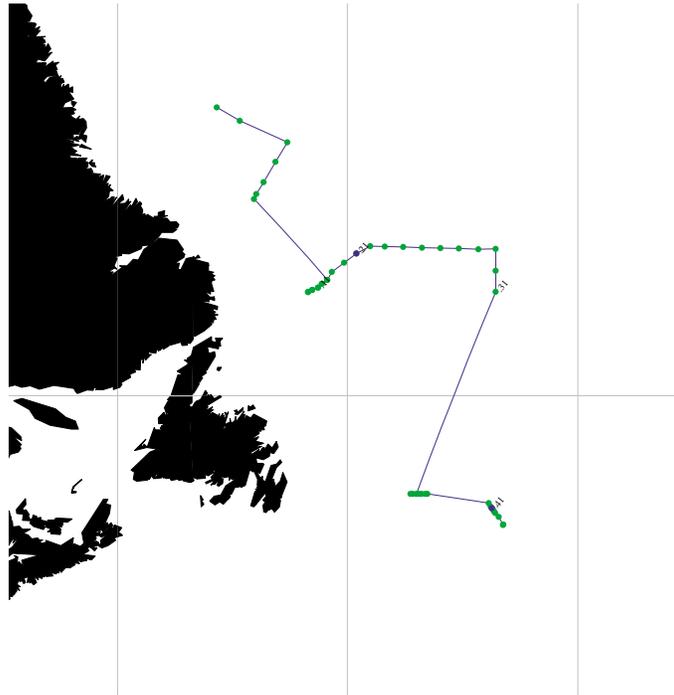


A. Cruise Narrative: AR13 and AR27



A.1. Highlights

WHP Cruise Summary Information

| | | | |
|---------------------------------------|---------------------------|--------------|------|
| WOCE section designation | AR13 and AR27 | | |
| Expedition designation (EXPOCODE) | 06AZ172 | | |
| Chief Scientist/affiliation | Monika Rhein/IfMK* | | |
| Dates | 1998.Jul.14 - 1998.Jul.30 | | |
| Ship | <i>RV Valdivia</i> | | |
| Ports of call | unknown | | |
| Number of stations | 47 | | |
| Geographic boundaries of the stations | 58°W | 59°N 46°N | 42°W |
| Floats and drifters deployed | unknown | | |
| Moorings deployed or recovered | unknown | | |
| Contributing Authors | M. Rhein | | |

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 Institut für Meereskunde • 24105 Kiel • Germany
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WHP Cruise and Data Information

Instructions: Click on headings below to locate primary reference or use navigation tools above. (Shaded headings were not available when this report was assembled)

| Cruise Summary Information | Hydrographic Measurements |
|---|---|
| Description of scientific program | Sample collection and technique Data calculation & calibration |
| Geographic boundaries of the survey | |
| Cruise track (figure) | Problems |
| Description of stations | Comments |
| Description of parameters sampled | |
| Bottle depth distributions (figure) | References |
| | |
| | Technical information |
| | |
| | Data Processing Notes |

Subpolar North Atlantic Chlorofluorocarbons: Labrador Sea

(Monika Rhein)

