
3 OV1	June 1984	Mud/Shell	63	1,000	111
4 OV1	June 1984	Sand/Mud	48	770	33
5 OV1	June 1984	Sand/Mud	51	670	145
DV (LT)	June 1984	Coarse Sand	94	207	14
DV (HT)	June 1984	Coarse Sand	93	484	124
GV (LT)	June 1984	Coarse Sand	97	866	128
GV (HT)	June 1984	Coarse Sand	101	406	38
HS (LT)	June 1984	Coarse Sand	89	98	3
HS (HT)	June 1984	Coarse Sand	96	61	2

*Expressed as dry weight of sediment.

Table 4.3

Sample Site	Date Collected	Pentane Eluate & Sulphur % age**	Total Alkanes % age**	Sulphur % age**	DCM Eluate % age**	Methanol Eluate % age**	Loss % age
AA44 (15)	June 1984	8.9	1.9	7.0	5.2	41.9	44.0
CC45 (16)	June 1984	7.1	1.0	6.1	5.7	45.9	41.5
CT1	June 1984	8.7	3.8	3.9	10.9	19.6	60.8
D4 (1)	June 1984	8.2	7.1	1.1	9.9	25.2	56.7
H13 (3)	June 1984	11.3	3.6	7.7	10.6	23.1	55.0
I19 (4)	June 1984	11.2	1.9	9.3	8.3	26.1	54.4
O23 (5)	June 1984	8.3	5.1	3.2	12.0	16.1	63.6
P31 (9)	June 1984	18.7	3.0	15.7	17.7	27.9	35.7
S39 (11)	June 1984	14.9	5.5	9.4	17.8	27.9	39.4
T27 (3)	June 1984	8.2	2.1	6.1	4.9	9.9	77.0
T44 (13)	June 1984	8.6	2.3	6.3	9.6	22.3	59.5
V45 (14)	June 1984	14.0	4.4	9.6	5.3	46.0	34.7
W27 (7)	June 1984	17.4	6.0	11.4	11.1	25.0	46.5
Z24 (6)	June 1984	2.5	1.9	1.6	12.9	33.9	50.7

Table 4.3 (contd)

Sample Site	Date Collected	Pentane Eluate & Sulphur % age**	Total Alkanes % age**	Sulphur % age**	DCM Eluate % age**	Methanol Eluate % age**	Loss % age
1 OV1	June 1984	33.1	9.6	23.5	21.2	22.6	23.1
2 OV1	June 1984	18.4	8.3	10.1	12.7	17.8	51.1
3 OV1	June 1984	21.9	11.1	10.8	9.5	30.0	38.6
4 OV1	June 1984	18.4	4.3	14.1	8.6	20.0	53.0
5 OV1	June 1984	21.8	21.8	Trace	12.3	45.0	20.9
DV (LT)	June 1984	17.4	6.7	10.7	24.1	36.4	22.1
DV (HT)	June 1984	31.3	25.6	5.7	21.6	27.1	20.0
GV (LT)	June 1984	19.3	14.8	4.5	14.4	36.9	29.4
GV (HT)	June 1984	11.0	9.3	1.7	14.9	30.2	43.9
HS (LT)	June 1984	5.2	3.4	1.8	12.6	39.0	43.2
HS (LT)	June 1984	3.6	2.4	1.2	23.7	35.6	37.1

**Expressed as percentage of the total extract

Table 4.4

SEDIMENT SAMPLES

Comparison of the total amounts of extractable organic matter (A) and saturated hydrocarbons (B) in the 1980, 1981, 1982, 1983 and 1984 sediment samples.

Sediment Sample Site	(A) Total Extract ppm dry wt.					(B) Total Alkanes ppm dry wt.				
	1 1980	2 1981	3 1982	4 1983	5 1984	6 1980	7 1981	8 1982	9 1983	10 1984
AA44 (15)	-	28	236	242	397		**	6	6	7
CC45 (16)	154	571	418	137	462	**	**	**	7	4
CT1	12,566	18,532*	13,666	19,940	14,182	592	194*	544	218	545
D4 (1)	9,156	6,456*	3,261	5,018	2,830	477	240*	126	249	202
H13 (3)	1,563	2,213	2,075	2,339	2,133	44	57	53	56	76
I19 (4)	2,338	5,382	6,795	2,154	6,250	199	175	191	89	120
O23 (5)	2,824	1,064	1,370	2,111	1,260	102	31	32	85	65
P31 (9)	977	1,025	1,268	1,090	1,740	58	62	110	42	53
S39 (11)	786	936	1,060	1,313	2,364	23	74	41	60	131
T27 (8)	1,117	1,606	3,140	1,175	2,690	56	29	67	42	57
T44 (13)	495	1,316	1,256	566	1,100	23	52	37	16	25
V45 (14)	676	505	467	524	580	26	29	11	17	26
W27 (7)	3,971	3,404	3,212	-	3,650	262	262	148	262	219
Z24 (6)	10,456	5,389	13,811	6,648	11,690	589	233*	188	242	225
10V1	-	1,027	-	-	1,650	-	137	-	-	159
20V1	-	680	2,293	1,570	2,020	-	79	284	333	167
30V1	-	2,438	738	1,757	1,000	-	507	46	100	111
40V1	-	1,419	577	1,253	770	-	204	26	34	33
50V1	-	611	549	991	670	-	57	20	74	145

N.B. Not provided for analysis in year shown -; Trace amounts only **; Average values *.

Table 4.5

Station (1)	Total alkanes (ppm)* (2)	(3)	Petrogenic hydrocarbons (4)
		(%)	ppm **
AA44 (15)	7	53	4
CC45 (16)	4	65	3
CT1	545	0	0
D4 (1)	202	2	4
H13 (3)	76	7	5
I19 (4)	120	56	67
O23 (5)	65	44	29
P31 (9)	53	30	16
S39 (11)	131	60	79
T27 (8)	57	10	6
T44 (13)	25	69	17
V45 (14)	26	63	16
W27 (7)	219	41	90
Z24 (6)	225	4	8
10V1	159	82	130
20V1	167	95	159
30V1	111	86	95
40V1	33	66	22
50V1	145	81	117
Dales Voe (HT)	14	0	0
Dales Voe (LT)	124	0	0
Gluss Voe (LT)	128	0	0
Gluss Voe (HT)	38	0	0
Houb Scatsa (LT)	3	73	2
Houb Scatsa (HT)	2	88	2

* ppm dry sediment weight

**approximated from figures in columns 2 and 3

Table 4.6

IDENTIFICATION OF HOPANES FROM RELATIVE RETENTION DATA AND MASS SPECTRA

(cf. Figs 4.26 to 4.30 for hopanograms)

1. C₂₇ 18 α (H) 22, 29, 30 trisnorneohopane (Ts)
2. C₂₇ 17 α (H) 22, 29, 30 trisnorhopane (Tm)
3. C₂₇ 17 β (H) 22, 29, 30 trisnorhopane
4. C₂₉ 17 α (H) 21 β (H) 30 norhopane
5. C₂₉ 17 β (H) α 21 (H) 30 normoretane
6. C₃₀ 17 α (H) 21 β (H) hopane
7. C₂₉ 17 β (H) 21 β (H) 30 norhopane
8. C₃₁ 17 α (H) 21 β (H) homohopane (22S)
9. C₃₁ 17 α (H) 21 β (H) homohopane (22R)
10. C₃₂ 17 α (H) 21 β (H) bishomohopane (22S)
11. C₃₂ 17 α (H) 21 β (H) bishomohopane (22R)
12. C₃₁ 17 β (H) 21 β (H) homohopane
13. C₃₃ 17 α (H) 21 β (H) trishomohopane (22S)
14. C₃₃ 17 α (H) 21 β (H) trishomohopane (22R)
15. C₃₄ 17 α (H) 21 β (H) tetrakishomohopane (22S)
16. C₃₄ 17 α (H) 21 β (H) tetrakishomohopane (22R)
17. C₃₅ 17 α (H) 21 β (H) pentakishomohopane (22S)
18. C₃₅ 17 α (H) 21 β (H) pentakishomohopane (22R)

Table 4.7

FIGURE NUMBERS OF GC AND GC-MS TRACES OF HYDROCARBONS ISOLATED FROM 1984
SEDIMENT SAMPLES

<u>Figure Number</u>	<u>GC Trace of Saturated Hydrocarbon</u>
4 . 1	AA44 (15)
2	CC45 (16)
3	CT1
4	D4 (1)
5	H13 (3)
6	I19 (4)
7	O23 (5)
8	P31 (9)
9	S39 (11)
10	T27 (8)
11	T44 (13)
12	V45 (14)
13	W27 (7)
14	Z24 (6)
15	10V1
16	20V1
17	30V1
18	40V1
19	50V1
20	DV (LT)
21	DV (HT)
22	GV (LT)
23	GV (HT)
24	HS (LT)
25	HS (HT)
	<u>Mass Chromatograms (M/z = 191) of</u>
	<u>Hydrocarbons</u>
26	CT 1
27	D4 (1)
28	P31 (9)
29	S39 (11)
30	T27 (8)
31	W27 (7)
32	Z24 (6)
33	20V1
34	50V1

Table 4.8 Ratio of peak heights (13/12 +13, Ratio A and 8/8 + 12 Ratio B) in the mass chromatograms showing the enhanced dilution of the biogenic by the heterogenic hydrocarbons.

RATIO A		RATIO B	
Station	Percentage	Station	Percentage
CT1	6	CT1	6
D4 (1)	20	D4 (1)	45
T27 (8)	26	Z24 (6)	55
Z24 (6)	29	T27 (8)	56
W27 (7)	45	W27 (7)	70
P31 (9)	47	P31 (9)	71
S39 (11)	63	S39(11)	84
50VI	83	50VI	94
20VI	93	20VI	99

These percentage values appear to bear out the increasing contamination in progressing from groups (i) to (iv).

