AMT8 Cruise Report

Halocarbons

Narrative

Leg 1 was used to set up the equipment, there being several teething problems setting up carrier gases and some of the automated systems. Consequently, no water samples were analysed during this leg.

During Leg 2, water, air and equilibrator samples were analysed at all depths (0 – 250m) between Stations 9 and 17, with an additional station (18) down to 3000m to permit an assessment of analytical blanks and reproducibility. At the start of Station 19 there was an accident with another piece of equipment, which resulted in seawater being sprayed onto some of the electronics, causing arcing and instrument failure. The ship's electrician managed to recover the situation prior to Station 21, but subsequent failure of the turbo pump on the mass spectrometer meant that this was the last station to be analysed on this leg. A new turbo pump was shipped out from the UK and was fitted following the boat transfers at Ascension Island.

On Leg 3 samples were analysed from Station 25 onwards but, following the rupture of the winch hydraulic line, contamination entered the system, becoming apparent during the analysis of Station 32, and severely compromised analysis thereafter. The contamination required the complete cleaning and rebuilding of the analysis system and replacement of the chromatography column and sampling syringes, with analysis being resumed at Station 43. Even so, there remained residual contamination that slowly degraded the instrument response, resulting in declining sensitivity as the cruise progressed. At this time we are unable to fully assess the effects on final data quality.

In total, 222 water samples were analysed, 108 on Leg 2 and 114 on Leg 3, together with 44 air and 22 equilibrator samples.

Methodology

The purpose of this work was to analyse a suite of halocarbons, both biogenic and anthropogenic, in the 0 – 250m depth range and to relate these measurements to the other biological and physical parameters measured on the cruise. Analysis was performed using a purge-and-trap GCMS (gas chromatography – mass spectrometry) system based on that described in Boswell and Smythe-Wright (1996). Water samples were collected from the rosette using ground glass syringes fitted with stainless steel luer stopcocks and were kept in a water bath until analysed. Approximately 80 ml of sample was introduced into the sparging tower and stripped for 8 min, the gases being absorbed onto a cryogenic trap. Chromatography was performed using a 30m x 0.32mm i.d. CB Sil-5 column (Chrompack) with helium as carrier gas. Mass spectrometry provides a very sensitive means of detecting compounds, the mass information providing a means of separating co-eluting components while achieving good signal to noise. The mass spectrometer (Hewlett Packard 5973)

was operated in selective ion monitoring (SIM) mode, with time windows set up with small groups of ions so as to obtain the maximum signal to noise. In all, 22 compounds were determined during AMT8 (see table below), although there are a number of other peaks that remain to be positively identified and from which data may subsequently be obtained. Both air and "Weiss equilibrator" samples were taken at regular intervals to enable determination of surface water saturations. An experimental automated underway sampling system was also tested during Leg 3. Calibration was by injections of known volumes of standard gases: for the main anthropogenic halocarbons (CFC-11, CFC-12, CFC-113, CCl_4) compressed air calibrated by CMDL (Climate Monitoring and Diagnostics Laboratory) was used, while a Kintek standards generator was employed for the other compounds.

Table 1. SIM ions used for compound determination

Compound	Ion	Compound	Ion
HCFC134a	69	Methyl chloride	50
HCFC-22	51	Methyl iodide	142
CFC-12	87	Methylene chloride	84
HCFC-142b	65	Vinylidine chloride	96
CFC-11	103	Dimethyl sulphide	62
HCFC-141b	81	bromochloromethane	130
CFC-113	103	Iodoethane	127
carbon tetrachloride	117	chloroform	83
Methyl bromide	96	trichloroethylene	130
Methyl chloroform	97	bromodichloromethane	83
		chloroiodomethame	176
		bromoform	173