Captions to figures

Figures 4.1 to 4.25 GC Traces of Saturated Hydrocarbons
at each sampling station

Fig 4.1

AA44 (15) 1984
saturated
hydrocarbons

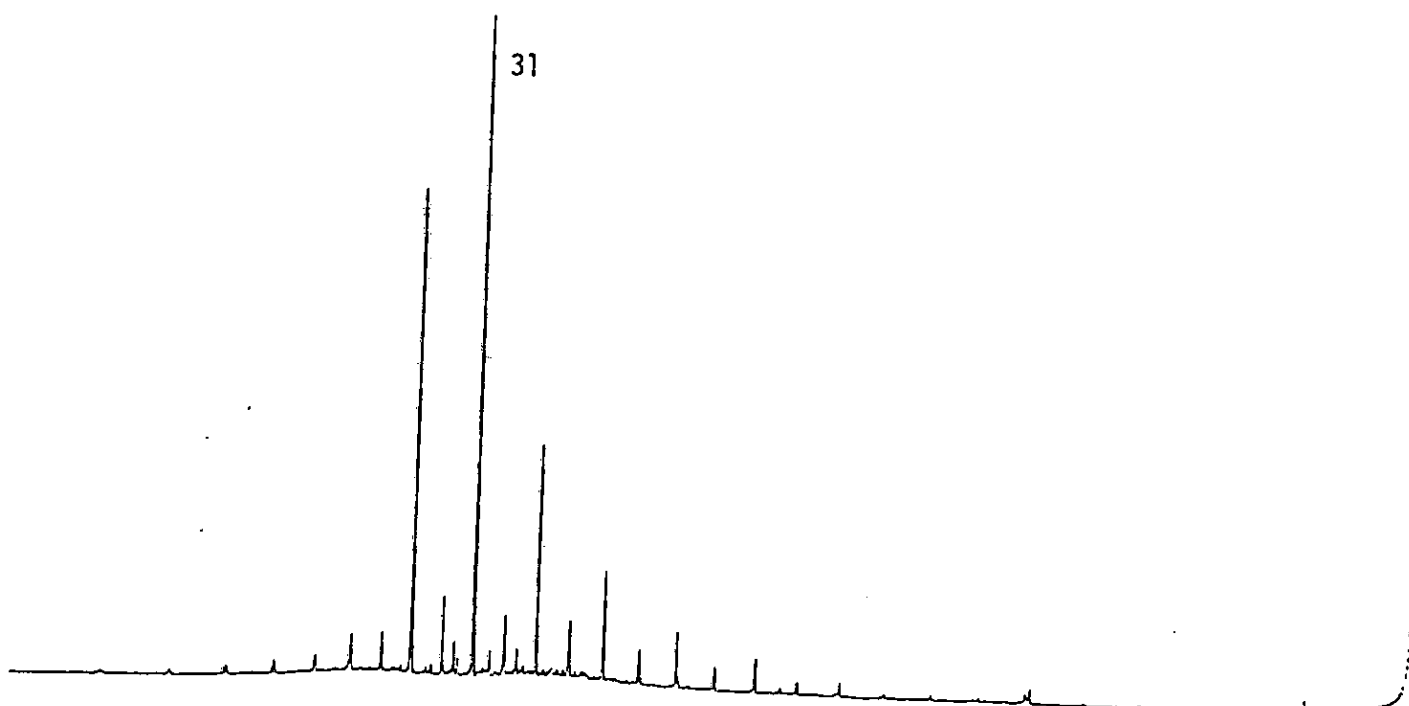


Fig 4.2

CC45 (16) 1984
saturated
hydrocarbons

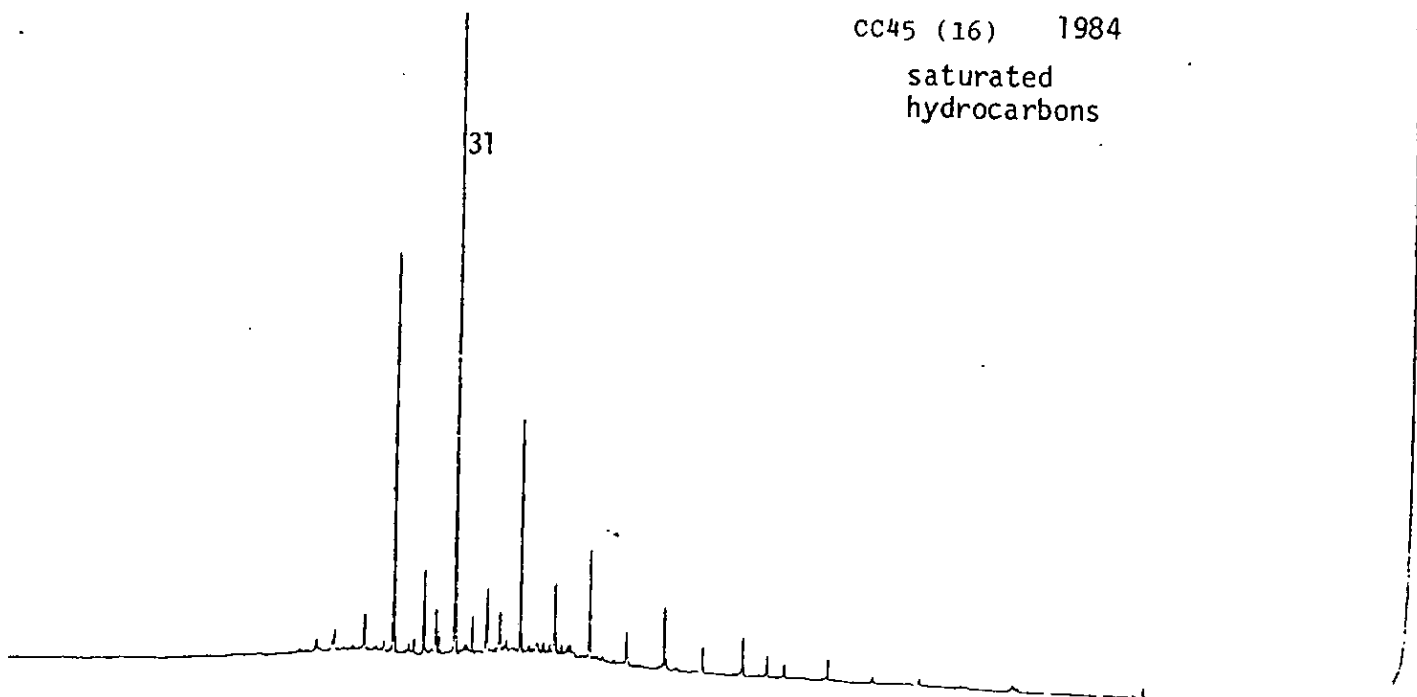


Fig.4.3

CT1 1984
saturated
hydrocarbons

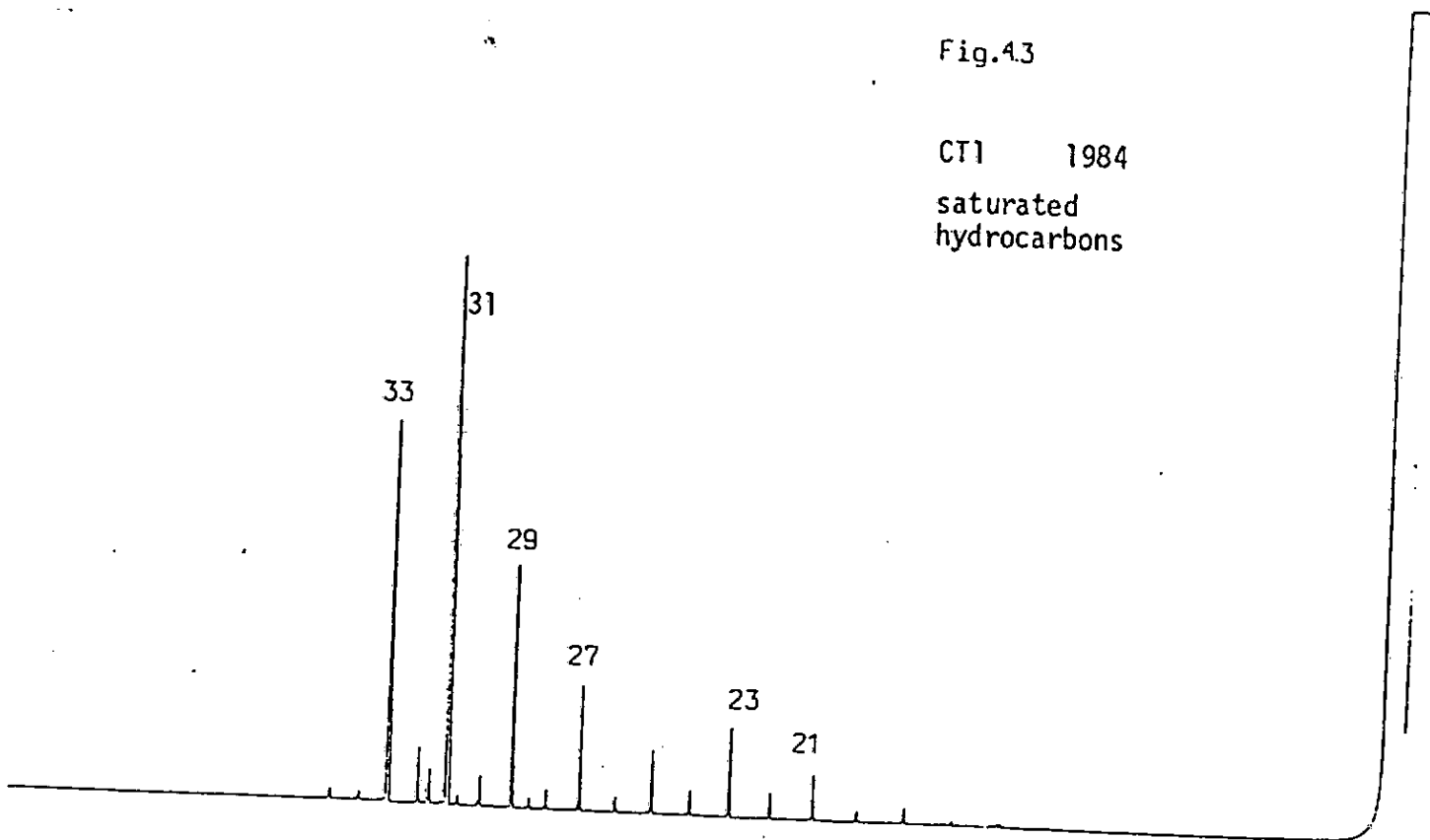


Fig.4.4

D4 (1) 1984
saturated
hydrocarbons

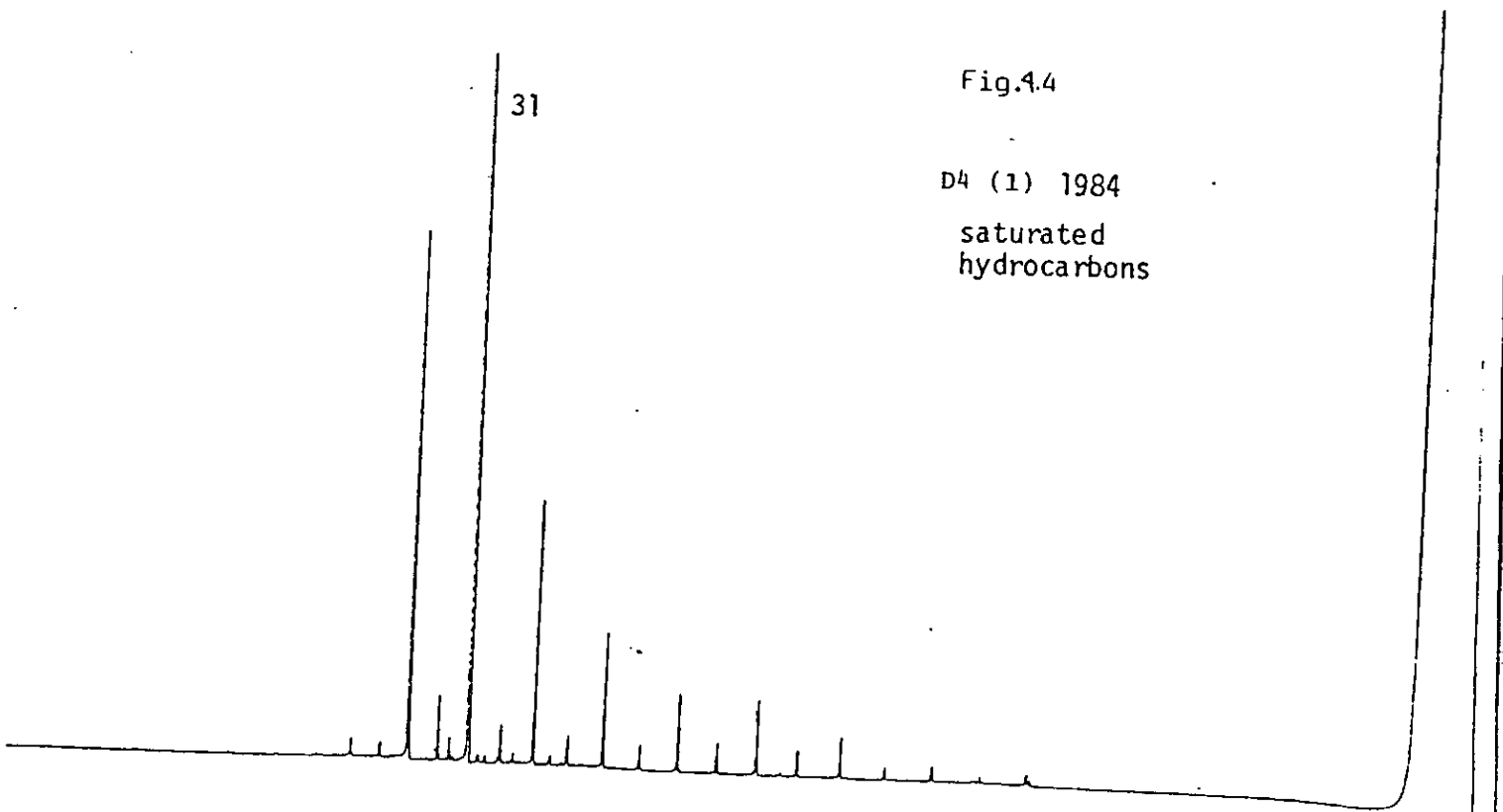


Fig.4.5

H13 (3) 1984
saturated
hydrocarbons

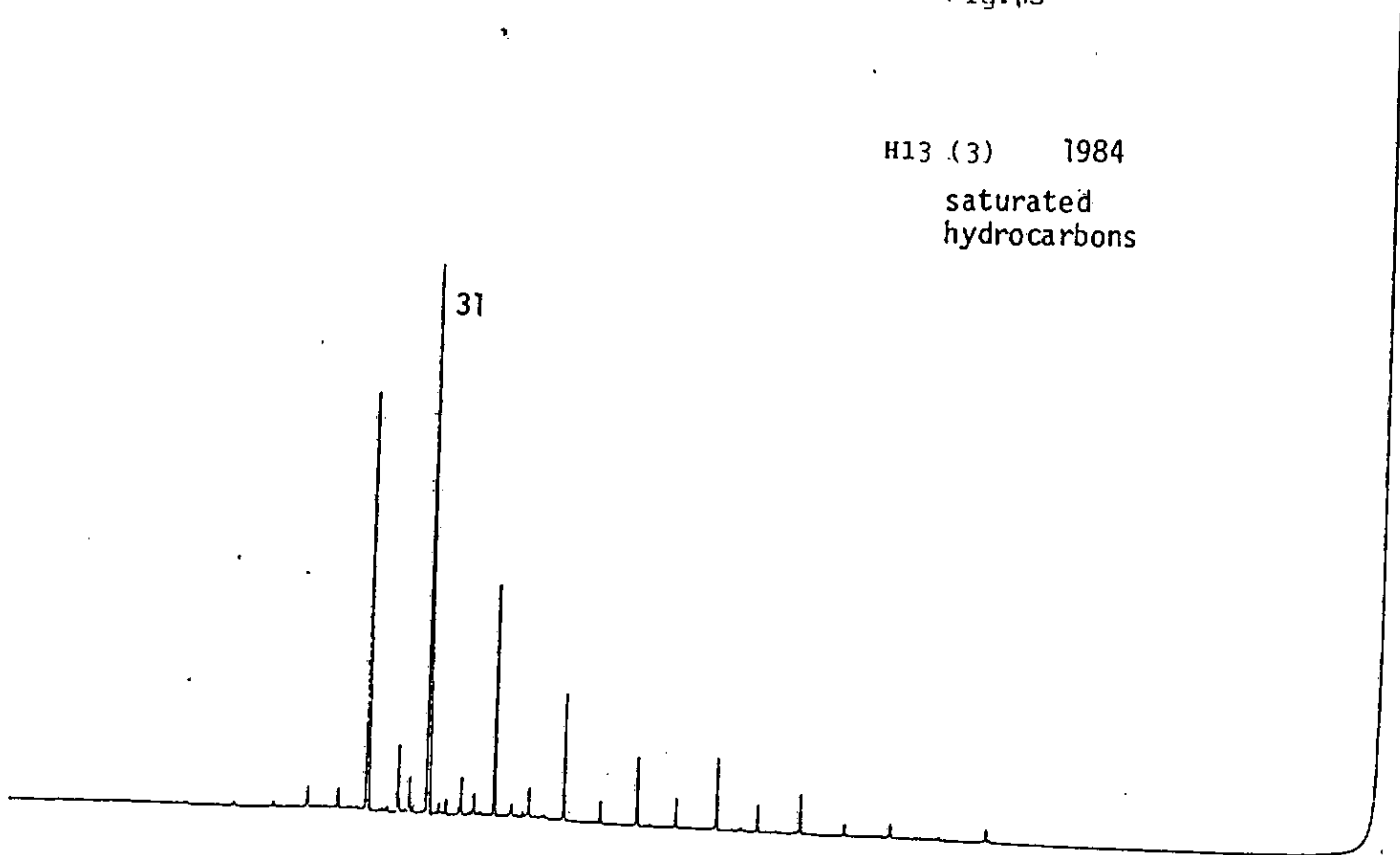


Fig.4.6

I19 (4) 1984
saturated
hydrocarbons

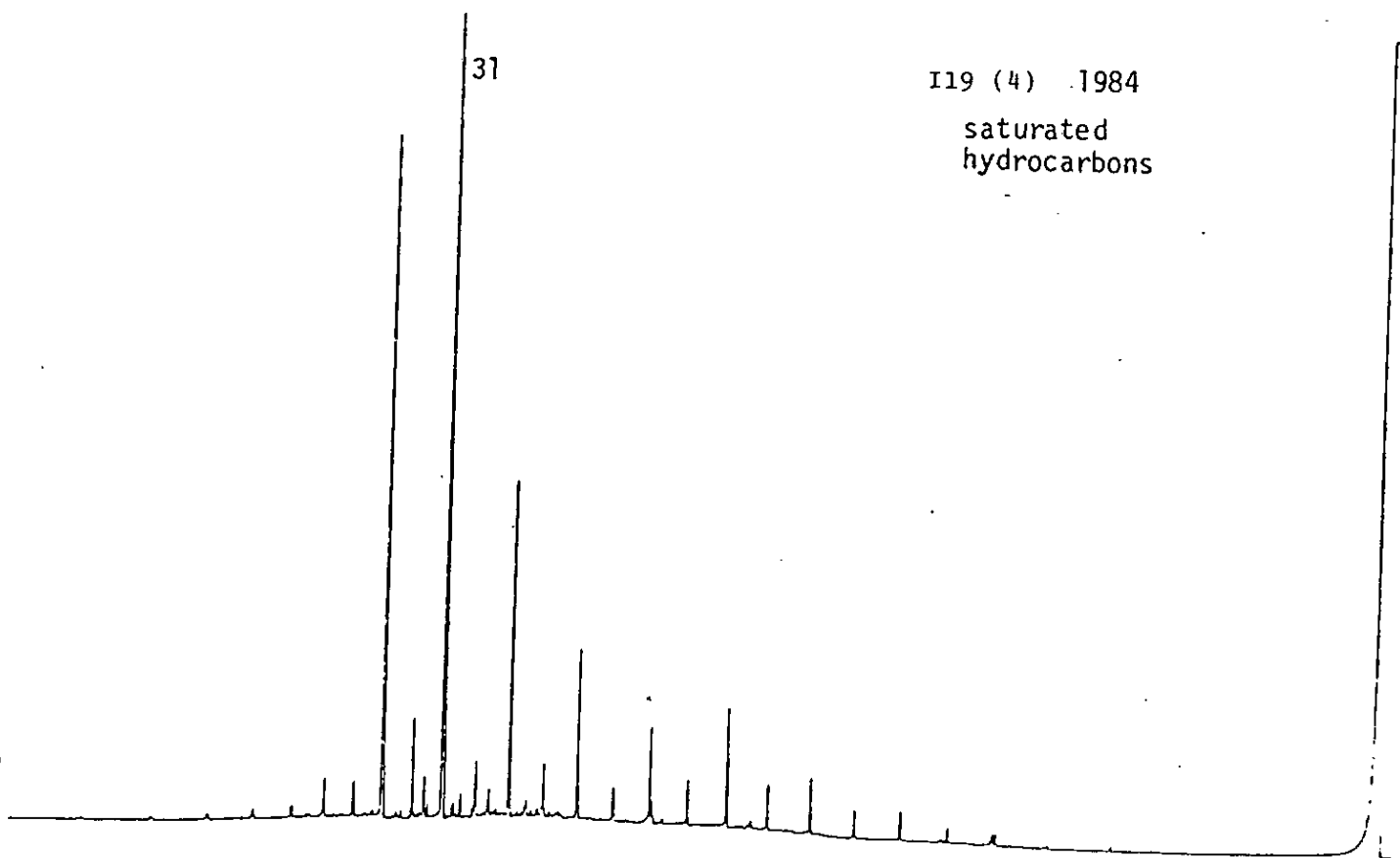


Fig.4.7

23 (5) 1984
saturated
hydrocarbons

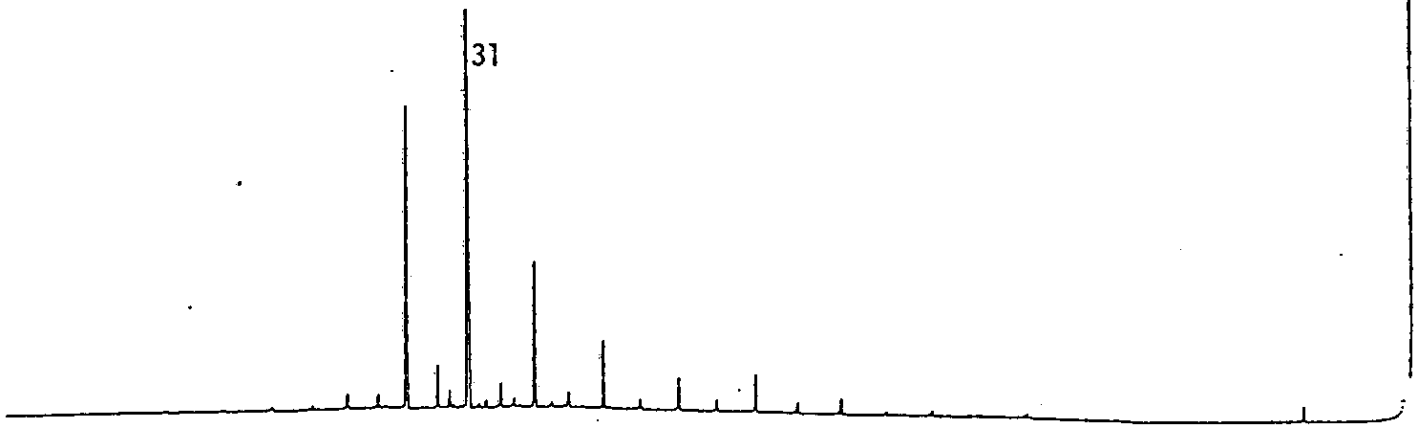


Fig 4.8

P31 (9) 1984
saturated
hydrocarbons

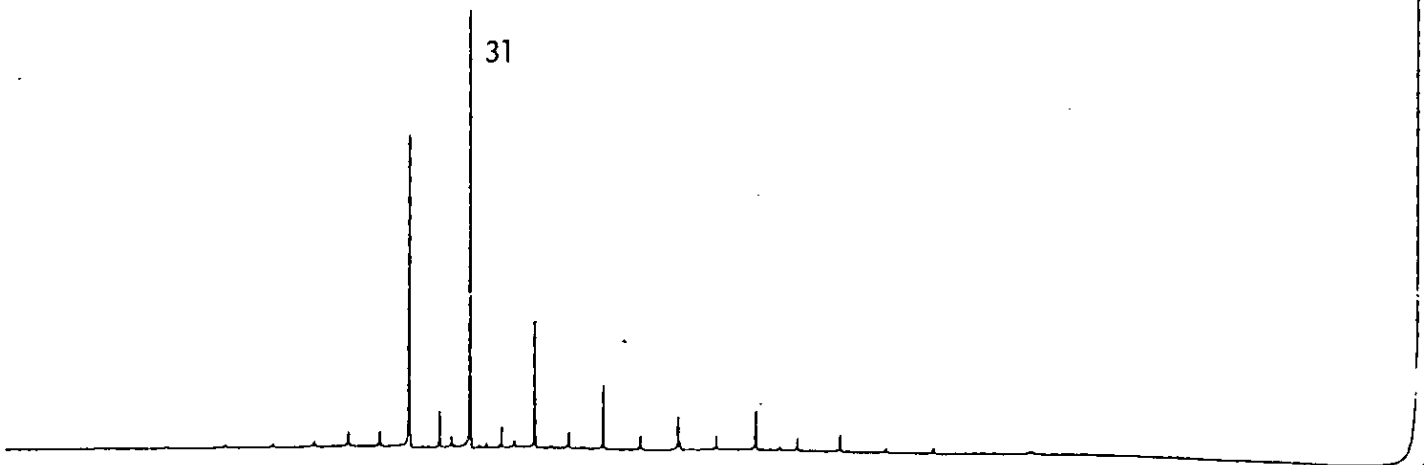


Fig.4.9

S39 (11) 1984
saturated
hydrocarbons

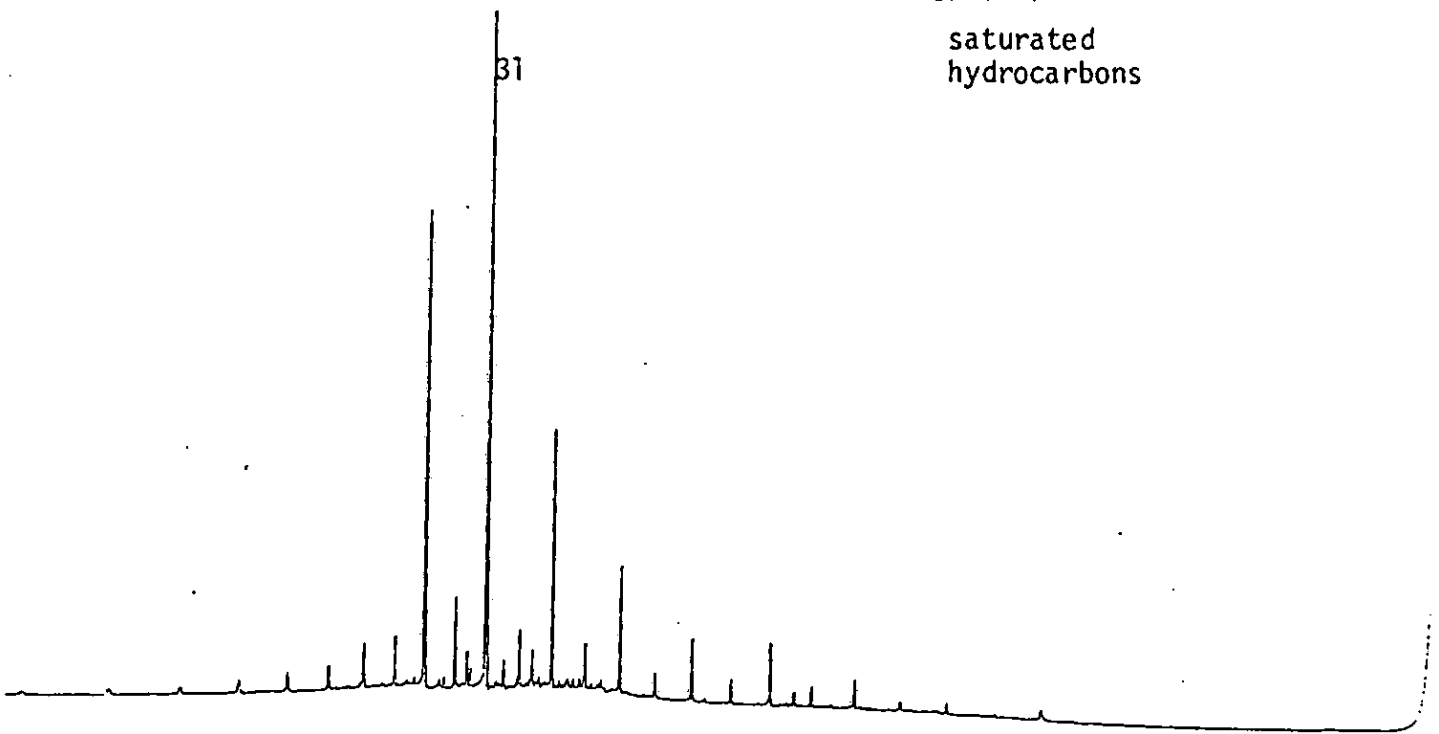


Fig.4.10

T27 (8) 1984
saturated
hydrocarbons

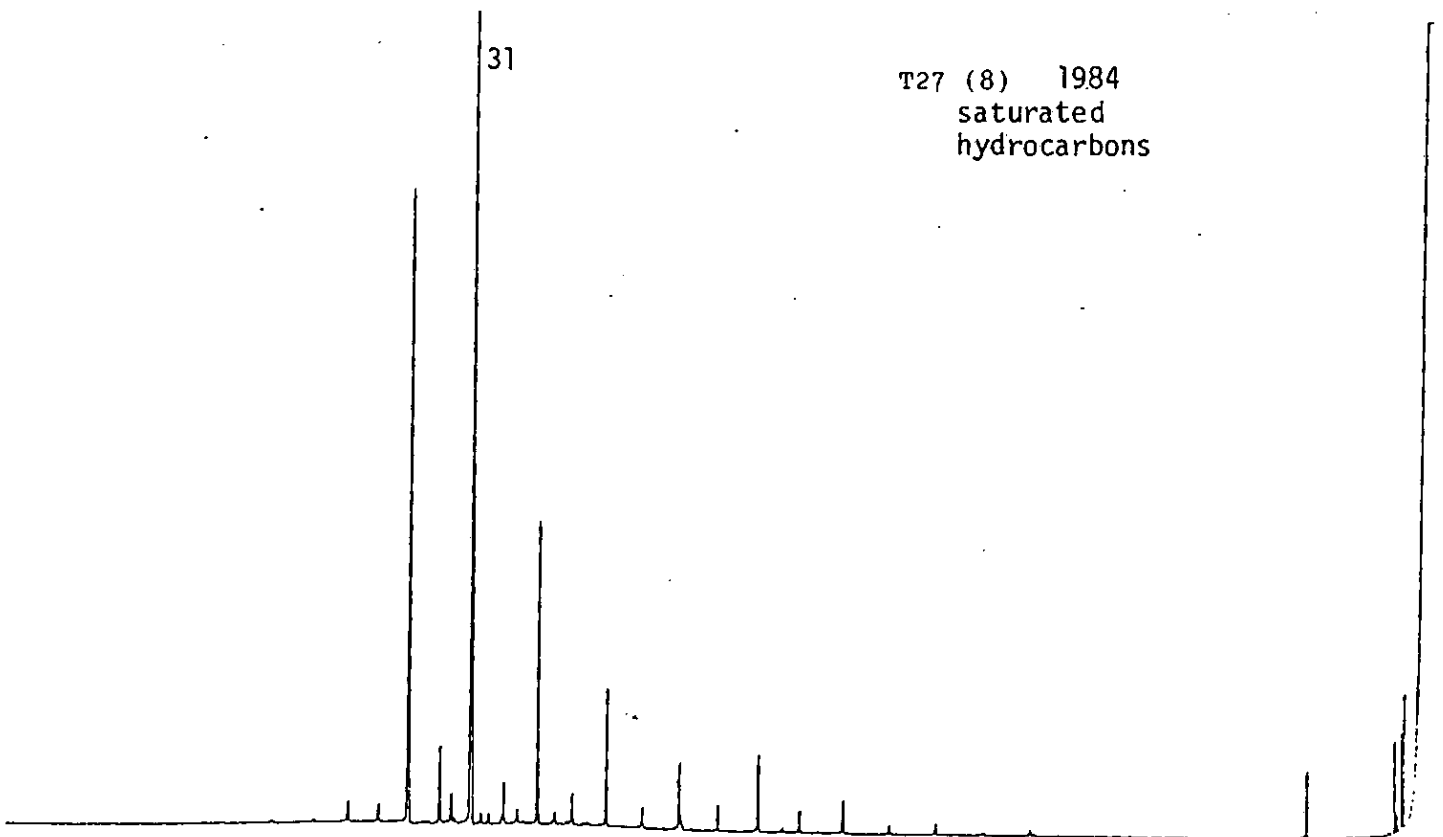


Fig.4.11

T44 (13) 1984
saturated
hydrocarbons

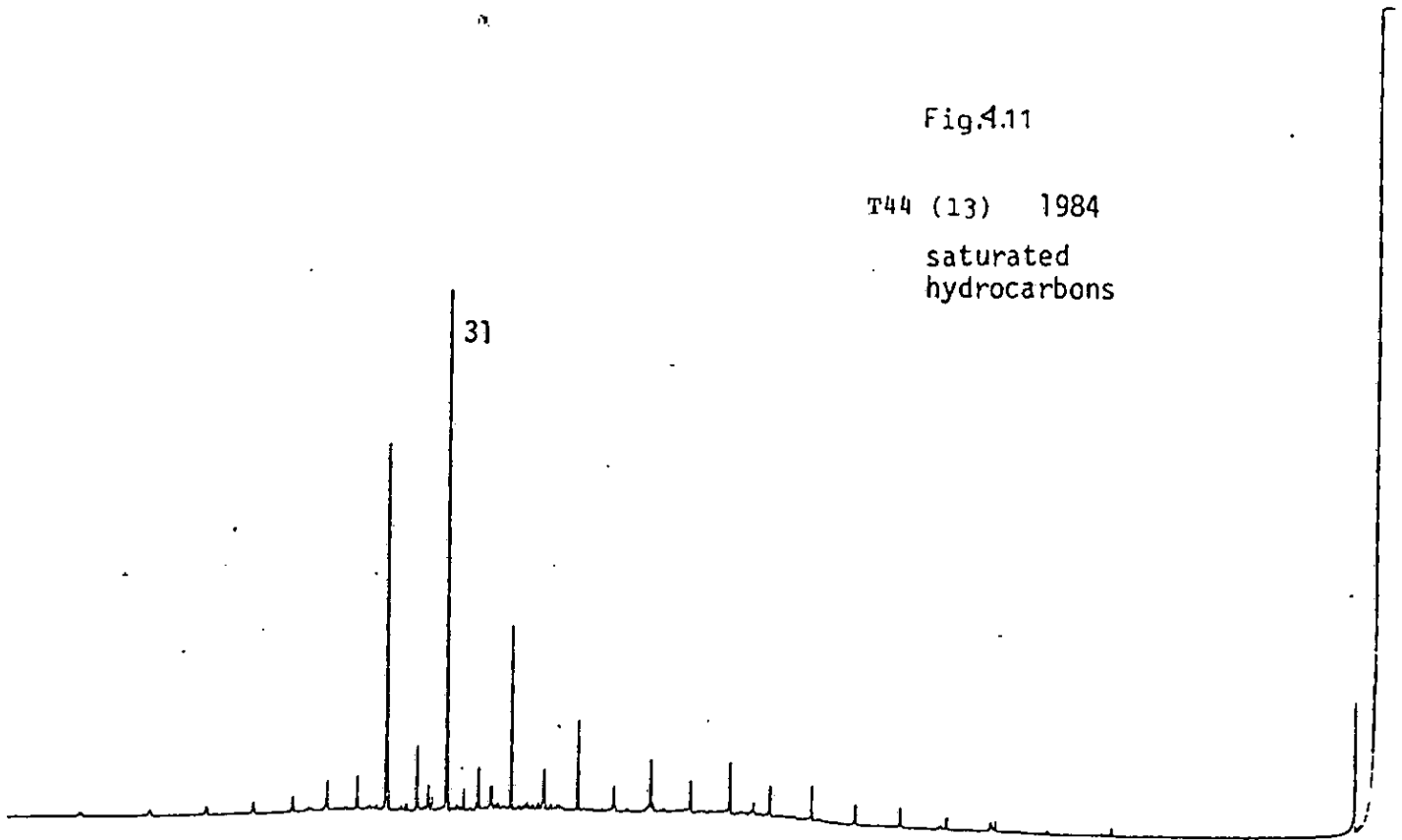


Fig.4.12

V45 (14) 1984
saturated
hydrocarbons

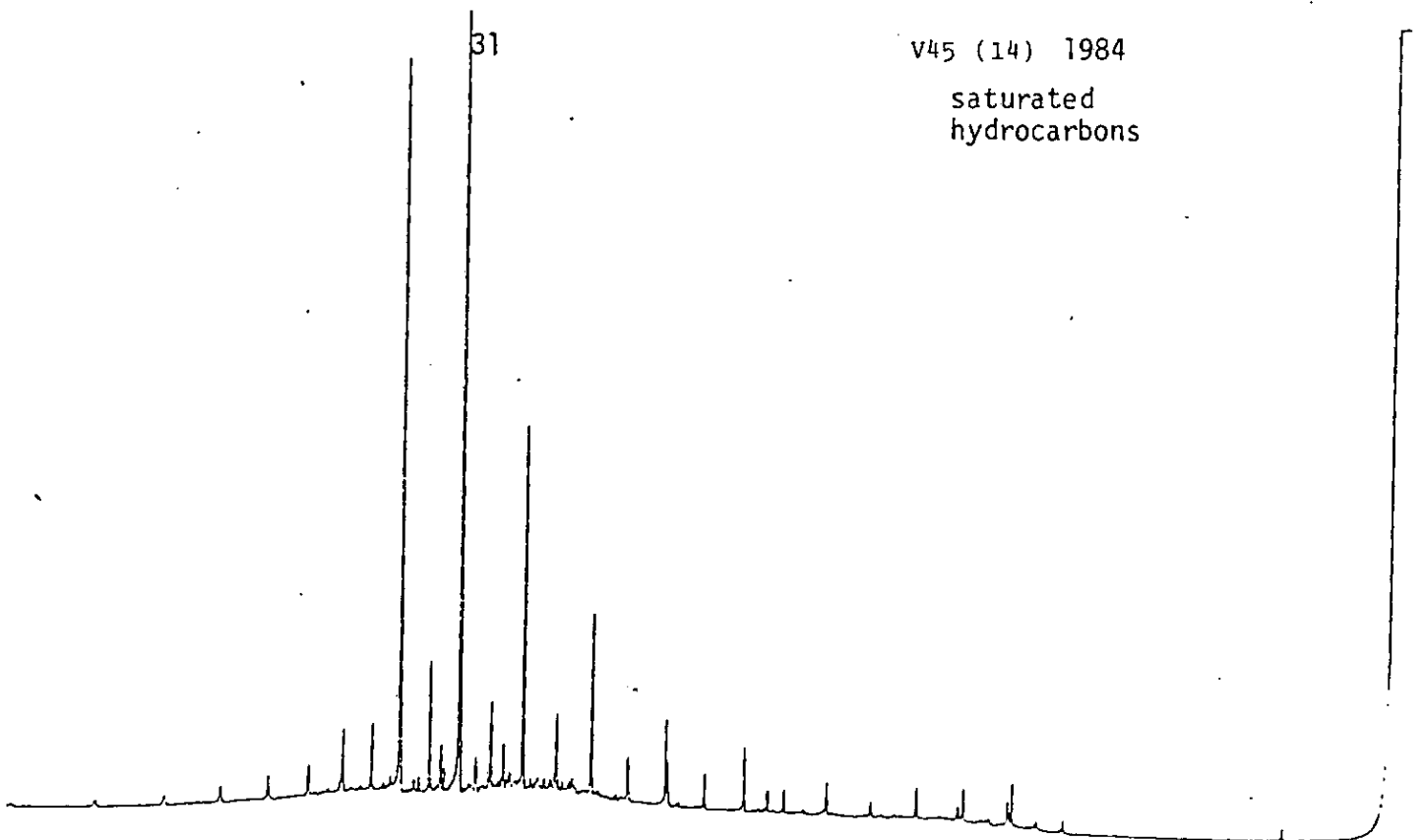


Fig.4.13

W27 (7) 1984
saturated
hydrocarbons

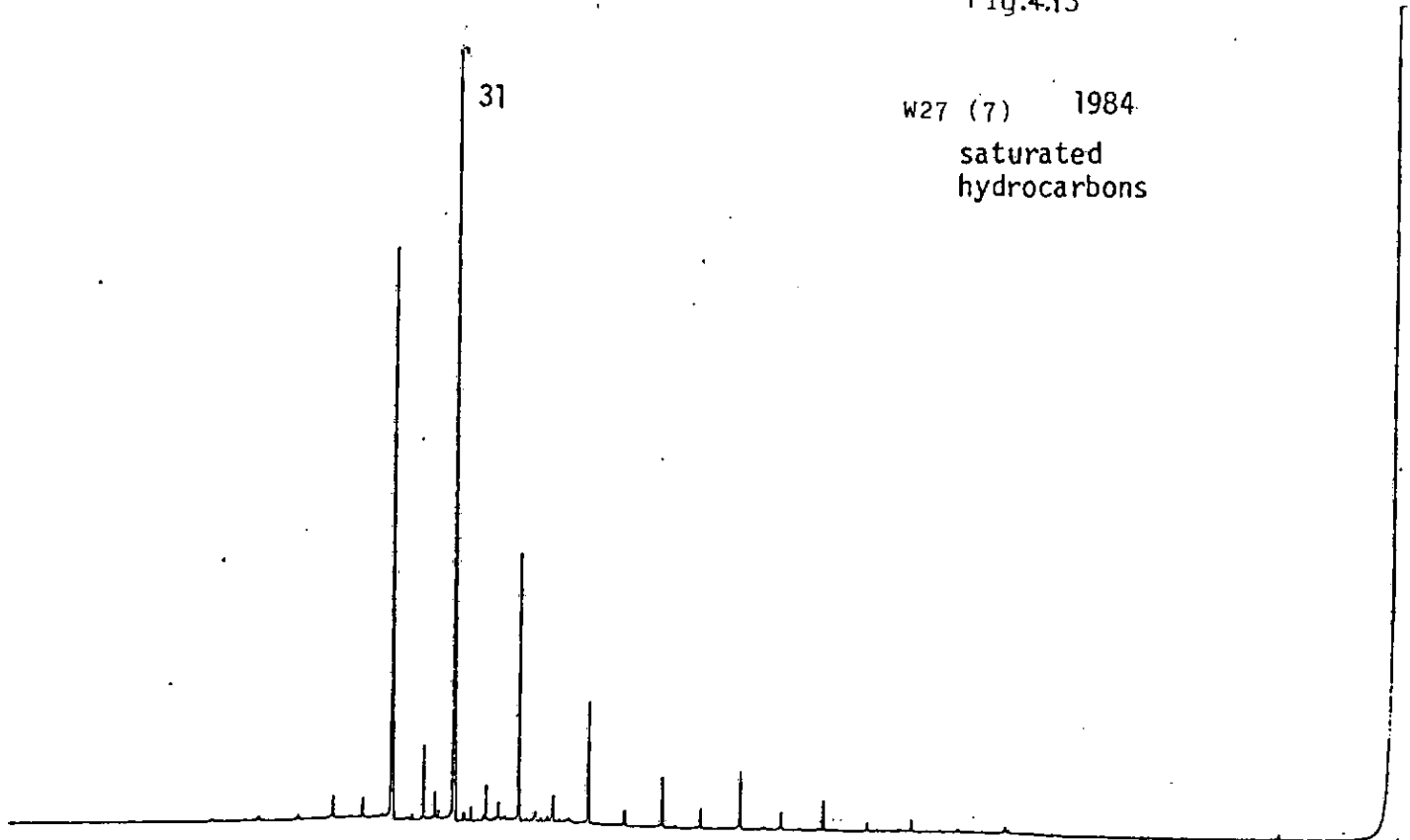


Fig.4.14

Z24 (6) 1984
saturated
hydrocarbons

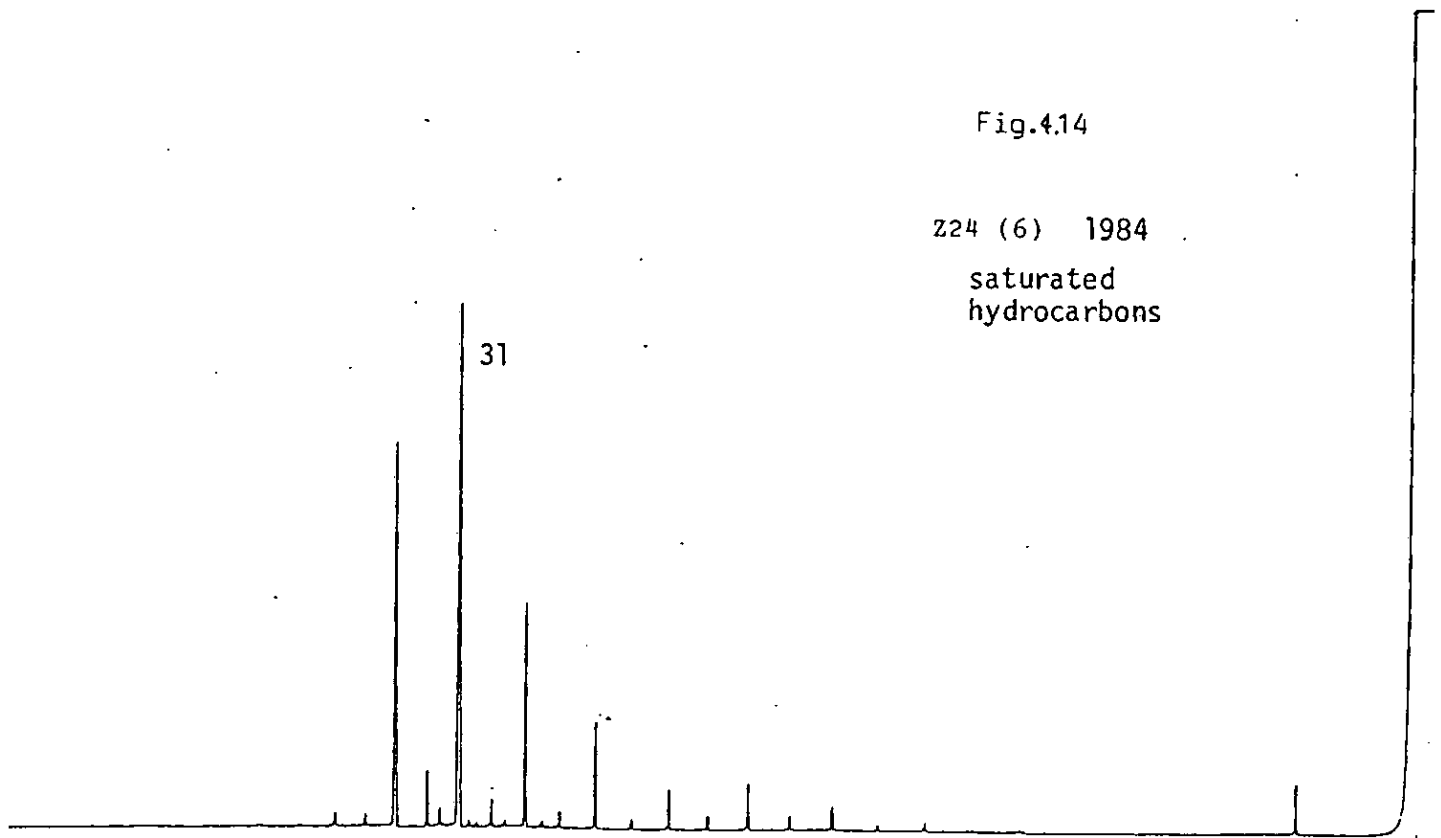


Fig 4.15

1 OV1 1984
saturated
hydrocarbons

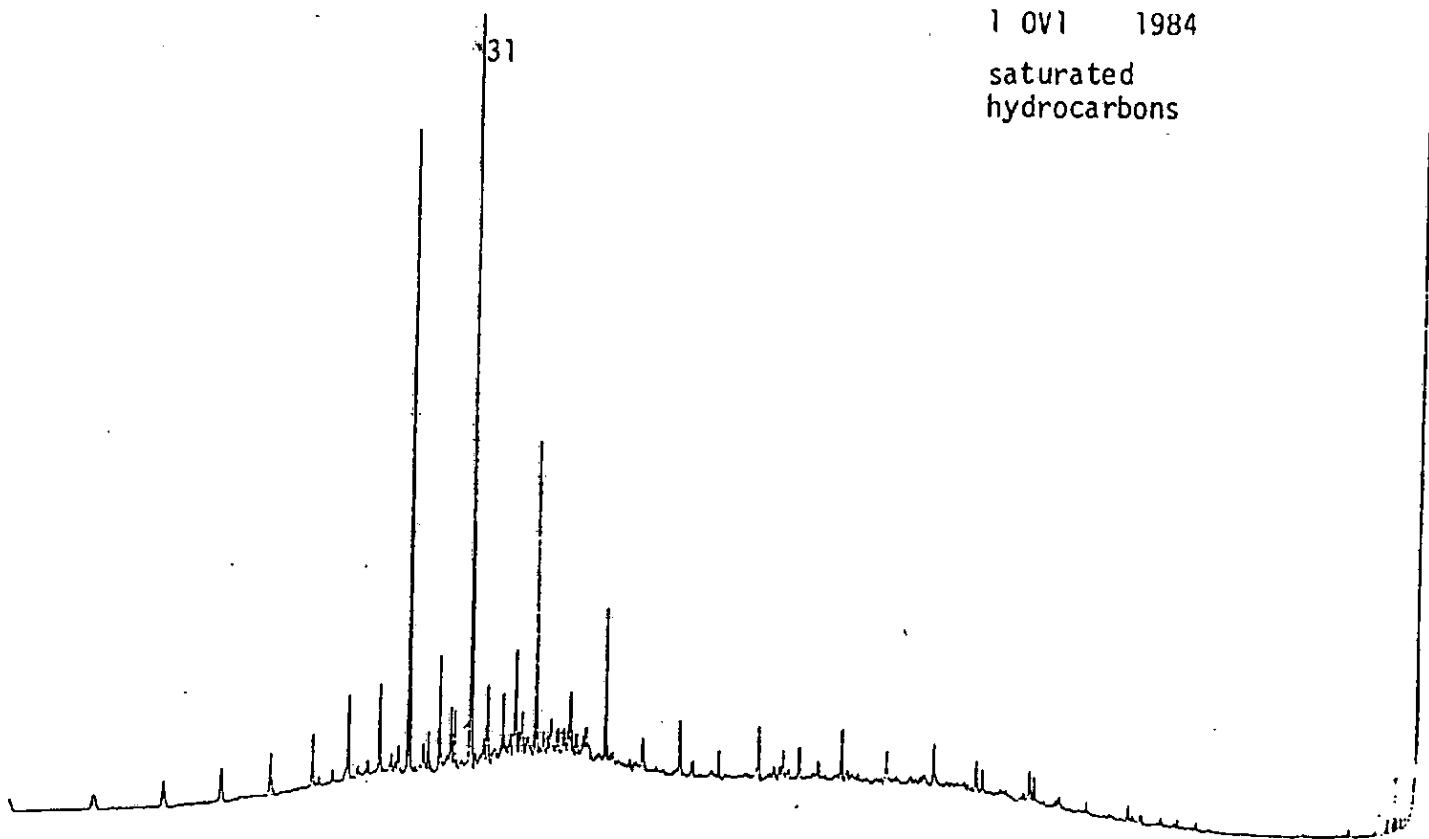


Fig.4.16

2 OV1 1984
saturated
hydrocarbons

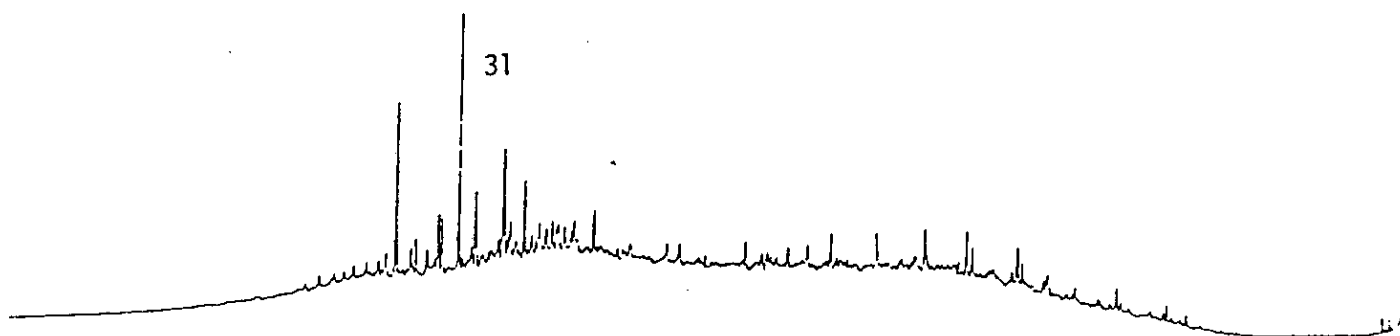


Fig.417

3 OV1 1984
saturated
hydrocarbons

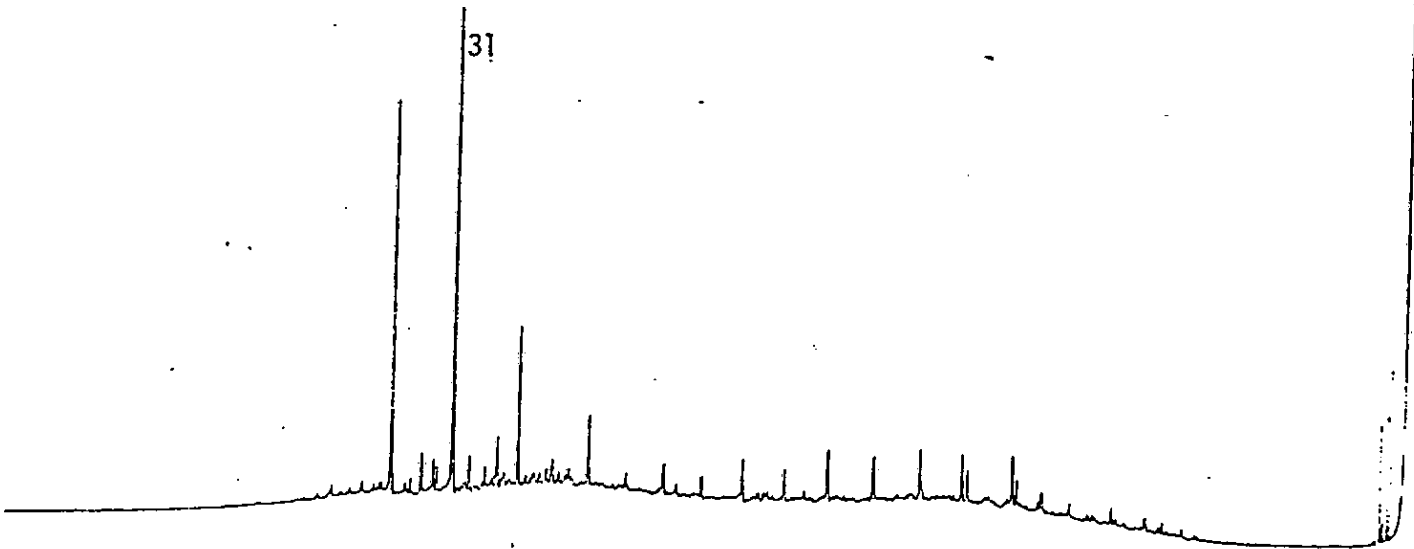


Fig.418

4 OV1 1984
saturated
hydrocarbons

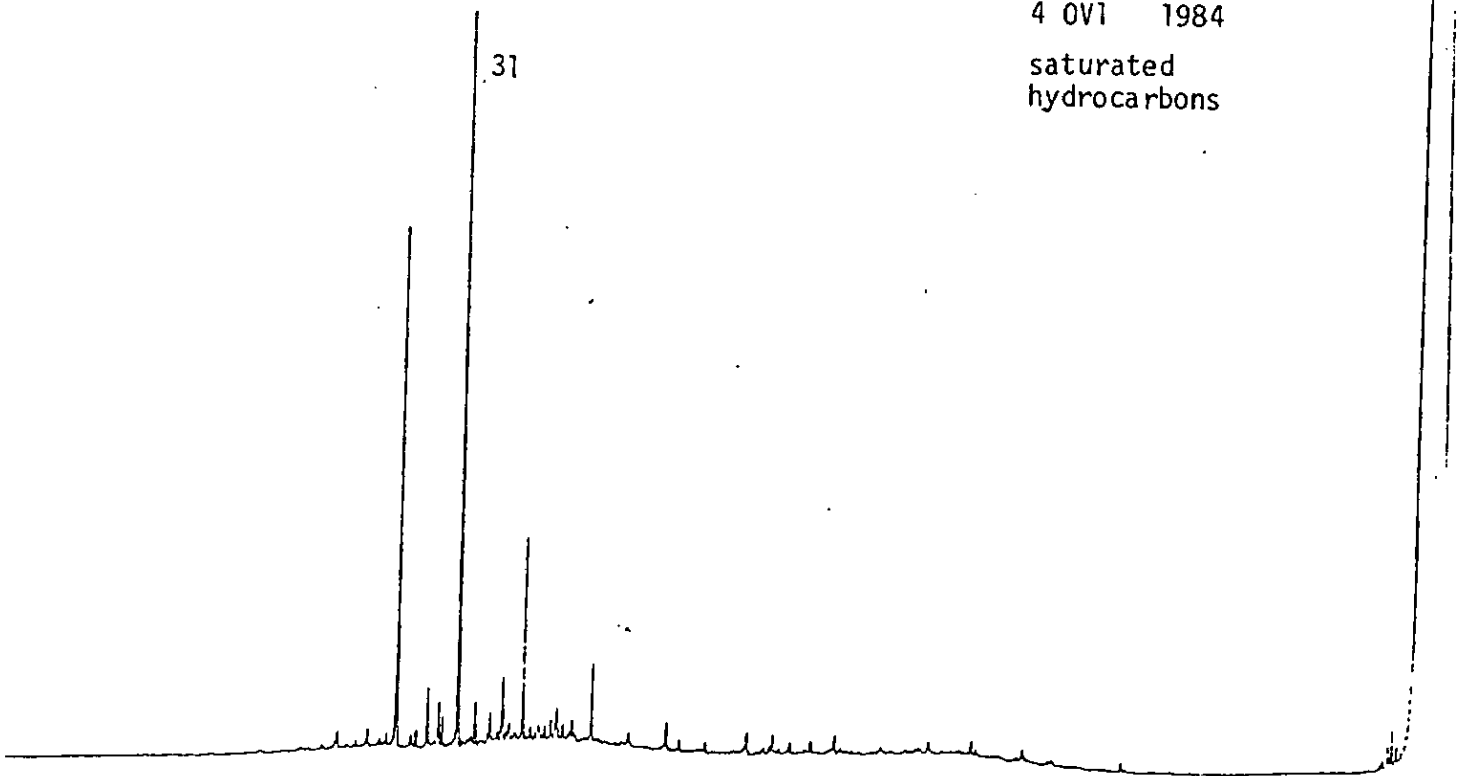