Results

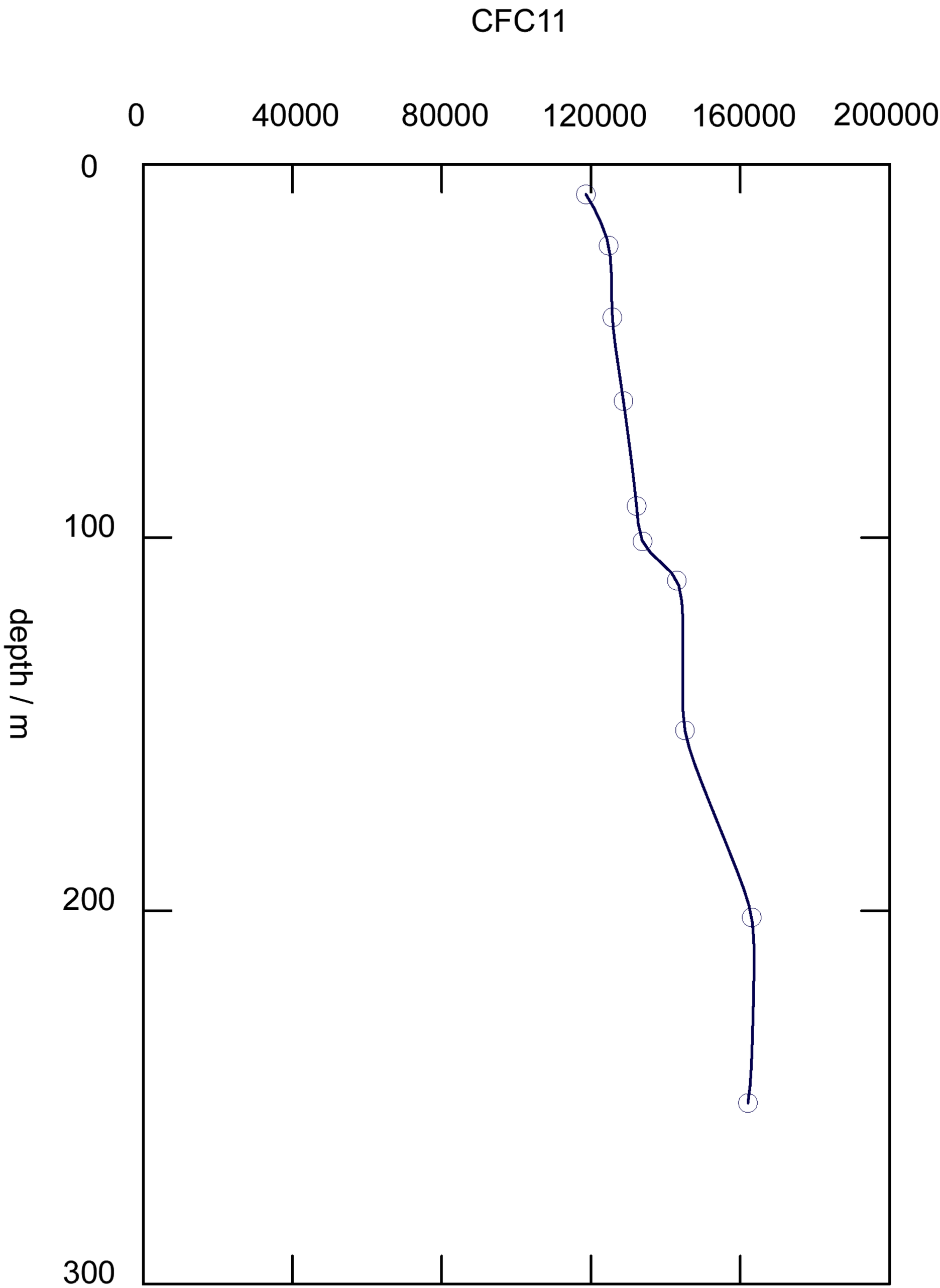
Calibration of this data set will take some time, especially those stations affected by the contamination problems that beset Leg 3. Therefore, only example plots can be presented here. Figure 1 shows a selection of the selected ion chromatographs obtained from a water sample. Figure 2 illustrates several depth profiles (uncalibrated) obtained from Station 13. CFC-11 is totally anthropogenic and its profile is primarily controlled by its solubility, a function of temperature and salinity, and therefore follows the T and S structure with concentrations increasing with decreasing temperature below the mixed layer. In contrast, methyl chloride is biogenic and its distribution is determined by factors that affect biological productivity, the highest values here lying between the fluorescence maximum and the transmission minimum. Other compounds exhibit maxima at different depths, eg DMS in the surface, reflecting the varying importance of species abundances, chemical degradation rates and the extent of