Fig.419

5 OV1 1984
saturated
hydrocarbons

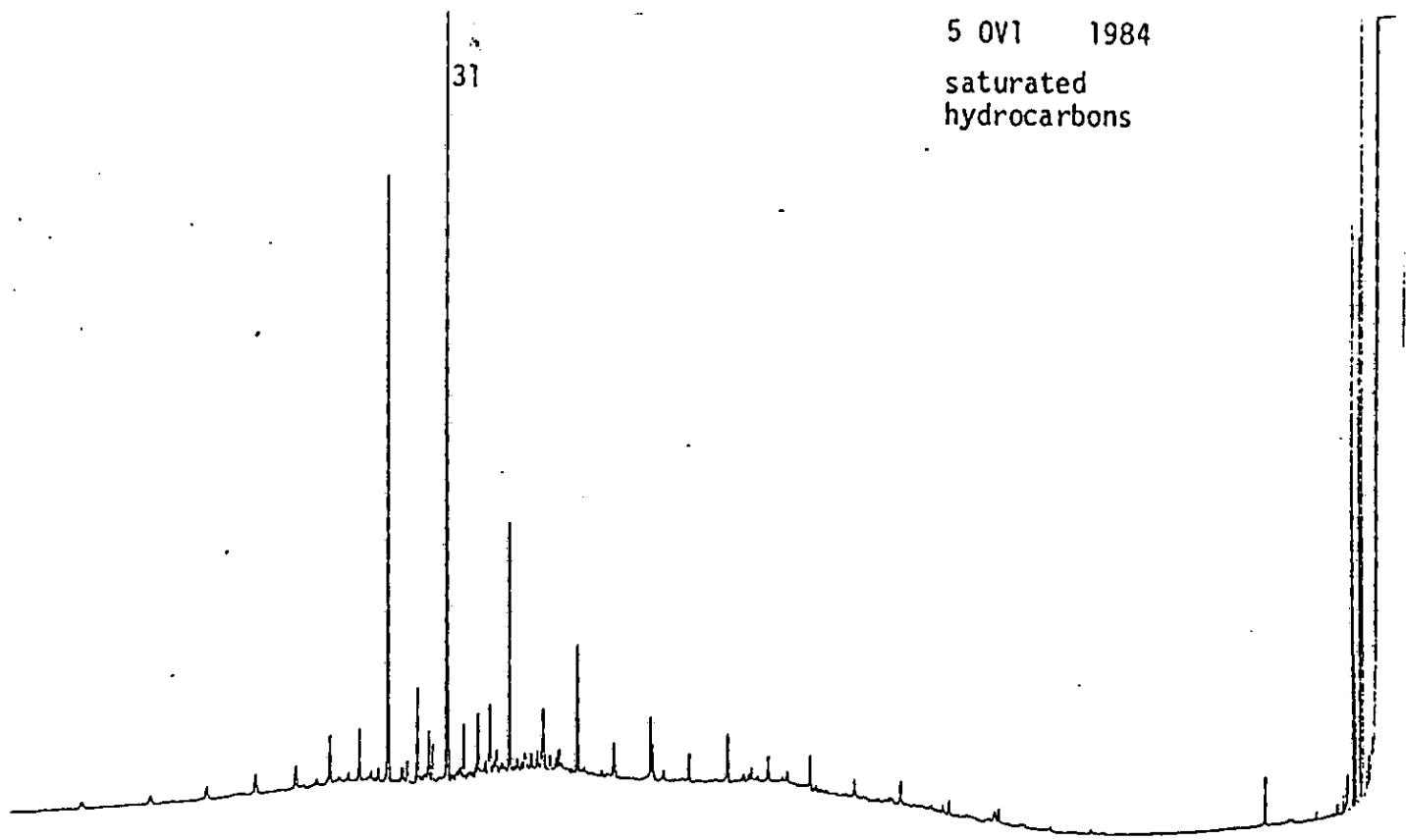


Fig.4.20

Dales Voe 1984
(Low Tide)
saturated
hydrocarbons

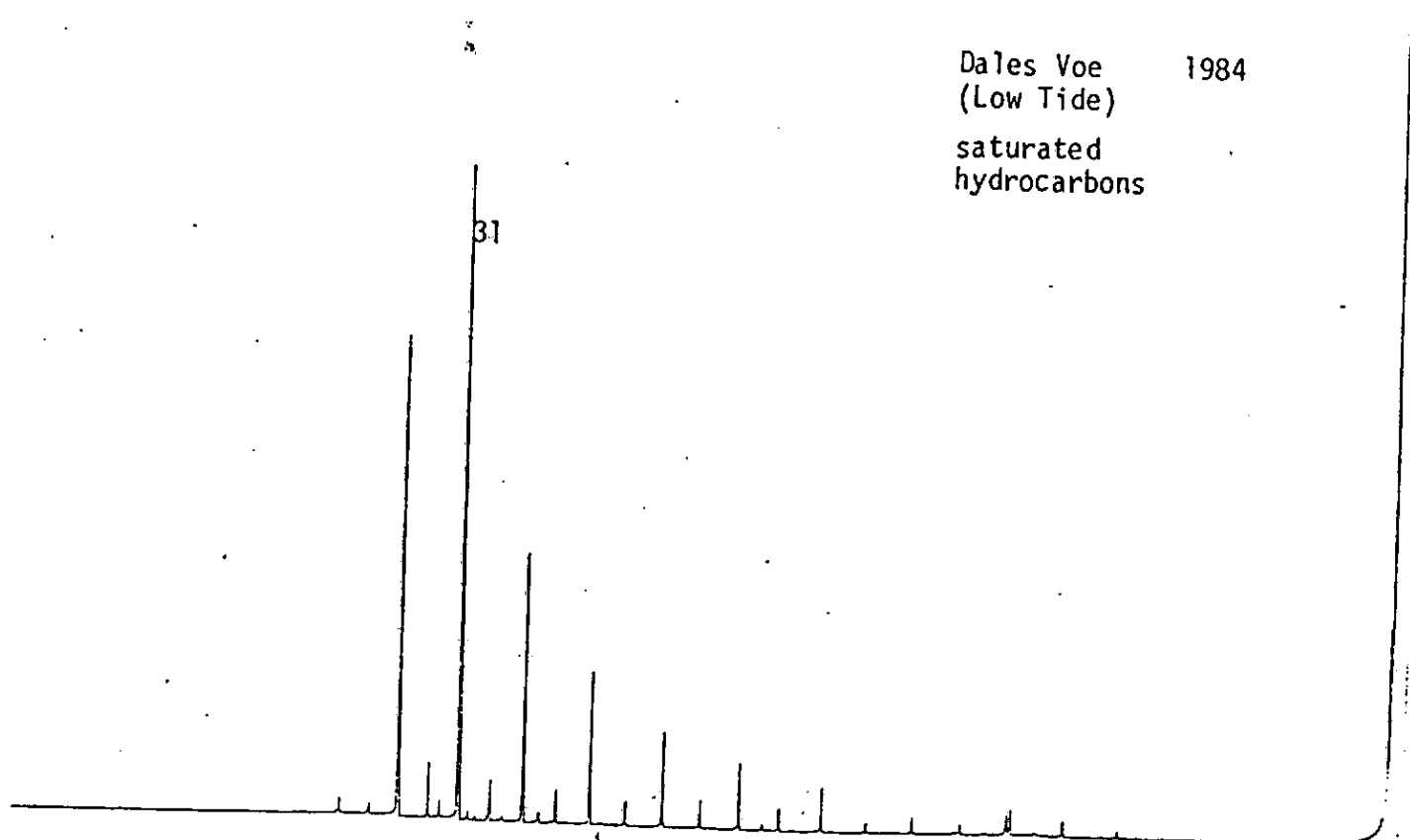


Fig.4.21

Dales Voe 1984
(High Tide)
saturated
hydrocarbons

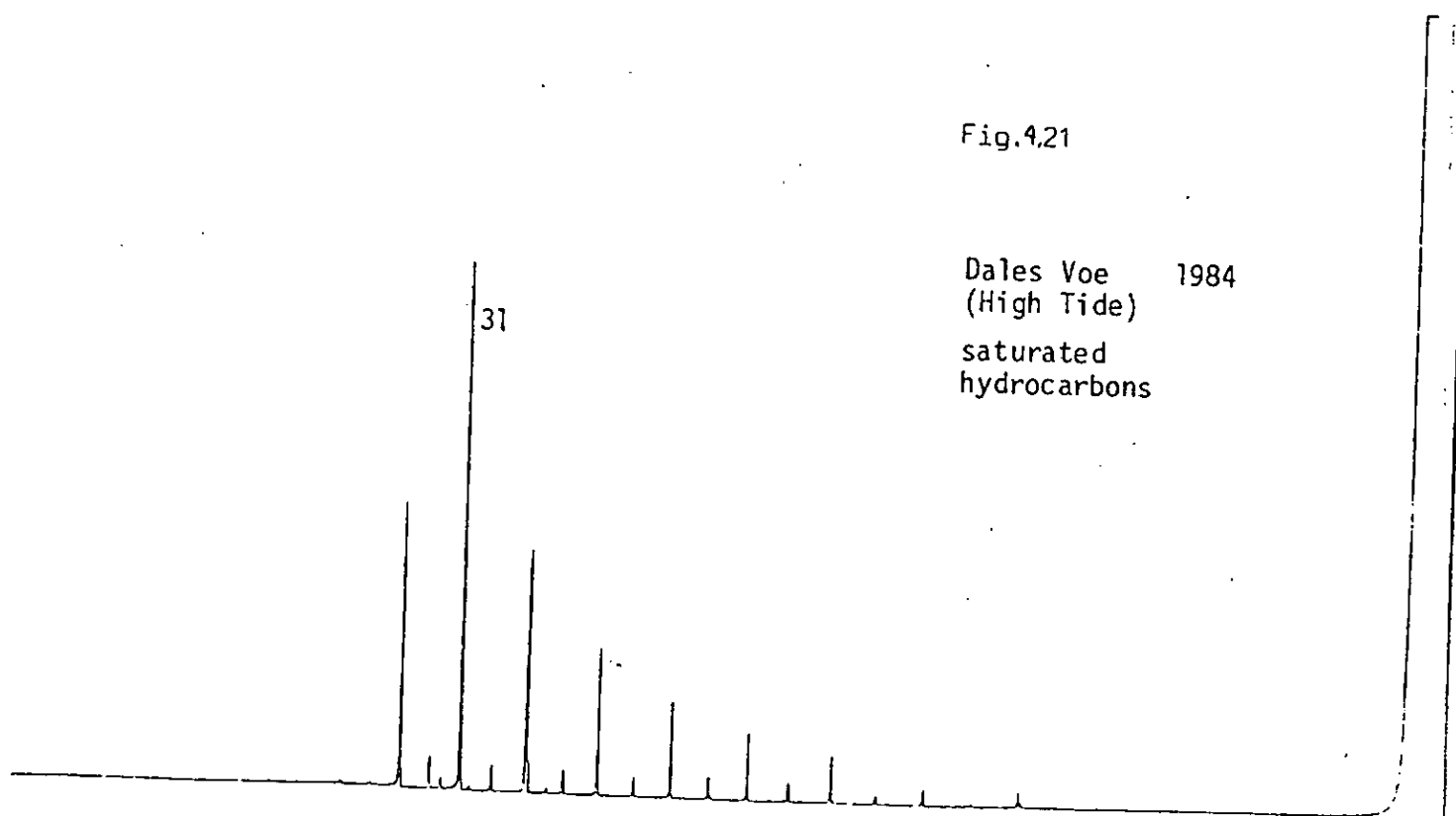


Fig.4.22

Gluss Voe 1984
(Low Tide)
saturated
hydrocarbons

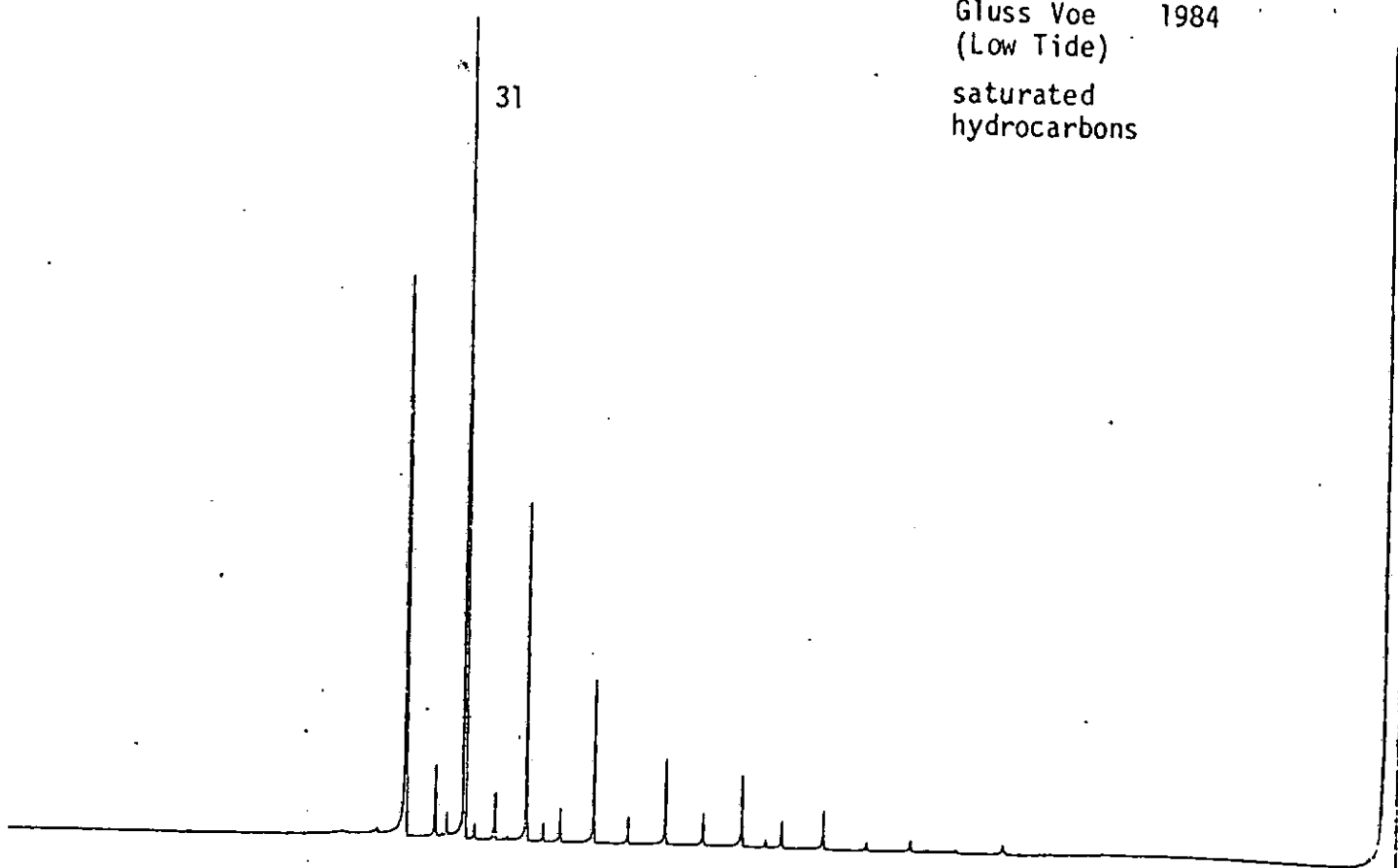


Fig.4.23

Gluss Voe 1984
(High Tide)
saturated
hydrocarbons

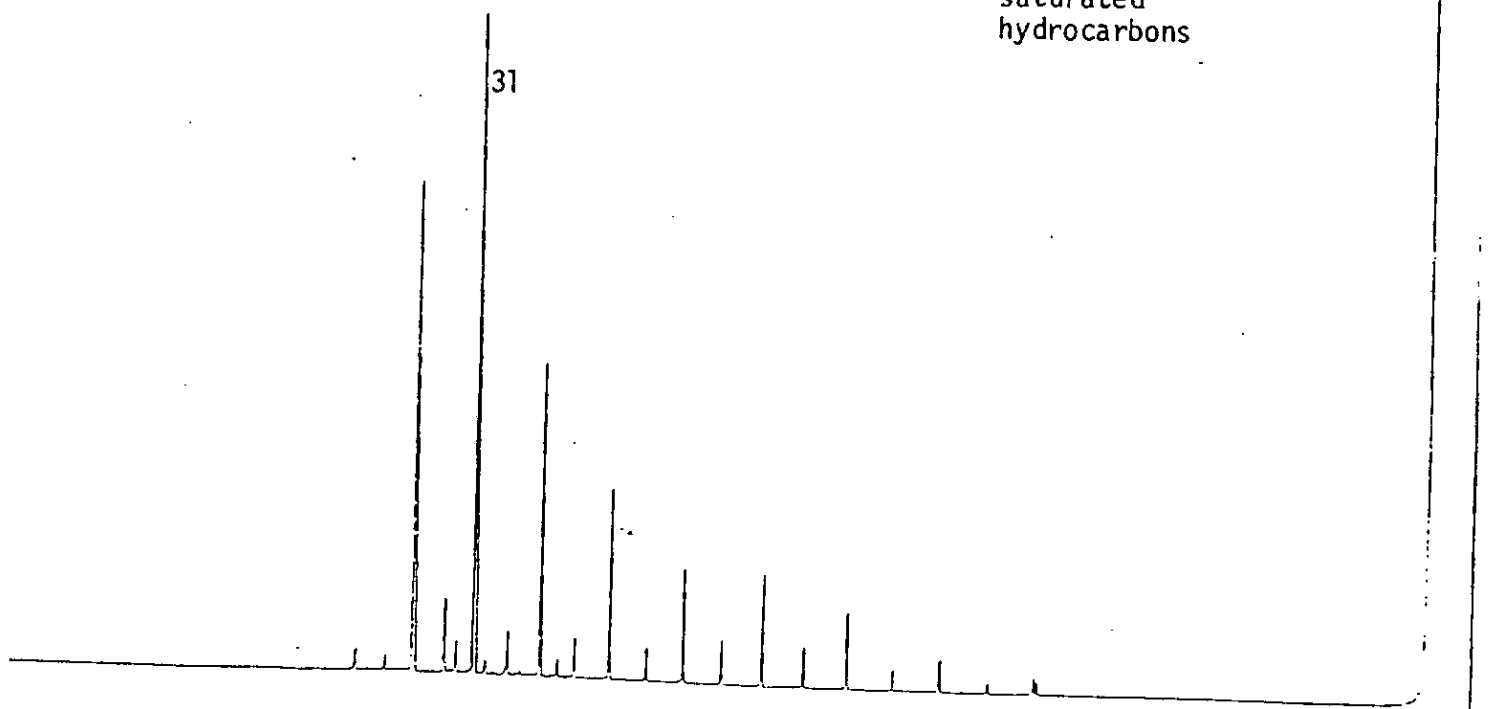


Fig 4.24

Houb Scatsa 1984
(Low Tide)
saturated
hydrocarbons

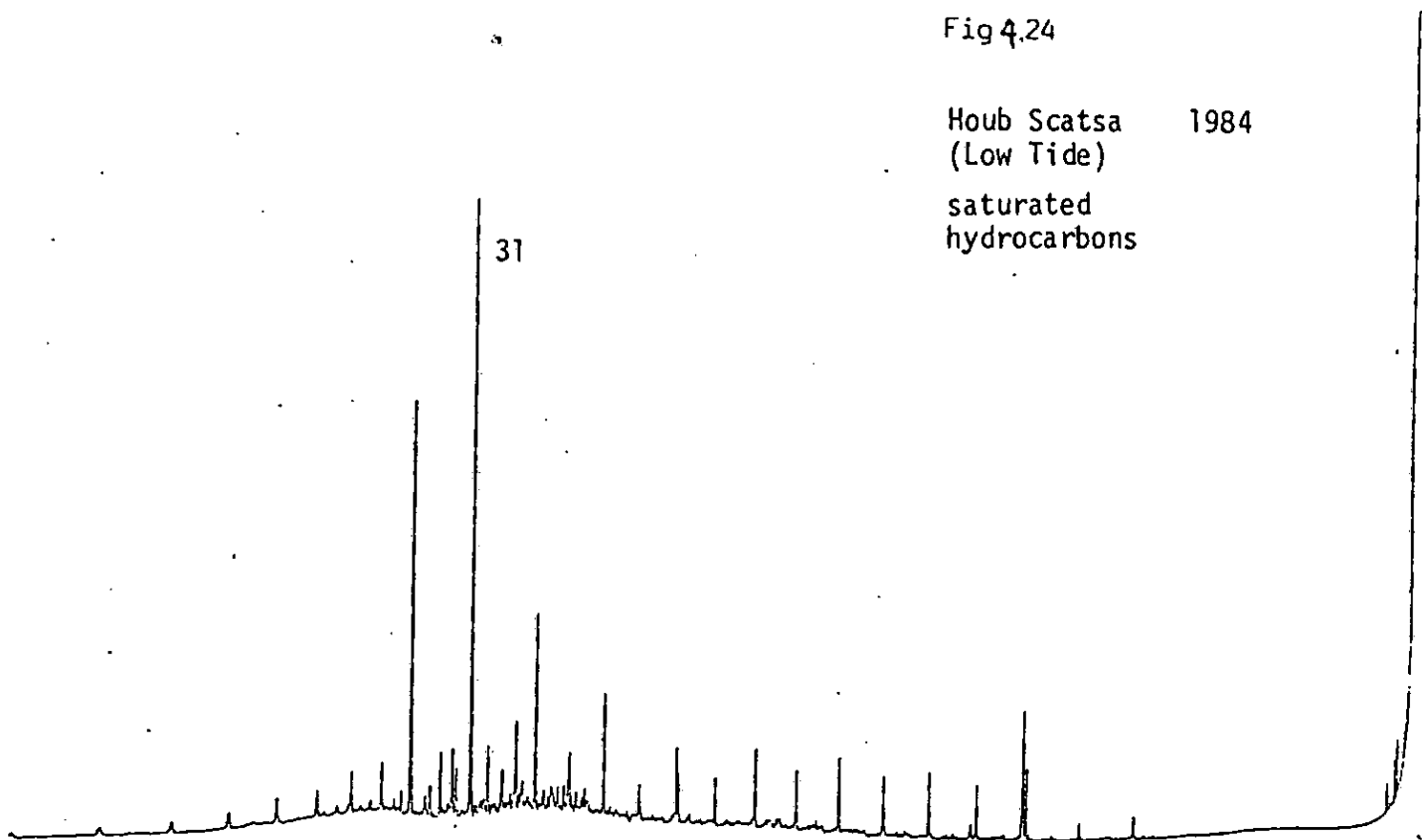
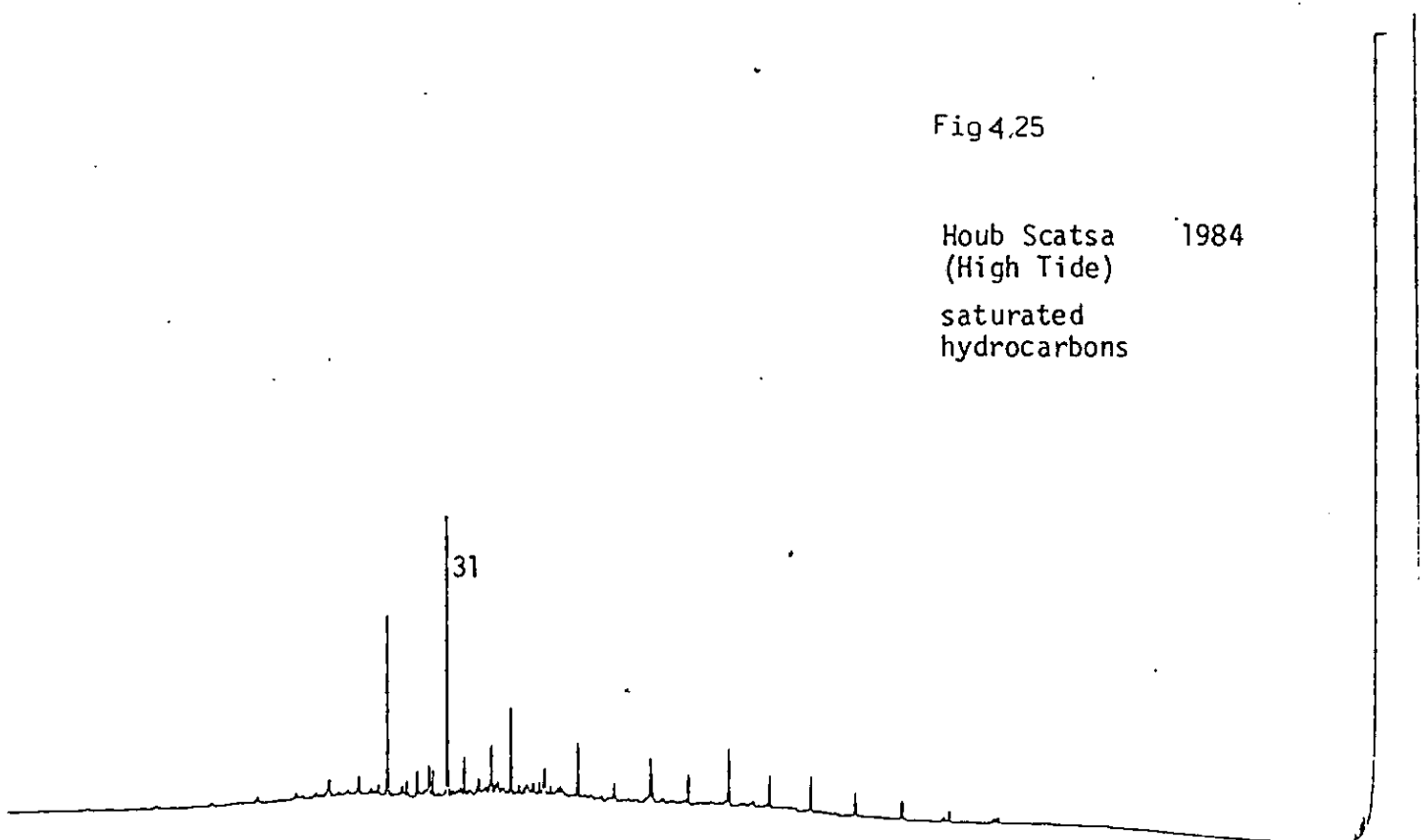


Fig 4.25

Houb Scatsa 1984
(High Tide)
saturated
hydrocarbons



Captions to figures :

Figures 4.26 to 4.34 Mass Chromatograms (M/Z = 191) of hydrocarbons
at selected sampling stations.

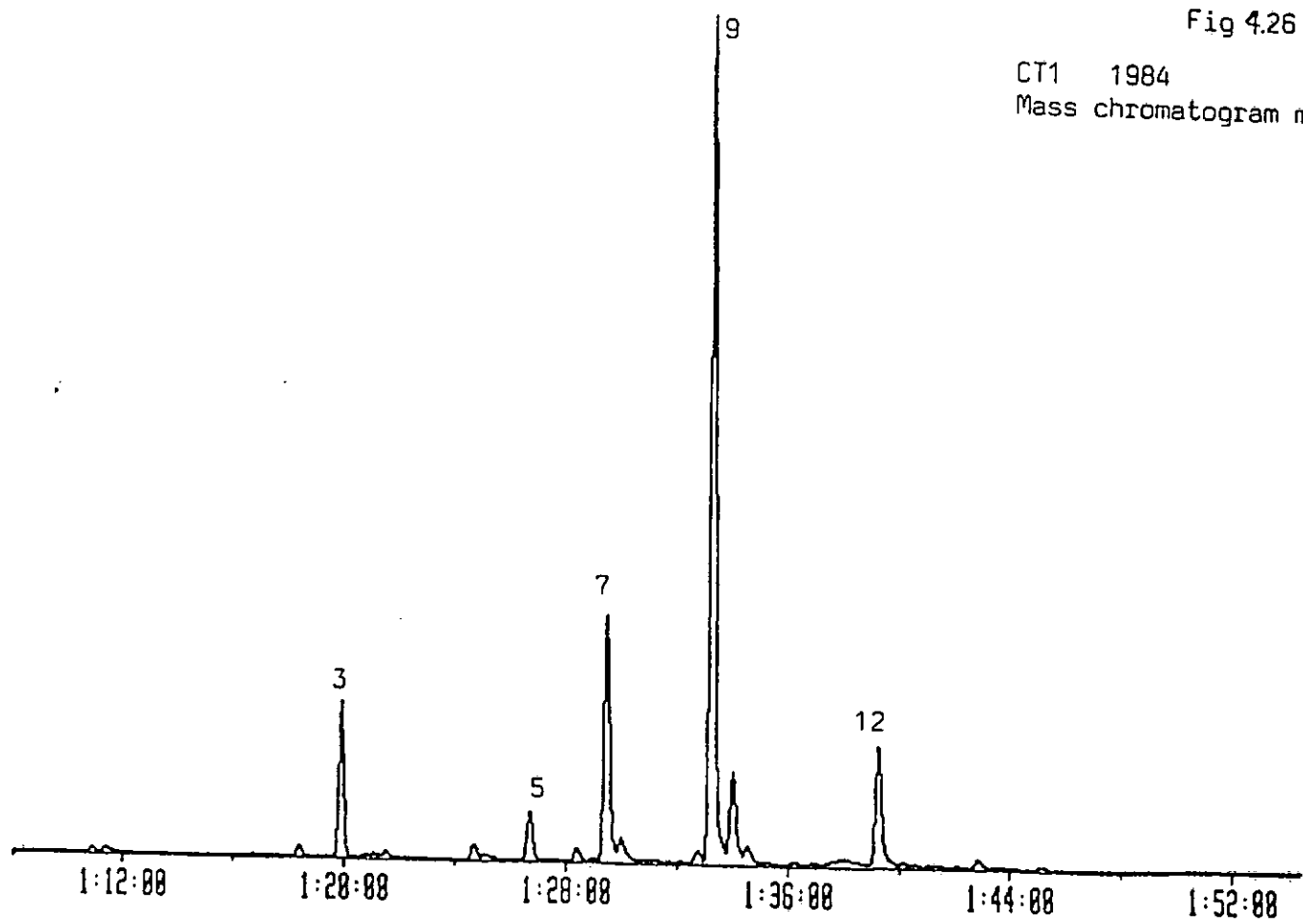


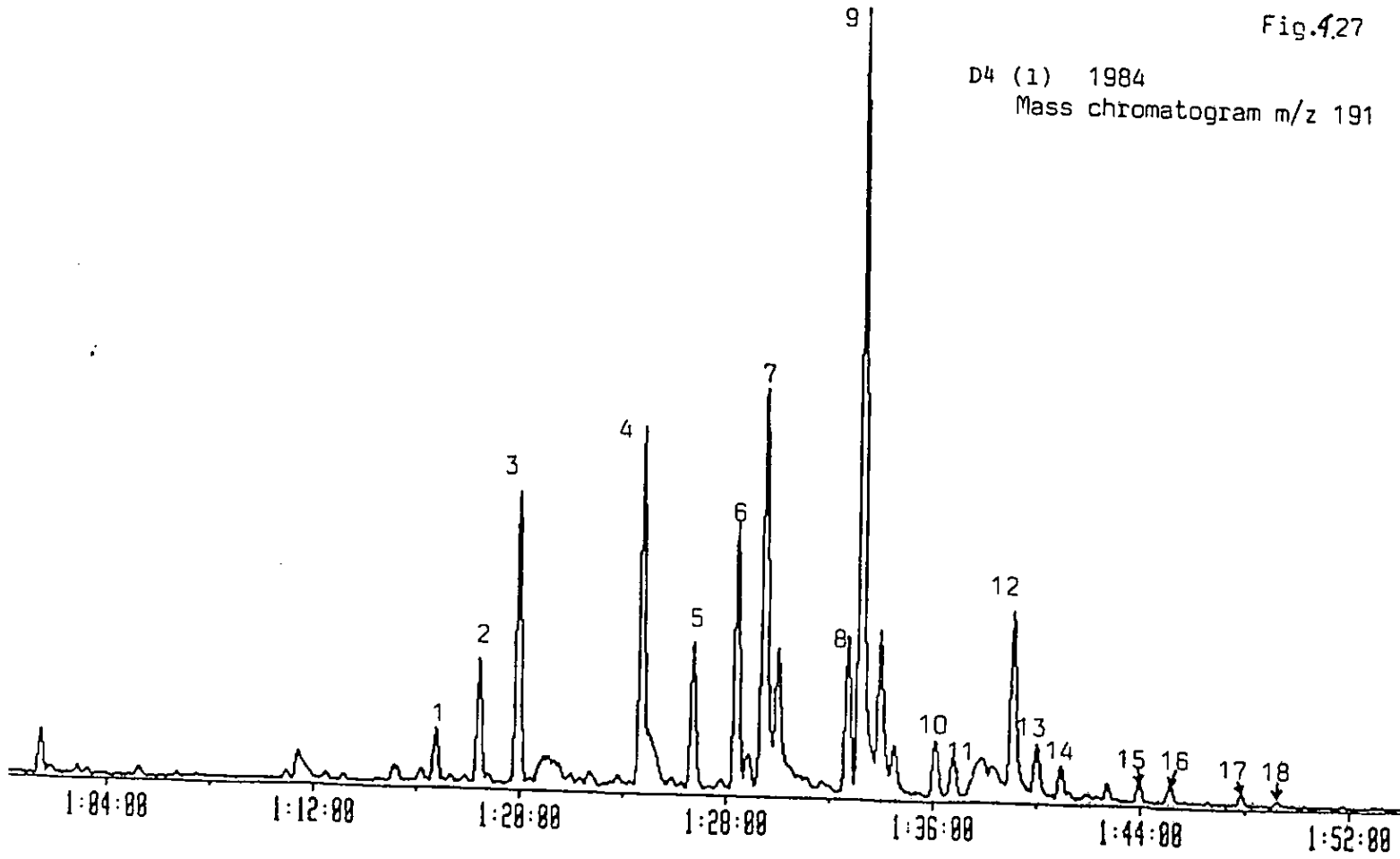
Fig 4.26

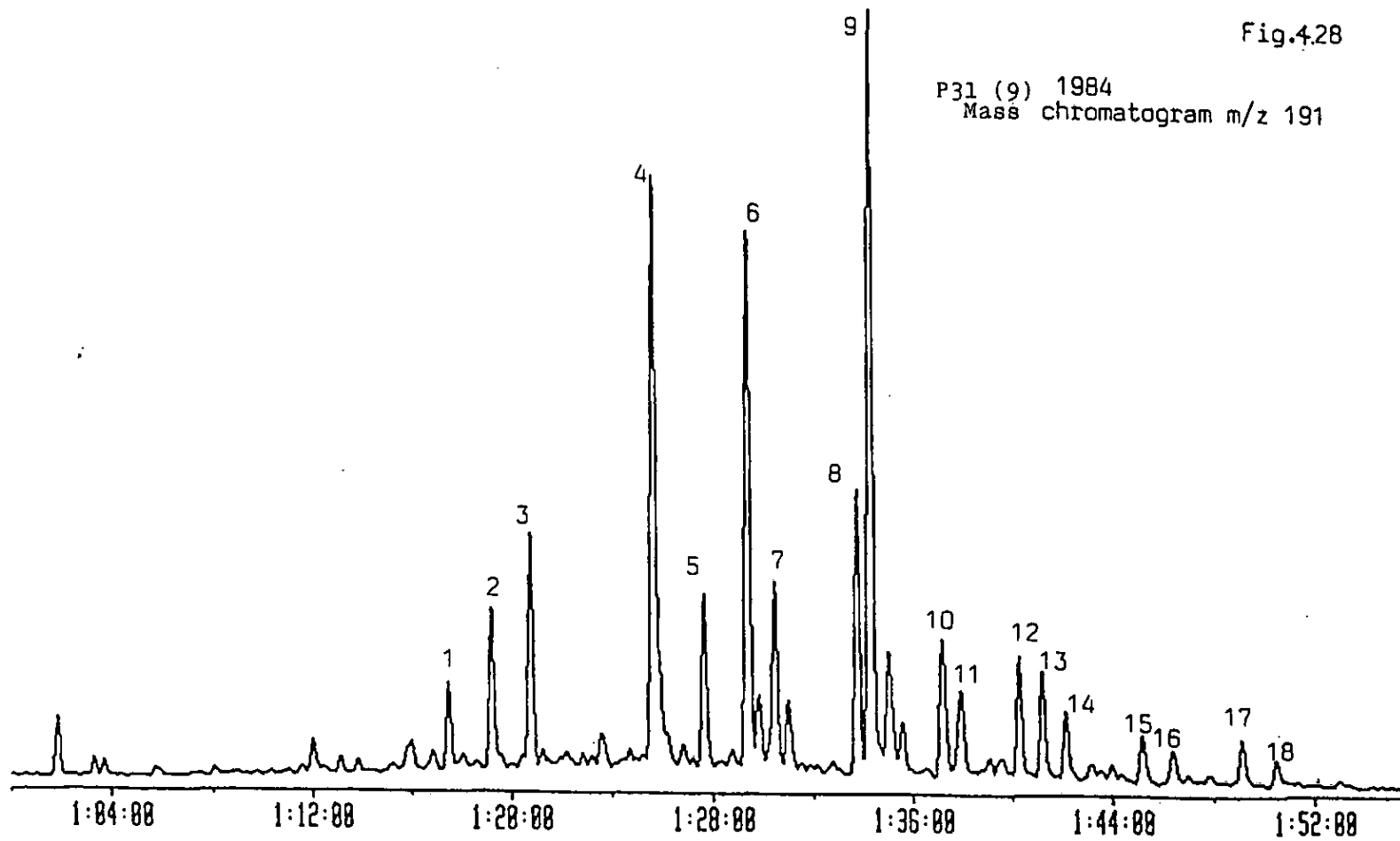
CT1 1984

Mass chromatogram m/z 191

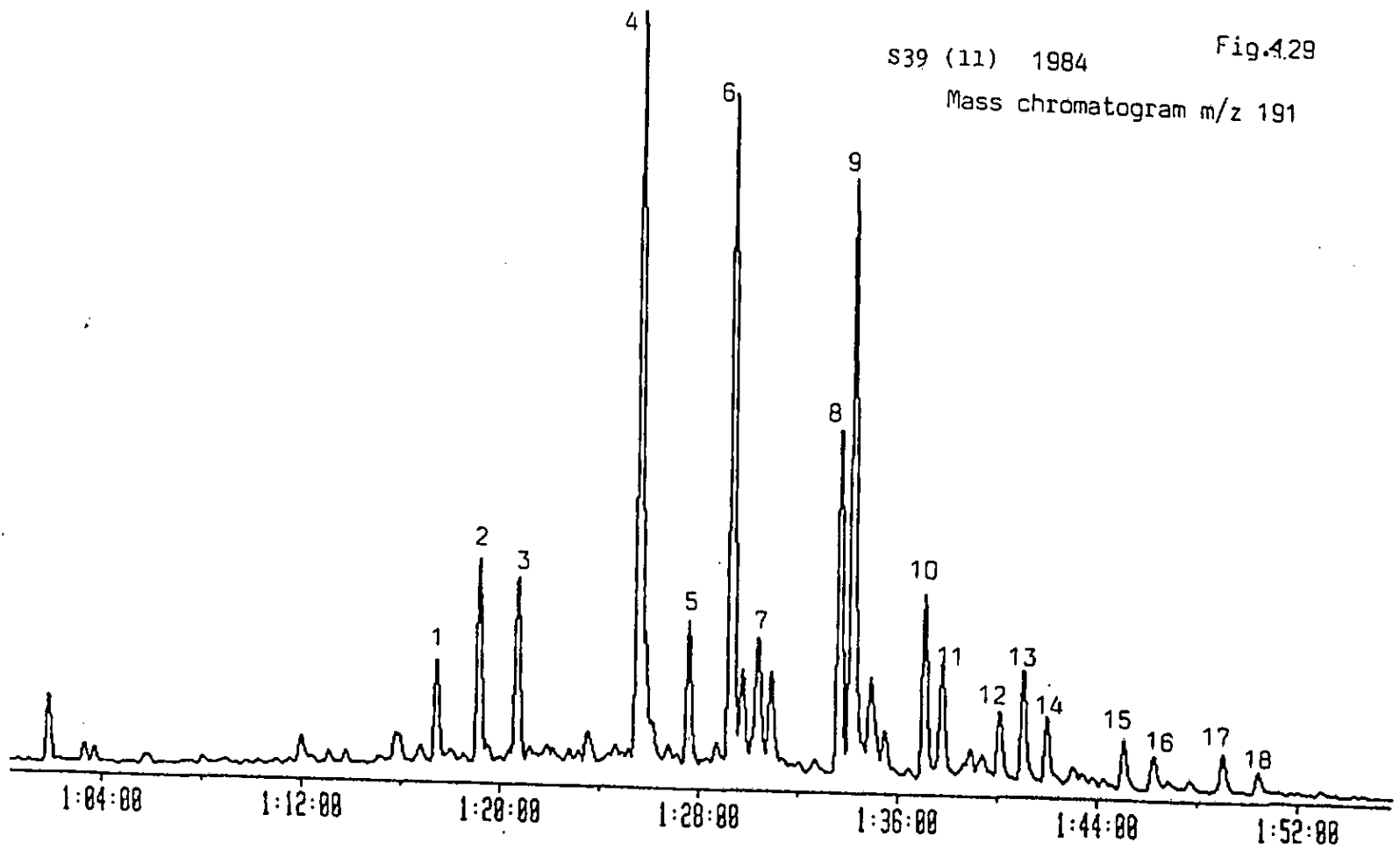
Fig.4.27

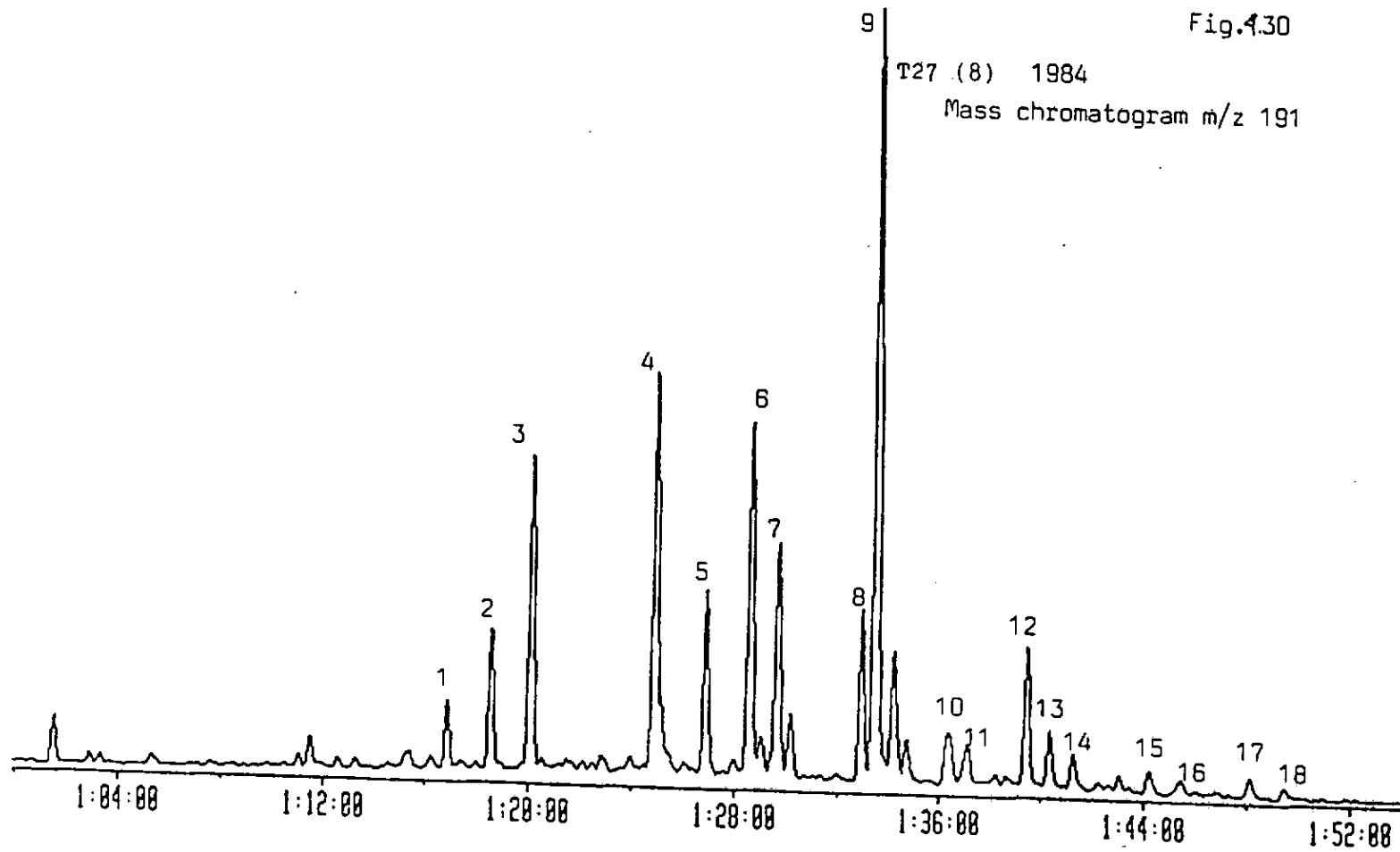
D4 (1) 1984
Mass chromatogram m/z 191





S39 (11) 1984 Fig.4.29
Mass chromatogram m/z 191





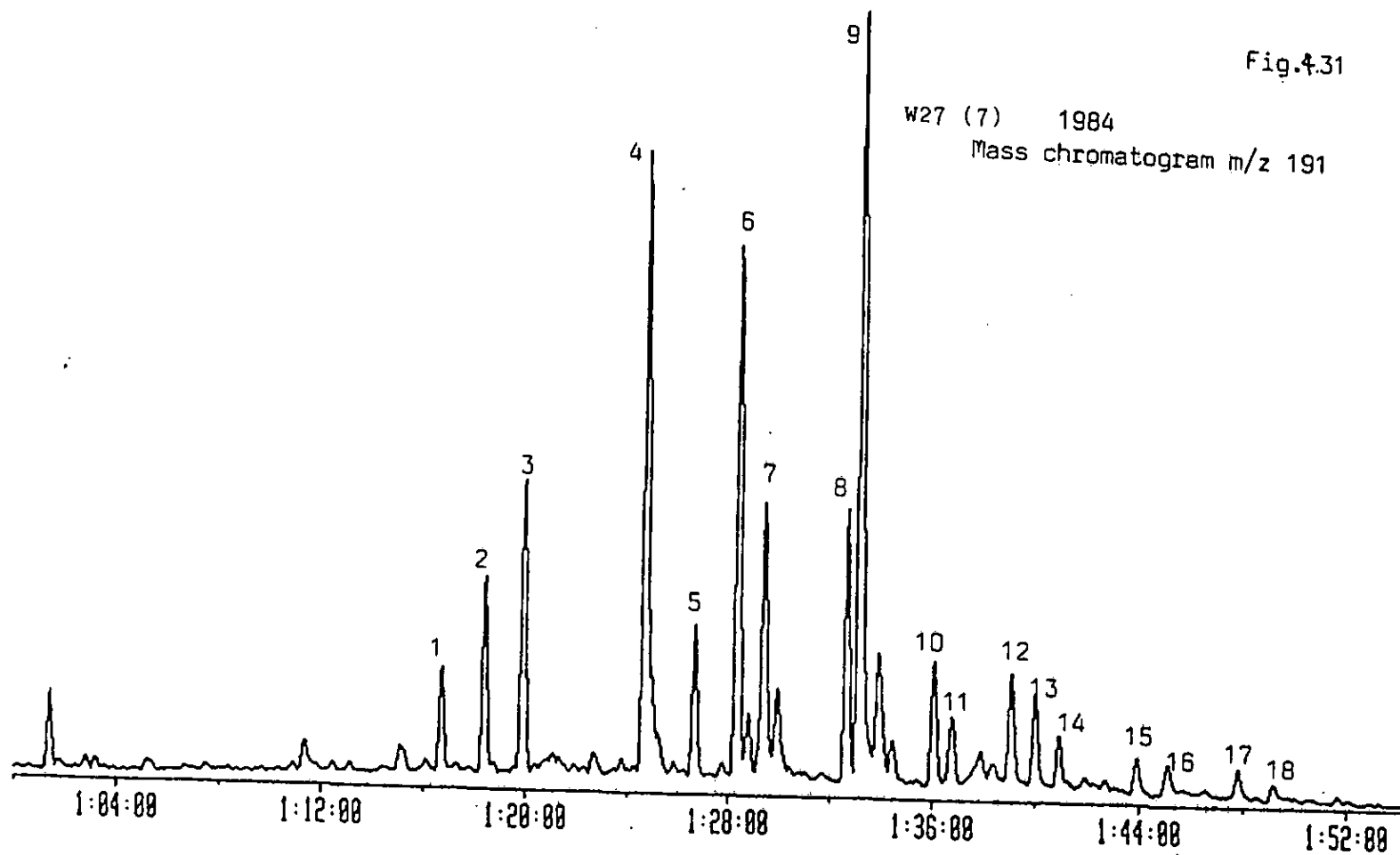
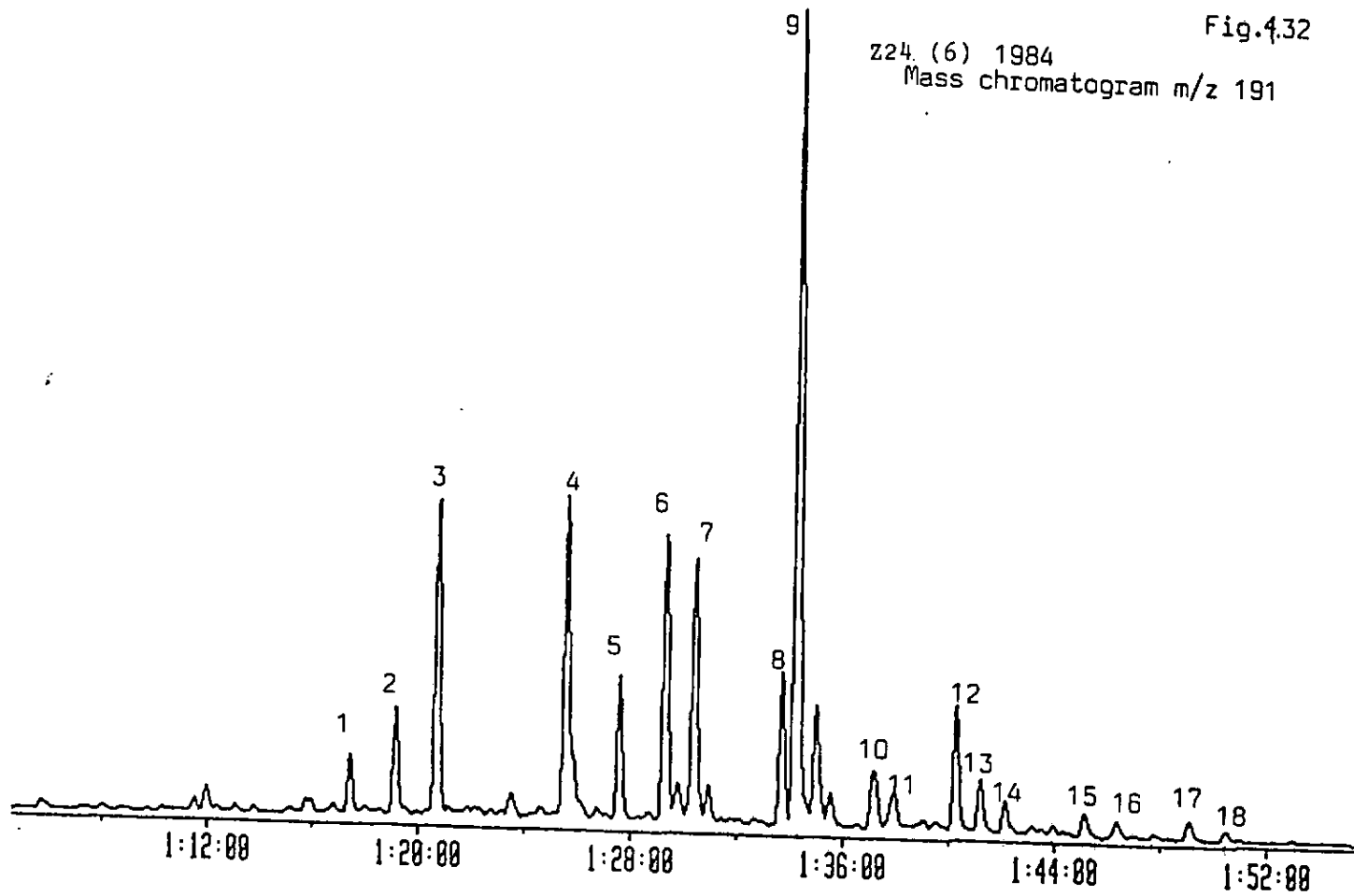


Fig.4.31

W27 (7) 1984

Mass chromatogram m/z 191



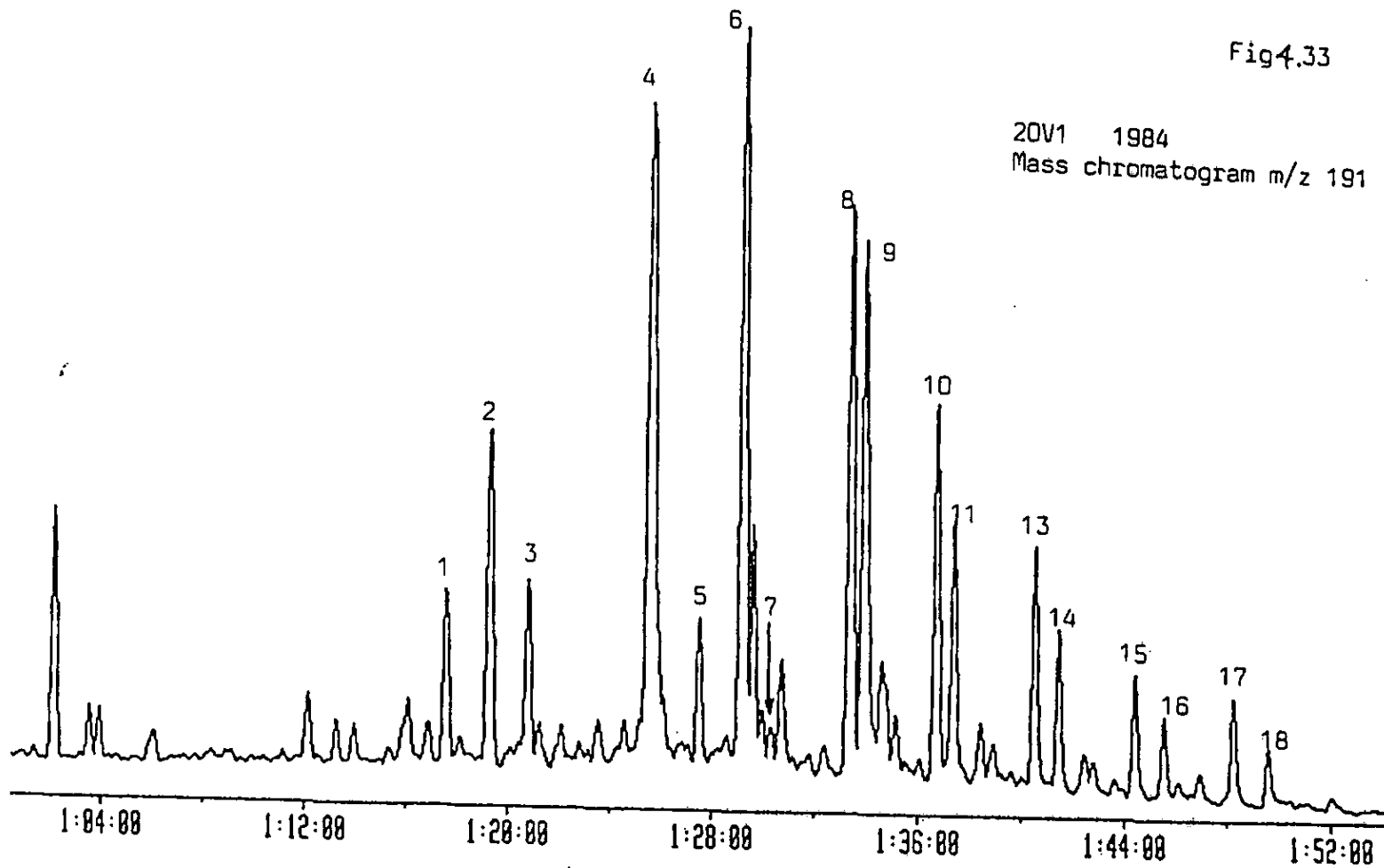
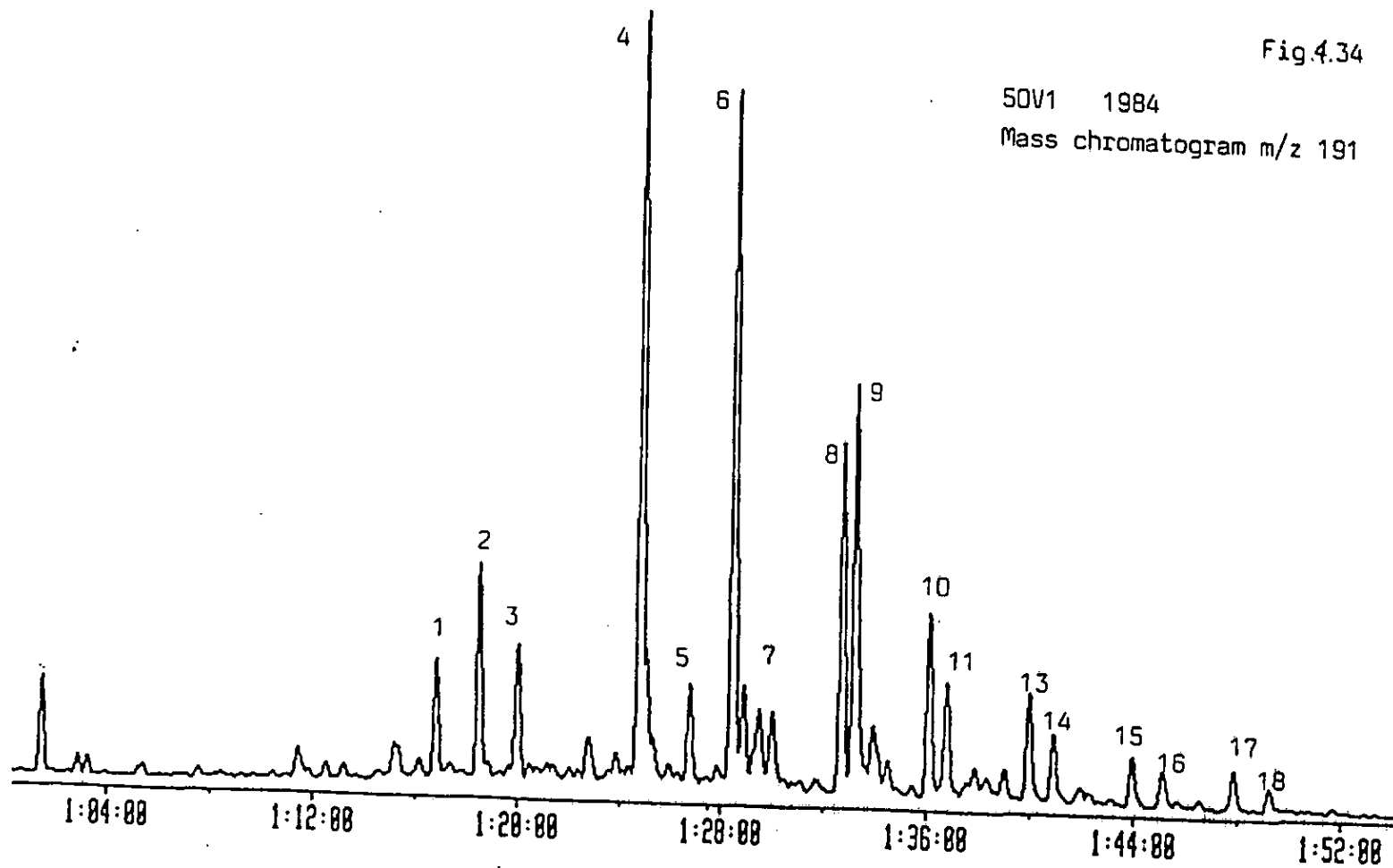


Fig4.33

20V1 1984
Mass chromatogram m/z 191



5. METALS IN SEDIMENTS

J. Blackstock & A. Maxwell

5.1 Introduction

Sediment samples from locations indicated in Table 1.1. were analysed by the Scottish Marine Biological Association. Sediments from eight stations were analysed in replicate to provide an indication of variation in metal content between different samples from the same locations. Sediment samples collected from shore sites at Dales Voe, Gluss Voe and Houb of Scatsta were also analysed.

5.2 Analytical methods

All estimations of metal concentrations were done by Atomic Absorption Spectrophotometry of acid digests of the sediment samples. The procedure for the analyses is detailed below.

5:2:1 Preparation of samples

Samples of sediment were collected with a Craib corer or a Day Grab. The upper 5 cm of sediment in the core samples were carefully extruded, mixed, transferred to a polythene bag and immediately frozen. Samples from Day grabs were taken from the centre of the grab with a polythene spatula and transferred to polythene bags for freezing. Prior to analysis the samples were freeze dried and then finely ground for 5 min in an agate cylinder in a ball mill. An accurately weighed portion of sediment (about 1 g) was used for the analyses.

To eliminate the possibility of contamination of the specimens, metal instruments were not used in any of the procedures detailed above and all laboratory ware was acid-washed.

5:2:2 /

5:2:2 Extraction of metals

All samples were digested four times in 10 ml of concentrated nitric acid at $74 \pm 0.7^\circ\text{C}$ (mean \pm S.E.). At each digestion with concentrated nitric acid the digest was evaporated to dryness. The residue remaining after the fourth digestion was extracted into 10 ml 1M nitric acid. After centrifuging to precipitate undissolved debris the supernatant fluid was transferred to a 10 ml volumetric flask and the volume was readjusted by addition of 1M nitric acid.

5:2:3 Analysis

The nitric acid extracts were analysed on an S.P.9 Atomic Absorption Spectrophotometer (Pye Unicam Ltd). For calibration, standard solutions containing 0.1-2.0 $\mu\text{g}/\text{l}$ of copper, nickel, zinc, lead, chromium and cadmium in 1M nitric acid were used.

A 'background correction' for non-specific absorbance was applied to the sediment atomic absorption analysis for all metals except chromium. This was achieved using a hollow cathode deuterium lamp which provided a uniform continuum spectrum. Absorption by chromium was outwith the wavelength range to which the 'background correction' was applicable.

5:2:4 Quality control

The 'quality control' system introduced in 1981 to facilitate assessment of variations between batches of analyses and to assist identification of analyses which may be in error has been continued. For this system use of the bulk preparation of pooled, freeze dried, sediments collected during the 1981 Sullom Voe Survey has continued. Two (occasionally three) /

three) 1 g portions of quality control sediment have been included with every batch of analyses of sediment samples.

The quality control analyses are summarised in Table 5:1 in which the 1983 'quality control' values are also shown. Student's 't' test was applied to the assessment of the significance of differences between the mean values found for each element in 1983 and 1984. Only mean lead concentrations are significantly different ($p < 0.05$). There were therefore no significant changes in mean copper, nickel, zinc, cadmium or chromium concentrations measured in the two consecutive years.

The decrease in mean lead concentration, from $9.1 \mu\text{g}\cdot\text{g}^{-1}$ in the 1983 group to $8.7 \mu\text{g}\cdot\text{g}^{-1}$ in the 1984 group, is not considered to represent a consistent trend towards decrease in the estimated lead concentrations because the mean lead concentrations measured in 1984 are not significantly different ($p < 0.05$) from that measured in 1982 ($9.0 \mu\text{g}\cdot\text{g}^{-1} \pm 0.7 \text{ S.D.}$). The observed fluctuation in mean lead concentrations in the quality control sediment are therefore not considered to be sufficiently large to merit further investigation at present.