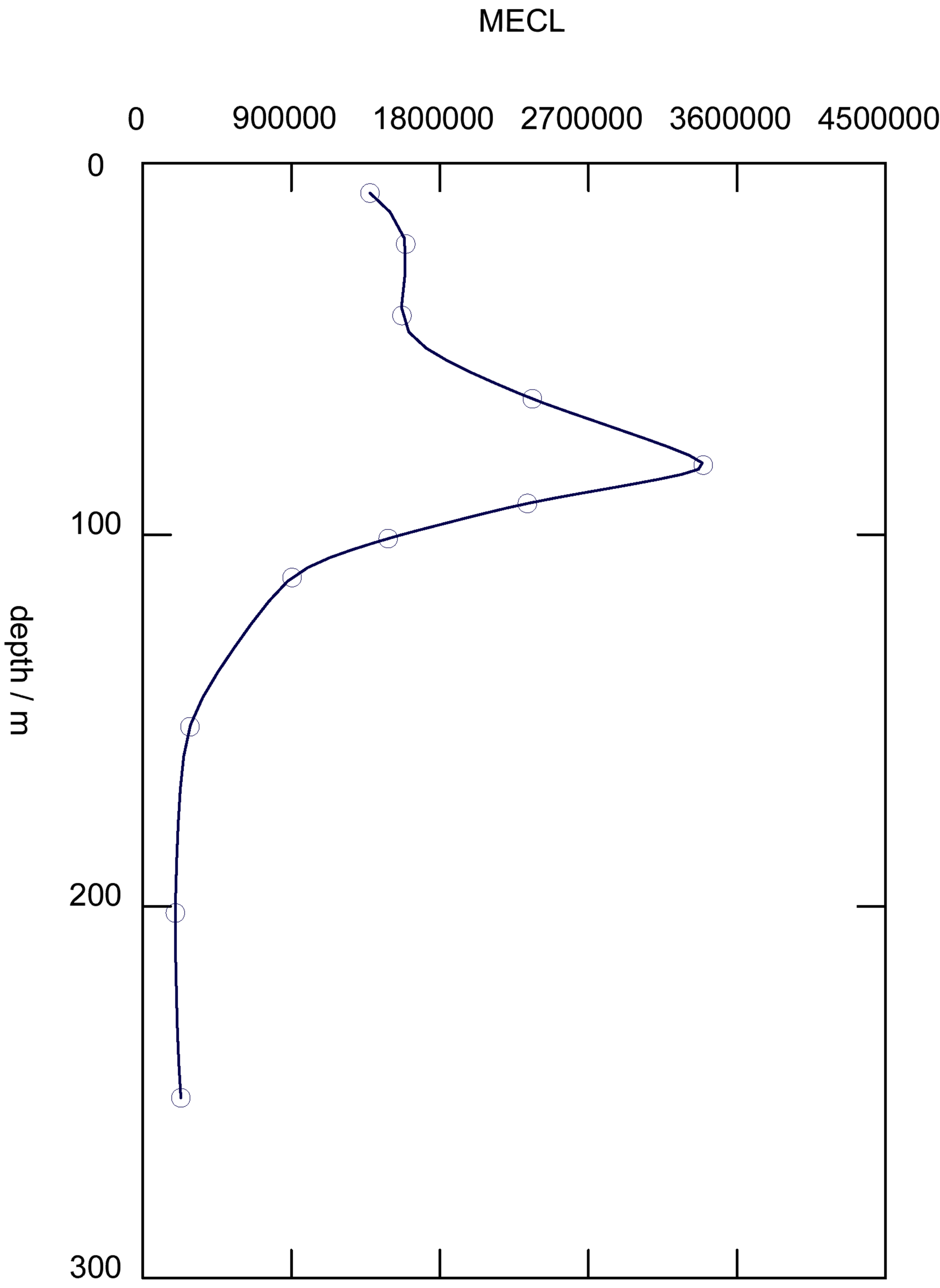
anthropogenic production. These halocarbon data will be analysed in the context of the biological data collected on the cruise to obtain a better understanding of the ocean's role as a source/sink of these compounds.