5.3 Sediment metal concentrations

Metal concentrations in the sediments from Sullom Voe remained generally similar to those found in the previous years of the survey (Table 5:2). The highest concentrations continue to be measured in sediments from Garth's Voe (Z24 (6)) and at station D4 (1) near the head of Sullom Voe. At the former station there is, however, evidence of a statistically significant decrease in mean copper sediment concentrations from $25.4 \mu\text{g}\cdot\text{g}^{-1}$ to $19.3 \mu\text{g}\cdot\text{g}^{-1}$ and mean chromium concentrations have increased from $45.8 \mu\text{g}\cdot\text{g}^{-1}$ in 1983 to $70.4 \mu\text{g}\cdot\text{g}^{-1}$ in 1984. At station D4 (1) a slight increase /

increase in copper concentrations from 18.8 ug.g^{-1} to 21.2 ug.g^{-1} was statistically significant ($p < 0.02$, student's 't' test) and there was an increase in zinc concentrations from 76.8 ug.g^{-1} in 1983 to 96.1 ug.g^{-1} in 1984. At station I19 (4), however, copper and nickel concentrations were lower than those measured in 1983.

Relatively high metal concentrations also persisted at Cat Firth (station CT1) outwith Sullom Voe but, with the exception of a small increase in chromium concentrations (from 21.7 ug.g^{-1} in 1983 to 27.4 ug.g^{-1} in 1984) there were no significant changes in metal concentrations in Cat Firth sediments since 1983.

Sediments were collected onshore at Dales Voe, Gluss Voe and Houb of Scatsta at sites selected by Dr Alan Jones of Dundee University. Metal concentrations in these samples are shown in Table 5:3. In the shore sediments from all the sites copper concentrations were somewhat lower than those measured in 1983. In addition nickel and zinc concentrations were lower and chromium concentration higher, than those measured in shore sediments from Houb of Scatsta in 1983. In all the shore sediment samples, however, metal levels were relatively low in both years and the noted changes may have little environmental significance.

Analyses of sediments from sampling stations in Orka Voe and in the channel at the entrance to Orka Voe (stations AA44 (15) and CC45 (16)) are summarised in Table 5:4. At station 20VI metal concentrations have increased to levels similar to that measured in 1981. At station 30VI concentrations of copper, nickel, lead, zinc and chromium are all intermediate between concentrations measured in sediments collected from this location in 1982 and 1983. Metal concentrations vary considerably between /

between replicate sediment samples from station 30VI (see Table 5:5) and the distribution of metals in the sediments from this area may now be rather patchy; the mean metal concentrations measured in 1984 do not differ significantly from those measured at this location in 1983 ($p < 0.05$, Student's 't' test). Further replication of the estimates of metal concentrations in sediments from Orka Voe is therefore required to allow valid statistical assessment of temporal changes in metal concentrations at the most affected location (20VI). At 500 m from the Bund and beyond (stations 40VI, 50VI, AA44 (15) and CC45 (16)) metal concentrations have consistently remained at relatively low levels.

Metal concentrations in five replicate sediment samples collected at each of eight sampling stations are listed in Table 5:5. With the exception of the relatively high variation in concentrations at station 30VI (see above) and in the zinc concentrations at station I19 (4), there are few indications of patchiness of sediment metal concentrations.

Table 5:1 Analyses of quality control sediment (QCl) in batches of analyses of Sullom Voe sediment samples collected in 1983 and 1984. Mean values (\bar{x}), standard deviation and 95% confidence limits (95%CL) are shown together with the number of individual portions of sediment analyzed (n). 'Background correction' was applied to all analyses except chromium.

Element	1983				1984			
	n	\bar{x}	S.D.	95% C.L.	n	\bar{x}	S.D.	95% C.L.
Copper (Cu)	37	9.7	0.6	9.5 - 9.9	13	9.4	0.8	8.9 - 9.9
Nickel (Ni)	35	14.0	1.1	13.6 -14.4	13	13.8	1.3	13.0 -14.6
Lead (Pb)	38	9.1	0.6	8.9 - 9.3	14	8.7	0.7	8.3 - 9.1
Zinc (Zn)	37	34.5	5.2	32.8 -36.2	14	35.1	4.0	32.8 -37.4
Cadmium (Cd)	40	< 0.1 (obs. range 0 - 0.3)			13	< 0.1 (obs. range 0 - 0.1)		
Chromium (Cr)	34	31.9	3.9	30.5 -33.3	14	31.0	4.4	28.4 -33.6

Table 5.2: Metal concentrations ($\mu\text{g}\cdot\text{g}^{-1}$ dry wt) in sediments after extraction in nitric acid. Mean values from 5 replicate samples are indicated by *.

Station	Year	Cu	Ni	Pb	Zn	Cd	Cr
D4 (1)	1979	18.4	26.9	31.8	75.8	0.9	47.2
	1980	18.1	29.7	26.8	74.5	1.1	53.8
	1981*	18.2	25.7	34.9	69.4	0.7	58.0
	1982*	21.0	28.8	28.2	81.2	1.1	59.4
	1983*	18.8	30.3	30.6	76.8	0.5	53.3
	1984*	21.2	27.8	30.6	96.1	0.8	50.9
H13 (3)	1979	8.2	13.2	10.1	33.8	0.7	25.9
	1980	5.7	14.7	7.4	27.5	nd	22.9
	1981	9.4	15.6	13.4	39.5	0.2	26.9
	1982	6.1	12.7	11.2	28.9	nd	22.8
	1983	6.0	10.9	9.1	32.3	nd	26.4
	1984	8.5	15.2	13.6	38.6	0.4	27.5
H19 (4)	1979	7.2	13.0	11.6	35.1	0.3	22.6
	1980	6.2	8.8	8.0	24.3	0.1	28.0
	1981*	5.8	10.1	9.6	27.5	nd	36.0
	1982	11.8	16.2	13.7	46.2	0.4	28.8
	1983*	11.7	22.2	13.8	37.4	nd	25.7
	1984*	6.0	9.4	10.8	32.4	0.2	22.6
O23 (5)	1979	7.5	10.4	17.0	27.8	0.1	18.1
	1980	9.1	13.2	12.0	46.6	0.2	27.7
	1981	6.5	9.0	7.9	18.5	0.3	26.0
	1982	7.3	9.9	11.9	32.8	nd	22.4
	1983	5.5	8.3	8.6	24.8	nd	32.6
	1984	7.3	12.0	9.9	24.2	0.2	19.5
Z24(6)	1979	30.3	22.1	18.1	73.1	0.3	48.5
	1980	23.1	26.8	22.0	75.0	nd	21.1
	1981	23.5	27.6	18.8	71.9	0.2	62.4
	1982	26.7	21.6	14.1	61.0	0.3	35.4
	1983*	25.4	18.5	13.7	74.5	0.2	45.8
	1984*	19.3	20.0	12.1	69.7	0.4	31.5

Table 5:2 (contd.)

Station	Year	* Cu	Ni	Pb	Zn	Cd	Cr
W27 (7)	1979	11.5	18.0	13.2	33.2	nd	25.0
	1980	12.1	16.2	14.6	55.6	nd	39.4
	1981	10.9	18.4	13.6	50.2	nd	41.7
	1982	11.7	14.4	15.1	43.6	0.1	34.4
	1983	12.8	15.4	16.4	40.0	0.2	31.4
	1984	9.1	12.4	10.8	45.3	0.2	26.5
T27 (8)	1979	8.1	11.0	13.3	32.7	0.2	19.4
	1980	6.5	11.8	10.8	33.9	0.1	25.2
	1981	6.1	7.2	7.6	25.1	0.2	27.3
	1982	6.6	8.4	7.9	27.3	0.1	21.7
	1983*	5.0	9.4	7.0	22.1	0.1	24.3
	1984*	5.3	8.7	6.1	27.1	0.2	23.8
P31(9)	1979	5.8	11.8	6.8	35.0	nd	18.2
	1980	7.0	12.2	6.3	19.0	nd	23.2
	1981	5.6	14.0	6.7	22.1	nd	22.2
	1982	5.2	13.2	6.5	28.2	nd	20.3
	1983	6.8	14.8	7.4	28.3	nd	22.3
	1984	4.5	10.6	5.0	20.2	0.2	23.4
S39 (11)	1979	8.2	14.4	8.0	34.8	nd	22.4
	1980	8.4	16.3	7.4	34.2	nd	30.1
	1981	6.5	15.6	8.1	31.2	nd	35.9
	1982	7.2	16.3	6.7	34.0	nd	21.9
	1983	5.2	14.2	6.9	30.1	nd	21.5
	1984	6.3	15.4	7.2	36.0	nd	32.0
T44(13)	1979	6.5	12.5	6.4	29.3	nd	22.3
	1980	6.4	11.3	5.4	31.0	0.1	21.4
	1981	5.8	14.4	4.9	18.1	nd	25.1
	1982	5.1	13.6	6.7	22.2	nd	25.8
	1983	5.4	13.1	5.3	28.8	0.3	25.9
	1984	4.6	11.9	5.0	26.2	0.1	22.3
V45 (14)	1979	6.0	11.9	5.6	29.0	nd	22.3
	1980	6.0	16.8	4.9	30.1	nd	21.6
	1981	5.6	12.4	5.9	24.7	0.2	30.2
	1982	4.6	13.0	4.7	27.5	0.2	21.0
	1983*	4.7	10.8	5.7	25.7	nd	19.4
	1984*	3.8	8.2	4.2	21.1	0.1	22.1

Table 5:2 (contd.)

Station	Year	Cu	Ni	Pb	Zn	Cd	Cr
AA44 (15)	1979	3.5	3.6	2.7	13.3	nd	11.2
	1981*	2.1	2.2	1.9	13.1	nd	11.7
	1982	2.2	4.4	3.6	12.2	nd	10.8
	1983*	3.6	6.3	4.1	12.6	nd	12.4
	1984*	1.7	2.8	1.8	10.8	0.1	11.1
CC45 (16)	1980	2.2	7.7	4.3	9.4	0.2	8.5
	1981	3.8	8.8	9.9	17.8	0.2	18.9
	1982	3.7	9.4	4.4	20.9	nd	9.9
	1983	4.6	8.6	3.8	21.6	0.1	12.8
	1984	2.4	5.4	3.1	14.2	0.1	20.3
CT1	1979	17.4	17.9	31.8	70.7	1.5	21.7
	1980	18.5	17.3	29.0	68.2	1.0	25.5
	1981*	15.3	17.1	31.4	66.1	1.2	32.6
	1982*	15.3	13.9	25.8	68.5	1.0	44.5
	1983*	13.1	15.1	23.4	70.8	1.0	21.7
	1984*	13.0	15.0	22.1	63.9	1.2	27.4

Table 5:3 Metal concentrations ($\mu\text{g.g}^{-1}$ dry wt.) in sediment samples collected on the shore at Dales Voe, Gluss Voe and Houb of Scatsta, July 1984.

Location	Shore level	Cu	Ni	Zn	Pb	Cd	Cr
Dales Voe	Low tide	5.6	7.9	38.0	4.8	nd	20.5
	High tide	5.9	8.3	41.9	4.5	nd	17.8
Gluss Voe	Low tide	7.1	14.6	43.0	4.0	nd	22.1
	High tide	6.9	14.4	35.9	2.8	nd	30.4
Houb of Scatsta	Low tide	3.8	9.5	20.4	2.5	nd	30.4
	High tide	3.2	8.5	24.0	1.9	nd	25.4

Table 5:4 Metal concentrations ($\mu\text{g}\cdot\text{g}^{-1}$ dry wt) in sediments collected from the vicinity of Orka Voe. Mean values from 5 replicate analyses are indicated by *.

Station	Distance from Bund (m)	Year	Cu	Ni	Pb	Zn	Cd	Cr
10V1	50	1981	24.7	30.8	32.5	74.8	nd	82.6
		1984	28.5	33.9	18.1	89.5	0.1	92.3
20V1	100	1981	30.8	35.7	16.7	81.9	nd	105.6
		1982	23.2	25.6	14.9	70.1	nd	70.6
		1983	17.5	20.0	13.4	67.1	0.1	67.3
		1984	31.7	31.9	19.9	92.0	nd	90.6
30V1	250	1980	33.2	20.0	18.8	98.6	nd	82.4
		1981*	27.9	33.0	19.1	79.6	0.1	92.8
		1982*	8.1	10.8	7.5	43.1	nd	24.6
		1983*	16.1	17.8	11.5	52.7	nd	44.2
		1984*	11.4	15.0	8.7	44.2	nd	38.7
40V1	500	1981	6.4	11.5	4.5	22.6	0.1	31.9
		1982	6.3	11.4	5.1	26.0	nd	27.8
		1983	3.4	5.3	3.4	14.1	0.1	16.9
		1984	7.6	12.6	6.3	32.2	nd	29.0
50V1	750	1980	8.0	16.0	6.0	30.8	nd	23.8
		1981*	7.9	11.8	7.0	24.5	nd	21.2
		1982	4.3	9.5	3.2	20.8	nd	16.8
		1983	3.6	6.5	4.4	39.4	0.1	16.9
		1984	5.3	8.2	4.4	23.6	nd	25.2
AA44 (15)	1600	1981*	2.1	2.2	1.9	13.1	nd	11.7
		1982	2.2	4.4	3.6	12.2	nd	10.8
		1983*	3.6	6.3	4.1	12.6	nd	12.4
		1984*	1.7	2.8	1.8	10.8	0.1	11.1
CC45 (16)	1600	1980	2.2	7.7	4.3	9.4	0.2	8.5
		1981	3.8	8.8	9.9	17.8	0.2	18.9
		1982	3.7	9.4	4.4	20.9	nd	9.9
		1983	3.9	4.1	3.2	11.3	nd	11.4
		1984	2.4	5.4	3.1	14.2	0.1	20.3

Table 5:5. Metal concentrations ($\mu\text{g.g}^{-1}$ dry wt) in 5 replicate sediment^a samples, July 1984.

Station	Sample No.	Cu	Ni	Pb	Zn	Cd	Cr
D4 (1)	1	23.5	33.2	31.2	102.4	0.8	57.6
	2	21.3	23.8	30.9	83.9	0.7	49.2
	3	20.7	31.3	31.5	103.4	0.7	56.6
	4	20.7	22.0	29.6	92.8	0.9	48.7
	5	19.9	28.9	29.6	97.8	0.9	42.3
	Mean	21.2	27.8	30.6	96.1	0.8	50.8
	S.E.M.	0.6	1.0	0.4	3.6	0.04	2.8
I19 (4)	1	5.8	8.5	11.5	29.4	0.1	20.4
	2	5.1	9.3	7.3	22.1	0.2	18.5
	3	5.0	8.8	7.3	22.4	0.2	27.3
	4	8.1	11.1	18.8	59.8	0.3	21.2
	5	6.1	9.4	8.9	28.5	0.2	25.8
	Mean	6.0	9.4	10.8	32.4	0.2	22.6
	S.E.M.	0.6	0.5	2.2	7.0	0.03	1.7
Z24 (6)	1	18.7	19.9	12.8	73.8	0.4	32.6
	2	18.4	19.5	13.7	69.1	0.3	28.6
	3	22.0	18.1	8.8	63.4	0.4	33.5
	4	19.5	23.1	15.5	76.8	0.4	36.5
	5	17.9	19.4	9.9	65.5	0.5	26.3
	Mean	19.3	20.0	12.1	69.7	0.4	31.5
	S.E.M.	0.7	0.8	1.2	2.5	0.03	1.8
T27 (8)	1	5.4	10.9	3.4	24.2	0.2	23.0
	2	3.8	7.4	3.7	18.5	0.2	18.6
	3	6.7	8.9	8.3	32.1	0.1	24.7
	4	6.4	7.9	8.2	31.8	0.3	23.4
	5	4.0	8.6	6.9	28.7	0.3	29.2
	Mean	5.3	8.7	6.1	27.1	0.2	23.8
	S.E.M.	0.6	0.6	1.1	2.6	0.04	1.7

Table 5:5 (contd)

Station	Sample No.	Cu	Ni	Pb	Zn	Cd	Cr
V45 (14)	1	4.0	8.5	4.5	19.7	0.1	23.2
	2	3.5	8.4	3.8	21.0	0.1	21.2
	3	3.5	8.2	4.1	21.5	0.1	21.3
	4	4.6	7.8	4.4	22.6	0.2	22.9
	5	3.5	8.2	4.2	20.6	0.1	21.7
	Mean	3.8	8.2	4.2	21.1	0.1	22.1
	S.E.M.	0.2	0.1	0.1	0.5	0.02	0.4
AA44 (15)	1	1.6	3.1	1.1	11.1	0.2	10.6
	2	1.7	3.0	1.1	10.2	0.2	13.2
	3	1.7	2.1	2.1	8.9	0.1	10.6
	4	1.7	2.3	1.8	10.2	nd	10.6
	5	1.8	3.6	2.8	13.6	0.1	10.6
	Mean	1.7	2.8	1.8	10.8	0.1	11.1
	S.E.M.	0.03	0.3	0.3	0.8	0.04	0.5
CT1	1	11.3	14.5	18.9	58.3	1.1	25.5
	2	13.5	14.5	23.0	64.3	1.2	26.6
	3	14.2	15.6	24.5	67.0	1.3	29.5
	4	12.7	15.0	21.2	64.1	1.2	24.9
	5	13.1	15.2	23.1	66.0	1.2	30.6
	Mean	13.0	15.0	22.1	63.9	1.2	27.4
	S.E.M.	0.5	0.2	1.0	1.5	0.03	1.1
30VI	1	8.3	10.9	6.8	34.4	nd	31.4
	2	10.4	13.3	8.3	41.3	nd	31.3
	3	18.5	24.0	12.9	64.4	nd	53.9
	4	8.8	12.7	7.0	36.3	nd	37.7
	5	10.9	14.1	8.3	44.7	0.1	39.1
	Mean	11.4	15.0	8.7	44.2	<0.1	38.7
	S.E.M.	1.8	2.3	1.1	5.4	-	4.1

6. MACROBENTHIC FAUNA AT REFERENCE STATION IN CAT FIRTH AND ORKA VOE

6:1 Introduction

Regular sampling at the reference station in Cat Firth was continued and in addition a series of samples was taken in Orka Voe. Sampling techniques were as described for previous years.

6:2. Cat Firth - CT1

Abundance levels were lower in 1984 than in any year but 1981, although biomass remained at a relatively high level. (Table 6:1). Bivalves remained as dominant species, with Tellina fabula, which first appeared as a dominant in 1983, now the most abundant species. Abra nitida was the next most numerous, but the population of Abra alba, the most abundant in 1983, was no longer present. The polychaete Capitomastus continued to be the third most abundant species present (Table 6:2). Species numbers were lower than in previous years. In general fewer small juvenile organisms were noted in the samples than in other years suggesting that the population is currently dominated by large, mature organisms.

Table 6:1 Faunistic data for station CT1 over eight years.

Year	Total biomass (g/m ² wet wt)	Total Species (numbers/m ²)	Total abundance
1977	31	22	2616
1978	18	33	1247
1979	18	34	3671
1980	8	30	1000
1981	5	34	592
1982	32	36	3637
1983	135	33	1194
1984	65	24	807

Table 6:2. The five dominant taxa (by number) for station CT1 over eight years, ranked in order of abundance.

SPECIES	YEAR							
	1977	1978	1979	1980	1981	1982	1983	1984
<i>Capitomastus minimus</i>	1	2	2	1	1	2	3	3
<i>Capitella capitata</i>	2					5		
Nematoda spp.	3	1	4	4				
<i>Peloscolex benedeni</i>	4		3	5	3		4	
Nemertea, Type 2	5	3	5		5			5
<i>Abra alba</i>		4			2		1	
<i>Ophelina acuminata</i> (<i>Ammytropane aulogaster</i>)		5						
<i>Polydora quadrilobata</i>			1	3		1		
<i>Prionospio malmgreni</i>				2		4	3	
<i>Abra nitida</i>					4		5	2
<i>Nucula tenuis</i>						3		
<i>Tellina fabula</i>							2	1
<i>Nephtys</i> spp.								4

A complete list of all organisms found is given in Appendix 6:1. Taxonomic authorities used in these analyses are : General, Plymouth Marine Fauna, Bruce, Colman & Jones, 1963; Mollusca, Tebble, 1966; Polychaeta, Fauchald, 1977; Oligochaeta, Brinkhurst, 1982; Echinodermata, Mortensen, 1927.

No attempt has been made to identify the small crustacean groups (Amphipoda, Isopoda, Crustacea and Copepoda) as these organisms are not sampled quantitatively by the collecting method used.

6.3 Orka Voe.

Five stations in Orka Voe were sampled along a 750 m transect line extending from the bund out into the Voe. (Fig. 6:3). Three grab samples were obtained at each station, sieved on a 1 mm sieve and the residue preserved in formalin and returned to the laboratory for analysis

The samples from the two inner stations, 10VI and 20VI were found to contain obvious globules of oil adhering to the sieved material. Samples from the three outer stations contained no visible oil. (Table 6:3). A full list of all the organisms found at each of the stations is given in Appendix 6:2. The principal faunal statistics from each station in 1983 and 1984 are listed in Table 6:4. There have been some notable changes along the transect between 1983 and 1984. No sample was obtained at 10VI in 1983 but at 20VI populations had more than doubled and total biomass and species numbers had also increased. At 30VI biomass and numbers had decreased but species numbers had increased, whereas at 40VI biomass and species numbers were lower but total abundance was higher. At the station furthest from the bund, 50VI, biomass was considerably lower, abundance slightly lower and species numbers the same. The variation in these statistics in 1984 is illustrated in Fig. 6:1. This reveals a pattern which suggests a fluctuating gradient of organic enrichment along the transect towards the bund. The characteristics of faunal change along such a gradient are defined in Pearson & Rosenberg (1978), and may be briefly summarized as follows. In highly enriched sediments a few small opportunist species flourish and may attain very high numbers. Thus biomass (B) and abundances (A) are high, but species numbers (S) are low. In moderately enriched sediments these species are superseded by a larger range of other organisms which /

which can take advantage of the more favourable sedimentary conditions. In such areas A and B are somewhat lower than in the highly enriched areas but S is higher. As enrichment decreases further B decreases rapidly and A and S more slowly. Reference to Fig. 6:1 suggests that by these criteria, station 20VI is the most enriched and station 50VI the least enriched along the sampling transect.

Simple statistics of this type are not capable of resolving the more subtle effects of organic enrichment however. To do this attention must be paid to changes in the populations of individual species. In the 1983 samples it was noted that some species characteristic of organically enriched sediments were amongst the most numerous (dominant) at stations 20VI and 50VI. Table 6:5 lists the dominant taxa found at each station along the transect in both 1983 and 1984. In general these dominants are typical of the organisms found in sand/mud sediments in shallow boreal areas. At the stations nearest the bund, however, two or three of the dominants are characteristically species associated with highly enriched sediments (Capitomastus, Tubificoides, Polydora) and the most numerous species found, Abra nitida, is known to predominate in moderately enriched areas (Pearson, 1975; Pearson & Rosenberg, 1978; Pearson et al 1983). Abra nitida occurs throughout the transect but in much lower numbers at the outer stations. A full list of all organisms found at the Orka Voe stations, together with their relative abundances is provided in Appendix 6:2. This data provides strong evidence of a progressive change in species composition along the transect from the inner area, near the bund, where the small opportunist polychaetes predominate, to the outer station (50VI), where the bivalve molluscs are abundant. Table 6:6 lists the species which reach their maximum populations at each station along the transect. At the station nearest the bund these are all small annelid worms, with the exception of the small bivalve Abra alba. Moreover, nearly /

nearly all are recognised as species particularly associated with organically enriched sediments (Pearson & Rosenberg, loc.cit.) These populations decline rapidly as distance from the bund increases (Fig. 6:2), and are replaced by small bivalve species, e.g. Thyasira, Abra nitida, Corbula, which peak 100 m from the bund. These in turn are superseded by other, predominantly bivalve species, e.g. Nucula, Venus, Mya, at 250 m. At 500 m larger bivalve species, e.g. Venerupis, Gari, larger polychaetes, e.g. Rhodine and the brittle star Ophiura have their maximum numbers. Very few species peak at 750 m where populations are declining to the levels characteristic of the normal unenriched sediment of the area. Figs 6:3 and 6:4 illustrate some of these population changes.

One notable characteristic of the populations present in 1984 was the predominance of juveniles in many of the species, particularly at the two inner stations 10VI and 20VI. At these stations the bivalve molluscs were almost entirely juvenile (Thyasira and Abra spp.), whereas the annelid species had mixed populations containing a range of age groups. This suggests that the molluscs had been recently recruited to these populations. In general, this analysis supports the contention that there is a clearly discernible gradient of organic enrichment in the sediments of Orka Voe, with the most enriched areas closest to the bund. The presence of visible oil globules in the residues from the two innermost stations suggests that one source of the organic enrichment is hydrocarbon contamination. It must be noted, however, that there is a gradient from coarse to fine sediments from the outer to the inner end of the sampling transect and that peat detritus is associated with the finer sediments (Table 6:3), and also provides a carbon source for benthic metabolic activity.

Conclusions /

Table 6:3 Observations on the appearance of material sieved at the stations in Orka Voe, June 1984.

<u>Station number</u>	<u>Description of Material</u>	<u>Degree of Contamination</u>
10VI	Fine mud with peat detritus	Numerous large globules of light brown oil throughout sample
20VI	Fine mud with peat detritus	Small globules of oil present
30VI	Mud, gravel and shell with a little detritus	No oil visible
40VI	Mud, gravel and shell with a little detritus	No oil visible
50VI	Gravel and shell	No oil visible

Table 6:4 Faunistic data from Orka Voe

Station	Total biomass (g/m ² wet wt)		Total species (No./m ²)		Total abundance	
	1983	1984	1983	1984	1983	1984
50VI	32.1	12.4	60	60	1647	1450
40VI	15.0	11.6	59	50	1774	2825
30VI	49.8	13.5	52	67	3179	2992
20VI	49.0	59.5	52	60	2248	5454
10VI	-	42.1	-	63	-	3467

Table 6:5 The five dominant taxa (by number) of stations in Orka Voe in 1983 and 1984 ranked in order of abundance.