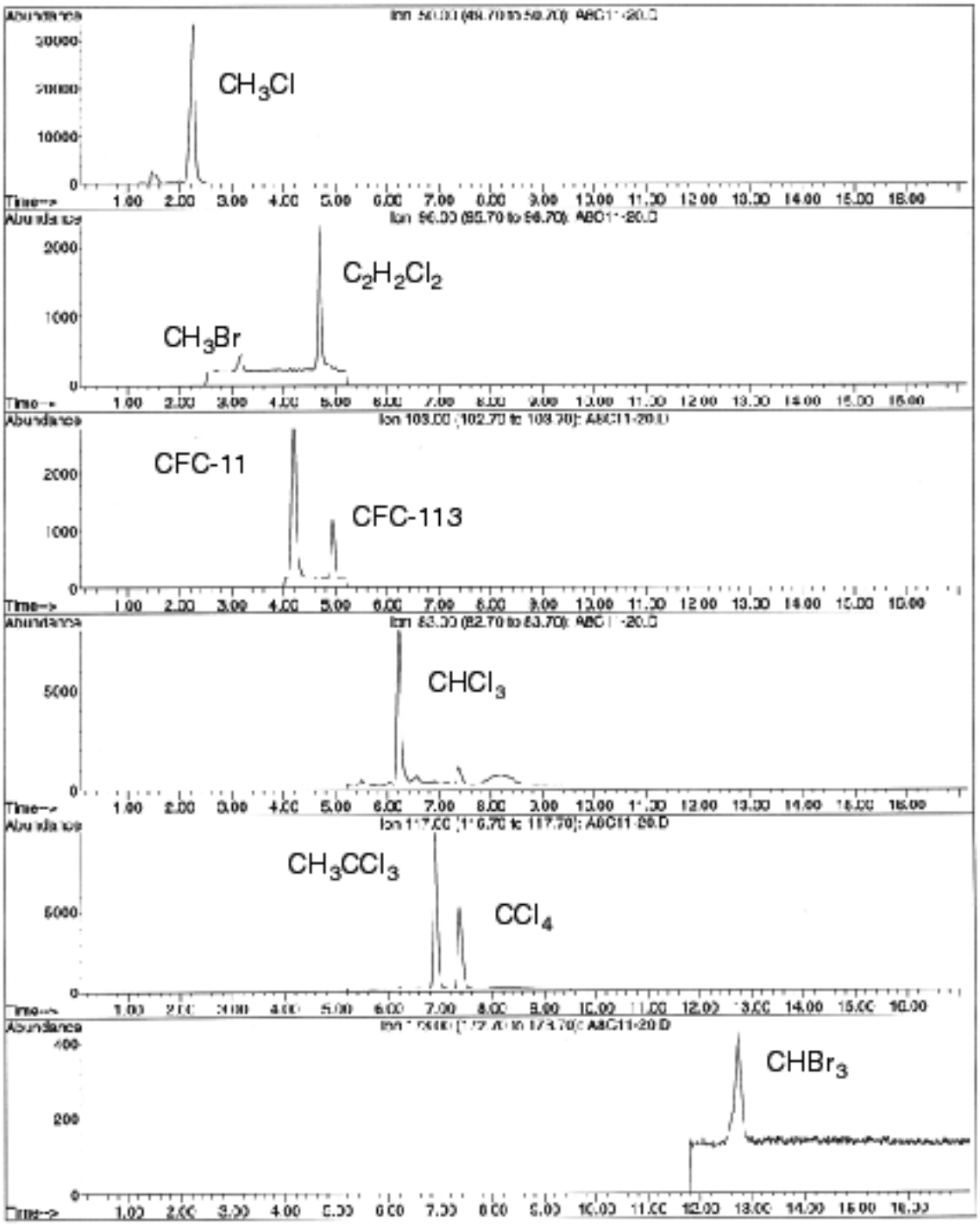
Boswell, S.M. and Smythe-Wright, D., (1996), Dual-detector system for the shipboard analysis of halocarbons in sea-water and air for oceanographic tracer studies, Analyst, 121, 505 – 509