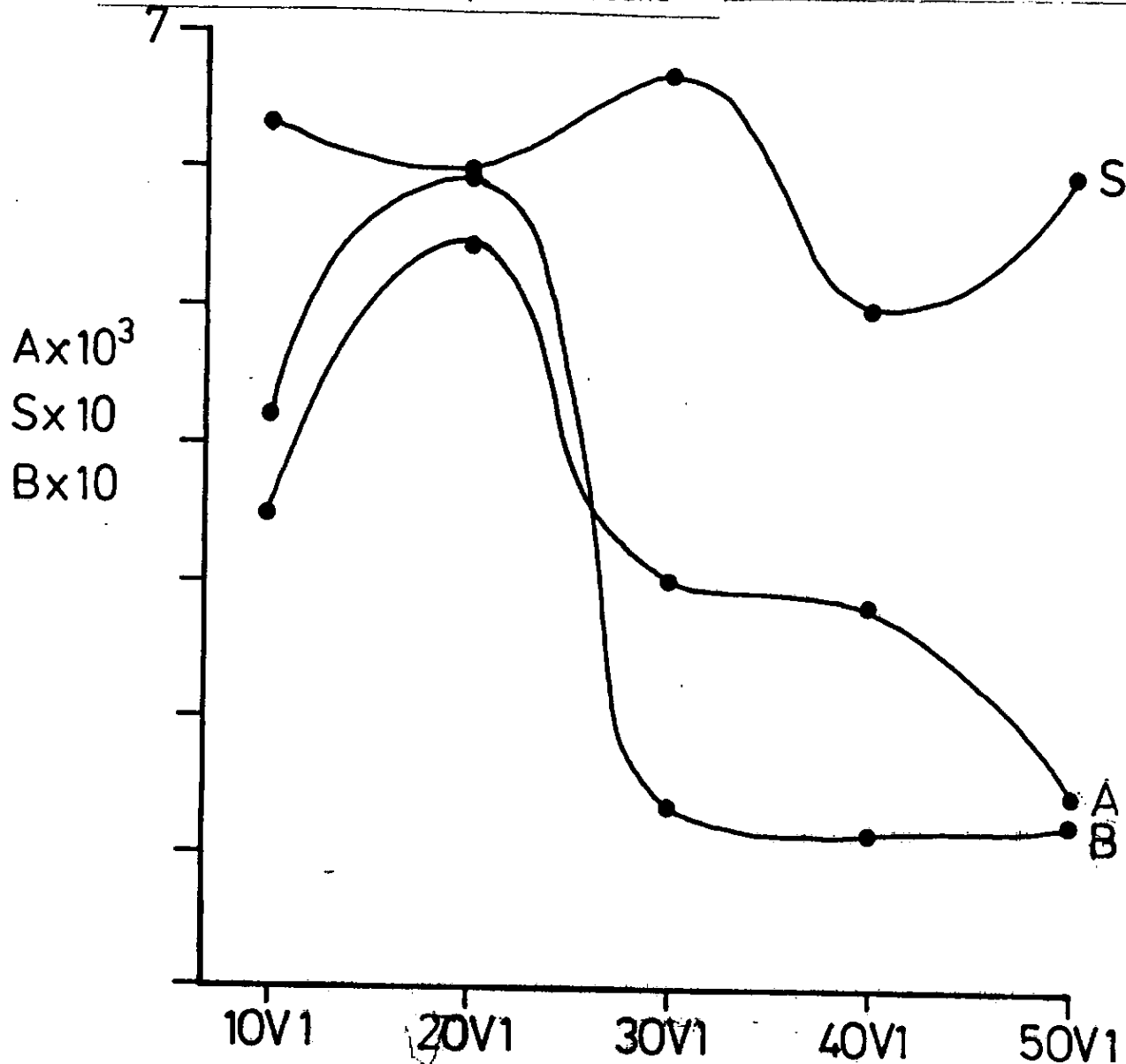
Station	Taxa	1983		1984	
		Rank	No/m ²	Rank	No/m ²
10VI	<i>Abra nitida</i>			1	902
	<i>Polydora</i> sp.			2	322
	<i>Ampharete</i> sp.			3	265
	<i>Tubificoides benedeni</i>			4	252
	<i>Capitomastus minimus</i>			5	217
20VI	<i>Abra nitida</i>	1	723	1	2977
	<i>Thyasira flexuosa</i>	2	477	2	628
	<i>Capitomastus minumus</i>	3	130	4	125
	<i>Mysella bidentata</i>	4	123	10	81
	<i>Ampharete</i> sp.	5	103	6	105
	<i>Nephtys</i> sp.	9	47	3	136
	<i>Polydora</i> sp.	13	30	4	125
30VI	<i>Thyasira flexuosa</i>	1	1120	2	323
	<i>Abra nitida</i>	2	493	1	886
	<i>Ampharete</i> sp.	3	280	16	34
	<i>Lumbrinereis hibernica</i>	4	210	3	120
	<i>Polydora</i> sp.	5	123	7	74
	<i>Exogone hebes</i>	-	-	4	115
	<i>Parvicardium ovale</i>	39	7	5	110
40VI	<i>Thyasira flexuosa</i>	1	247	2	312
	<i>Lumbrinereis hibernica</i>	2	230	7	92
	<i>Mysella bidentata</i>	3	143	4	100
	<i>Abra nitida</i>	4	107	1	529
	<i>Pholoe minuta</i>	5	77	8	77
	<i>Polydora</i> sp.	7	53	3	192
	<i>Ophiura affinis</i>	30	7	5	98
50VI	<i>Thyasira flexuosa</i>	1	337	1	202
	<i>Maloceros fuliginosa</i>	2	147	16	18
	<i>Abra nitida</i>	3	143	2	176
	<i>Mysella bidentata</i>	4	80	5	53
	<i>Polydora</i> sp.	5	77	4	82
	<i>Myriochele</i> sp.	6	63	3	94

Table 6:6. Comparative list of those species reaching their highest populations at each station along the transect.

STATION	DISTANCE FROM BUND (m)	SPECIES WITH PEAK POPULATIONS AT THAT STATION
10VI	50	Scoloplos armiger Polydora sp. Capitella capitata Capitomastus minimus Scalibregma inflatum Eteone longa Ampharete sp. Tubificoides benedeni Maloceros fuliginosa Notomastus latericeus Abra alba
20VI	100	Chaetozone setosa Nephtys sp. Terebellides stroemi Thyasira flexuosa Abra nitida Cultellus pellucidus Corbula gibba
30VI	250	Prionospio malmgreni Exogone hebes Lumbrinereis hibernica Nucula sulcata Parvicardium ovale Venus casina Mya truncata
40VI	500	Rhodine loveni Pholoe minuta Mysella bidentata Venerupis pullastra Gari fervensis Ophiura affinis Diplocirrus glaucus
50VI	750	Phacoides borealis Harmothoe sp. Myriochele

Comparison of the principal macrobenthic population statistics along the transect sampled in Orka Voe.
A, total abundance of organisms (N/m^2);
B, total biomass of all organisms found (g.wet wt./ m^2).
S, total number of species found

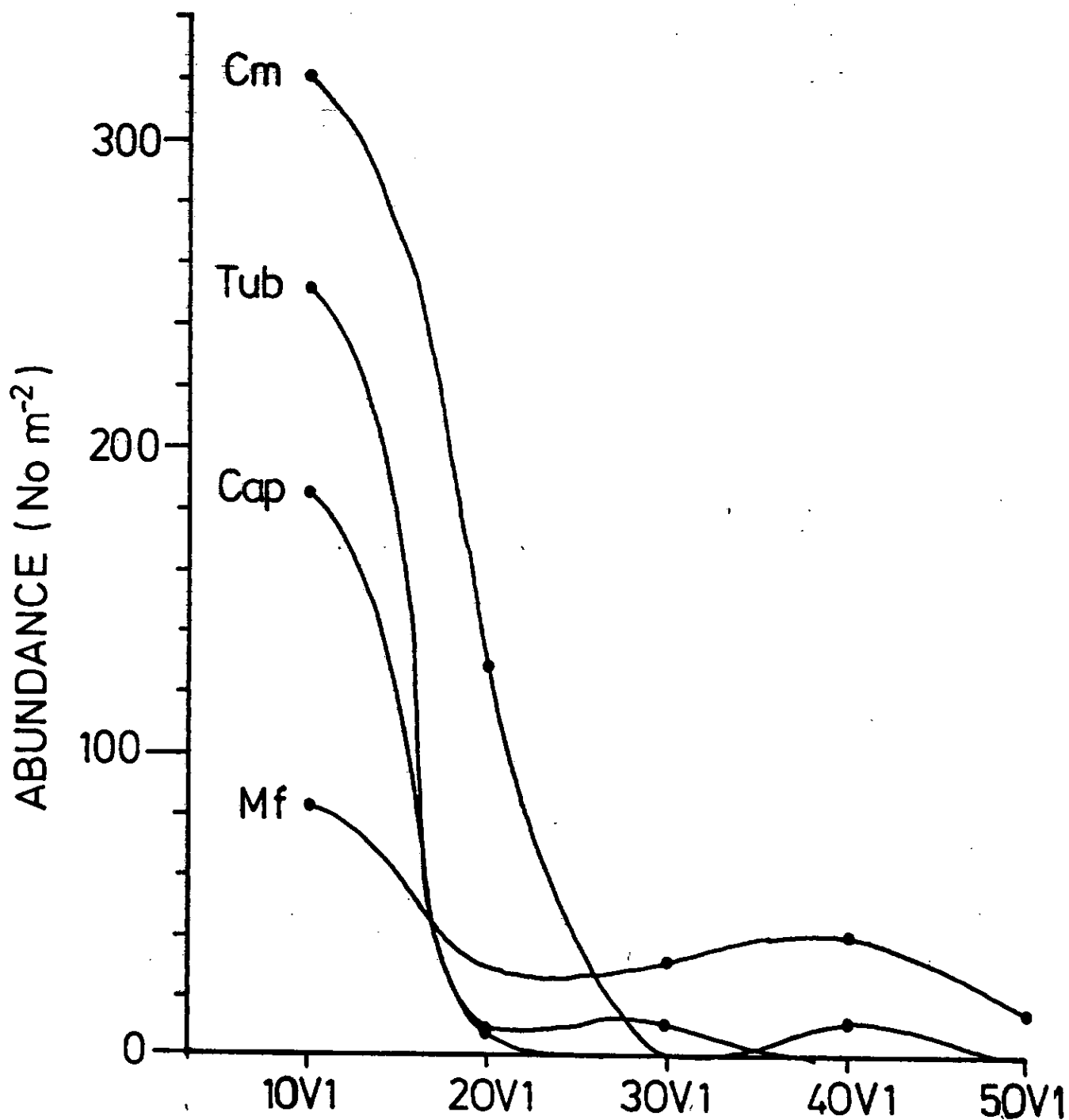
FIG 6.1



Variation along the Orka Voe transect in the populations of some species associated with highly enriched sediments.

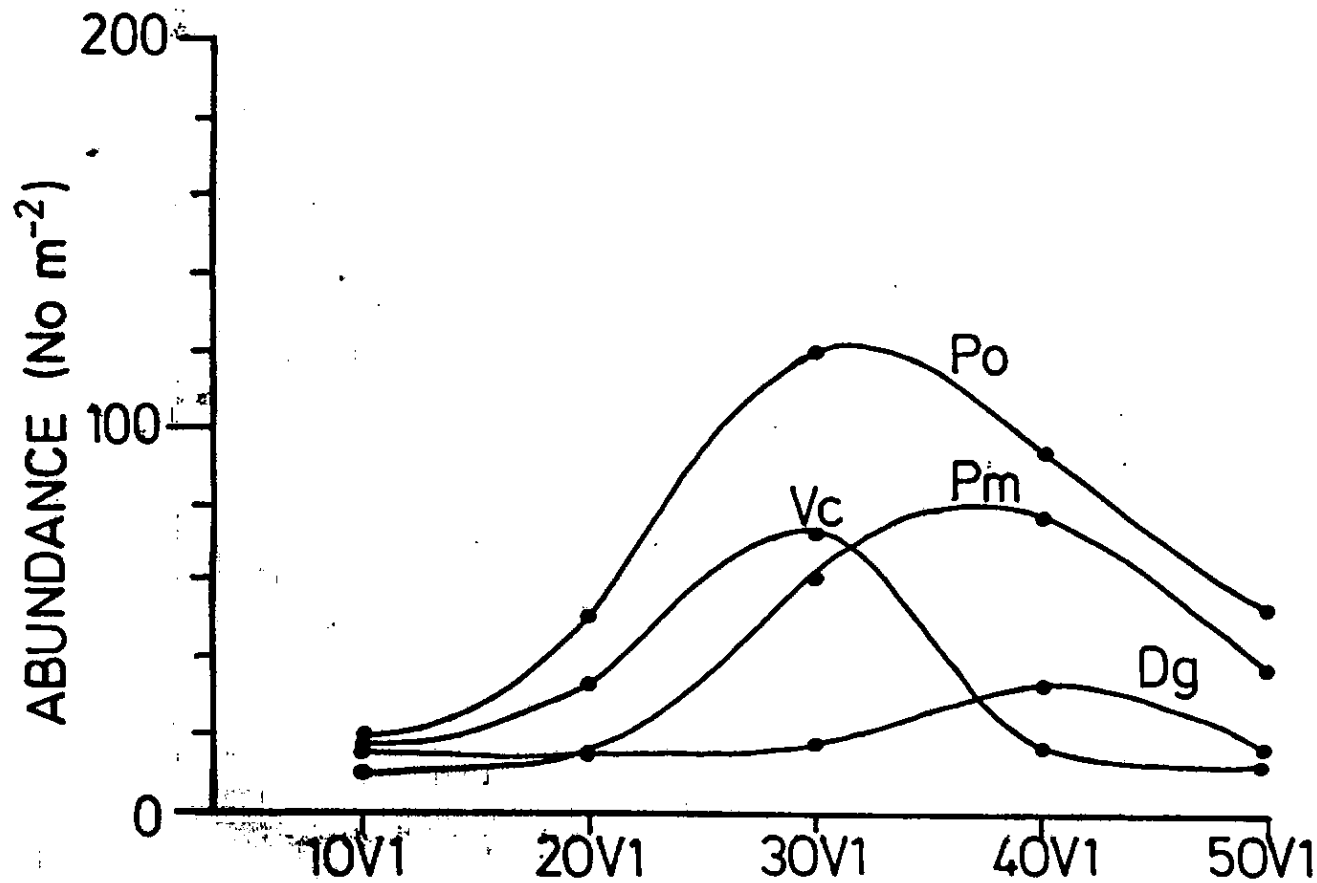
Cap, Capitella capitata; Tub, Tubificoides benedeni;
Cm, Capitomastus minimus; Mf, Maloceros fuliginosa.

FIG 6.2



Variation along the Orka Voe transect in the populations of some species characteristic of normal sediments in the area. Po, Parvicardium ovale; Pm, Pholoe minuta; Vc, Venus casina; Dg, Diplocirrus glaucus.

FIG 6.3



Appendix 6.1 List of all organisms taken at reference station CT1 in 1984.

CAT FIRTH STATIONS		ABUNDANCES per m ²
TAXA		CT1
Nematoda		6
Nemertini	sp A	5
	sp B	29
	sp C	11
Annelida		
	Prionospio malmgreni	9
	Capitella capitata	5
	Capitomastus minimus	106
	Ophelina acuminata	2
	Glycera alba	4
	Nephtys spp	35
	Ampharete	5
	Tubificoides benedeni	16
Sipunculoidae		
	Gofingia sp	4
Priapulioidea		
	Priapulus caudatus	2
Crustacea		
	Amphipoda	28
Mollusca		
	Thyasira flexuosa	9
	Mysella bidentata	6
	Venus casina	5
	Gari fervensis	4
	Abra nitida	185
	Tellina fabula	316
	Corbula gibba	4
Echinodermata		
	Amphiura chiajei	5
	Ophiura texturata	4
Total number of species (S)		24
Total abundance (A) (No. per m ²)		807
Total biomass (B) (g. wet wt per m ²)		65.1
Abundance ratio A/S		34
Size ratio B/A		81

Appendix 6:2 List of all organisms taken at stations in Orka Voë, June 1984.

TAXA	ABUNDANCE per M ²				
	10VI	20VI	30VI	40VI	50IV
Coelenterata	12	5			
Pennatulacea					
<i>Virgularia mirabilis</i>	5	14	27	8	10
Nemotoda	10				
Nemertini sp. A	5		6		
sp B					
sp C					
Annelida					
<i>Scoloplos armiger</i>	42	3	8	18	10
<i>Aricidea catherinae</i>	5				
<i>Cirrophorus lyra</i>	2	5		10	7
<i>Cossura</i> sp.	2				
<i>Polydora</i> sp.	322	125	74	192	82
<i>Spiophanes kroyeri</i>	5		3		
<i>Spio filicornis</i>	15	12	9	12	3
<i>Malacoceros fuliginosa</i>	93	30	30	40	18
<i>Prionspio malmgreni</i>	30	51	52	38	
<i>Prionspio cirrifera</i>		24	10		13
<i>Chaetozone setosa</i>	37	86	10	19	6
<i>Caulleriella</i> sp.	2	5			
<i>Cirratulus filiformis</i>	15				3
<i>Capitella capitata</i>	185	10	11		
<i>Capitomastus minimus</i>	217	125		15	
<i>Notomastus latericeus</i>	27	21	6	10	
<i>Praxillella affinis</i>	12	22	3	8	8
<i>Praxillella</i> sp.		17	20		
<i>Rhodine loveni</i>	12			41	2
<i>Rhodine gracilor</i>		20			
<i>Ophelina acuminata</i>	2				
<i>Scalibregna inflatum</i>	55	54	17		
<i>Anaitides groenlandica</i>	12				3
<i>Eteone longa</i>	42	5			
<i>Eulalia viridis</i>	5		2		8
<i>Mystides</i> sp.	10	5		3	4
<i>Aphrodita aculeata</i>			2		
<i>Harmothoe</i> sp.	20	11	25	18	43
<i>Pholoe minuta</i>	15	15	60	77	36
<i>Neremyra punctata</i>					2
<i>Ophiodromus flexuosus</i>	2				
<i>Exogone hebes</i>			115	40	17
<i>Syllis armillaris</i>			3		
<i>Nereis virens</i>	15	5			
<i>Glycera alba</i>	52	55	47	60	35
<i>Goniada</i> /					

Appendix 6:2 (contd)

OVI STATIONS TAXA	ABUNDANCE per m ²				
	10VI	20VI	30VI	40VI	50VI
Goniada maculata	5	4			
Nephtys spp.	35	136	41	48	20
Lumbrinereis hibernica	50	41	120	92	28
Ophryotrocha puerilis	5	5			
Myriochele sp.	2		5	62	94
Diplocirrus glaucus	10	15	18	33	17
Ampharete spp.	265	105	34		10
Amphitrite sp.					4
Lanice conchilega	2				
Scionella lornensis			4	2	
Terebellidae sp A			7		
Terebellidae sp.B			9		1
Terebellidae sp.C			3		
Terebellides stroemi	42	105	43	60	8
Sabella pavonina	12	9	8	7	
Sabellidae sp A			2	12	6
Sabellidae sp. B			4	5	7
Sabellidae sp. C			3	11	9
Hydroides norvegica			3	4	
Pomatoceros triqueter	2		28	27	
Serpulidae sp. A			3		6
Tubificoides benedeni	252	5			
Sipunculoidea					
Golfingia sp.		2			
Priapuloida					
Priapulus caudatus		2			
Crustacea					
Copepoda	2				18
Leptostraca					
Nebaliopsis bipes			9		
Cumacea	12	13	10		8
Isopoda	5	7	15		22
Amphipoda	27	55	124	82	167
Decapoda	2				2
Eupagurus bernhardus			4		
Mollusca					
Solenogastres					
Chaetoderma nitidulum		6	8		
Gastropoda					
Acmaca					17
Turritella communis		13			
Gastropoda sp A		8	50		4
sp B	15	15	33		
Lamellibranchiata /					

Appendix 6:2 (contd)

OVI STATIONS	ABUNDANCE per m ²				
	TAXA	10VI	20VI	30VI	40VI
Lamellibranchiata					
Nucula sulcata	5	21	87	69	40
Modiolus sp.		5	18	10	13
Musculus mamoratus				9	
Crenella decussata			29		
Astarte sp.					8
Arctica islandica		28	23	18	2
Thyasira flexuosa	207	628	323	312	202
Phacoides borealis		6			20
Myrtea spinifera		5	14		3
Mysella bidentata		81	54	100	53
Laevicardium crassum			2		
Parvicardium ovale	20	49	110	93	52
Dosinia lupinus				3	
Venus casina	20	36	73	16	13
Venus ovata				2	
Venerupis pullastra		5	2	19	17
Veneridae spp.	11				
Gari fervensis		10	17	21	7
Abra alba	200			2	
Abra nitida	902	2977	886	529	176
Tellina donacina					4
Tellina fabula	2				
Cultellus pellucidus		62	20		16
Corbula gibba	20	95	16	41	20
Mya truncata	15	51	71	48	20
Mya arenaria		68	57		
Thracia sp.				19	
Phoronidea					
Phoronis mulleri				12	
Echinodermata					
Asteroidea/Asterias rubens	1				
Ophuroidea/Amphiura filiformis					3
Ophiura affinis	7	25	67	98	17
Holothuridae					
Leptosynapta decaria	8	4		9	2
<hr/>					
Total number of species (S)	63	60	67	50	60
Total abundance (A)(No.per m ²)	3467	5454	2992	2825	1450
Total biomass (B)(g. wet wt. per m ²)	42.1	59.5	13.5	11.6	12.4
A/S	55	91	45	56	24
B/A	0.012	0.011	0.004	0.004	0.008

7. Conclusions and general comments.

No great changes have been found in Sullöm Voe in 1984 when compared with previous years. Note should be taken of the increase in hydrocarbon contamination at station S39 (11), however. A careful check of the benthic communities in that area should reveal whether the measured levels have had any impact on the fauna.

There appears to be a continued source of hydrocarbon contamination in Orka Voe, which has had some effect on the distribution of the benthic communities in the area. The discernible faunal succession along the transect sampled is undoubtedly related to increasing organic enrichment as the bund is approached. However, despite the higher hydrocarbon levels recorded at station 50VI, the fauna there contained fewer species known to be associated with organically enriched sediments than in 1983. Moreover, the somewhat lower total carbon levels at the two inner stations and the fact that the populations there contained a recent settlement of small bivalves, suggests that conditions at the inner end of the transect were slightly improved over those observed in 1983. It may be concluded that, in the fine sediments of the inner part of Orka Voe, a fauna that is naturally adapted to relatively high organic carbon levels, probably stemming from a combination of both planktonic and terrestrially derived detritus, has been further affected by hydrocarbon inputs. This has favoured the development of a population dominated by small opportunistic polychaetes. Recolonisation by a more diverse fauna does appear to have begun in 1984, however.

8. References.

- BRINKHURST, R.O., 1982. British and other marine and estuarine oligochaetes. Synopses of the British Fauna, No 21. Edited by D.M. Kermack & R.S.K. Barnes, Cambridge University Press.
- FAUCHALD, K., 1977. The polychaete worms. Definitions and keys to the orders, families and genera. Natural History Museum of Los Angeles County, Science Series 28: 1-190.
- MARINE FAUNA OF THE ISLE OF MAN, 1963. Edited by J.R. Bruce, J.S. Colman & N.S. Jones. Memoir No. 36, Liverpool University Press.
- MORTENSEN, Th., 1927. Handbook of the echinoderms of the British Isles. Oxford University Press, 471 pp.
- PEARSON, T.H., 1975. The benthic ecology of Loch Linnhe and Loch Eil, a sea-loch system on the west coast of Scotland. IV. Changes in the benthic fauna attributable to organic enrichment. J. exp. mar. Biol.Ecol., 20, 1-41.
- PEARSON, T.H. and R. Rosenberg, 1978. Macrobenthic succession in relation to organic enrichment and pollution of the marine environment. Oceanogr. Mar.Biol. Ann.Rev. 16, 229-311.
- PEARSON, T.H., G. Duncan & J. Nuttall, 1982. The Loch Eil Project: Population fluctuations in the macrobenthos. J.exp.mar.Biol.Ecol., 56, 305-321.
- PLYMOUTH MARINE FAUNA, Third Edition 1957. Marine Biological Association of the U.K. 457 pp.
- TEBBLE, N., 1966. British Bivalve Sea shells. The British Museum (Natural History), London. 212 pp.