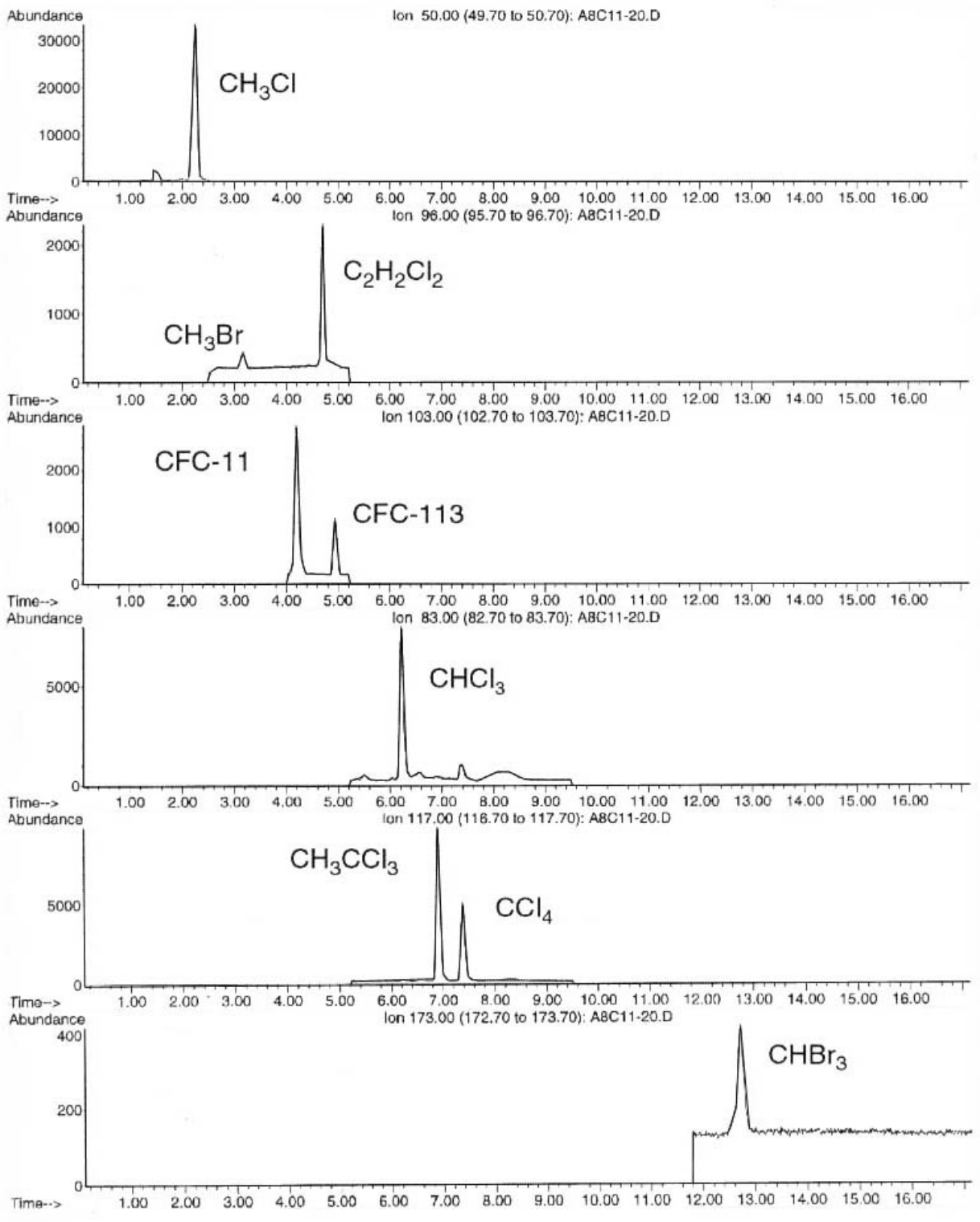
TOC

A total of 113 samples were collected for both TOC and POC analysis. 100ml of water was filtered through pre-ashed (500°C, 4hrs) GF/F glass-fibre filters into similarly treated bottles. These were then sealed, using sulphuric acid-cleaned PTFE inserts in the caps, and stored at –20°C. A further volume of water (up to 2 litres or until the filter clogged) was filtered and the GF/F placed in a "Cryovial" for storage at –80°C. Both sets of samples will be analysed for carbon and nitrogen content back at the SOC.


CFC11
0
40000
80000
120000
160000
200000
0
100
200
300
depth / m


MECL
0
900000
1800000
2700000
3600000
4500000
0
100
200
300
depth / m


Abundance
Time-->
CH_3Cl
$C_2H_2Cl_2$
CH_3Br
CFC-11
CFC-113
$CHCl_3$
CH_3CCl_3
CCl_4
$CHBr_3$


Abundance
Ion 50.00 (49.70 to 50.70): A8C11-20.D
30000
20000
10000
0
CH3Cl
Time-->
1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00
Abundance
Ion 96.00 (95.70 to 96.70): A8C11-20.D
2000
1000
0
C2H2Cl2
CH3Br
Time-->
1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00
Abundance
Ion 103.00 (102.70 to 103.70): A8C11-20.D
2000
1000
0
CFC-11
CFC-113
Time-->
1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00
Abundance
Ion 83.00 (82.70 to 83.70): A8C11-20.D
5000
0
CHCl3
Time-->
1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00
Abundance
Ion 117.00 (116.70 to 117.70): A8C11-20.D
5000
0
CH3CCl3
CCl4
Time-->
1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00
Abundance
Ion 173.00 (172.70 to 173.70): A8C11-20.D
400
200
0
CHBr3
Time-->
1.00 2.00 3.00 4.00 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00

Station	Halicarbons	TOC
1	NA	NA
2	NA	NA
3	NA	NA
4	NA	NA
5	NA	NA
6	NA	NA
7	NA	NA
8	NA	NA
9	11	NA
10	NA	NA
11	9	NA
12	NA	NA
13	11	NA
14	10	NA
15	11	NA
16	11	NA
17	11	NA
18	11	NA
19	NA	NA
20	NA	NA
21	11	NA
22	NA	NA
23	1	NA
24	NA	NA
25	11	NA
26	NA	NA
27	NA	NA
28	10	6
29	NA	NA
30	11	6
31	NA	NA
32	4	6
33	NA	NA
34	NA	6
35	NA	NA
36	NA	6
37	8	6
38	NA	NA
39	5	6
40	NA	NA
41	NA	NA
42	NA	NA
43	7	6
44	NA	NA
45	10	6
46	NA	NA
47	9	6
48	NA	NA
49	8	6
50	NA	NA
51	7	6
52	NA	NA
53	3	6
54	7	6
55	NA	NA
56	8	6
57	NA	NA
58	3	6
59	11	5
60	NA	NA
61	3	6
62	NA	6