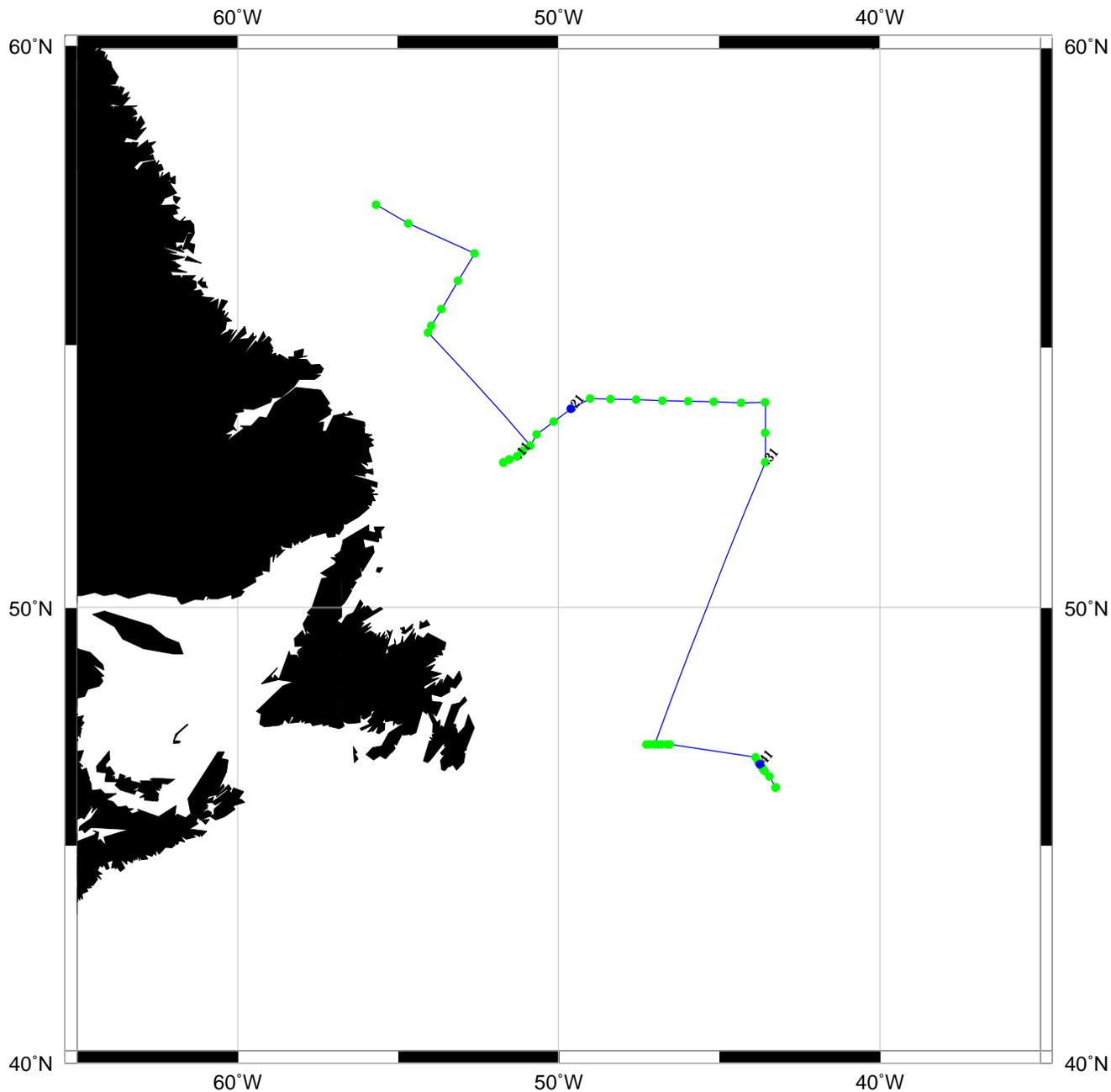
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Sample collection and technique

The water samples were drawn from precleaned 10 L Niskin bottles with gas tight 100 mL glass syringes (Becton and Dickinson). CFCs were measured on board with a GC-ECD (Electron Capture Detector) technique first described by Bullister and Weiss [1988]. About 15-25 mL were transferred to a purge and trap unit. The CFCs were separated on a packed stainless steel column filled with Porasil C and detected with an ECD. The carrier gas is ECD pure Nitrogen, which was additionally cleaned by molsieves (13X mesh 80/100).

All 'O' rings and valves as well as the nylon stopcocks (of the syringes) were removed and washed in isopropanol and baked in a vacuum oven for 24 hours prior the cruise. The Niskin bottles were cleaned with isopropanol. The rubber bands on all bottles were replaced by stainless steel springs. The personnel for all water sampling and handling procedures at the bottles wore one-way gloves to protect the valves from grease. A standard gas (kindly provided by D. Wallace, IfM Kiel) was used to convert the ECD signal in concentrations. The CFC concentrations are reported in pmol kg^{-1} on the SIO93 scale (R. Weiss, SIO).

Station Locations for AR13 and AR27, 1998



Performance

The cruise was split into three legs. During the first leg (stations 1-12) mooring work were carried out, and the CFC system was not on board. On leg 2 (stations 13-48), the Kiel CFC system worked continuously and a total of 410 CFC-12 and 510 CFC-11 water samples were measured. The survey was dedicated to the circulation of the deep water masses. During periods of dense station spacing, sampling was focused on the water column below 800 m depth.

Accuracy of the data was checked by analysing 70 CFC-11 and 47 CFC-12 samples twice and the mean rms was 0.8% for CFC-12 and 0.6% for CFC-11 (Figure 1). The system and syringe blanks were checked by purging ECD clean Nitrogen permanently through 5 L seawater. The blanks were lower than $0.005 \text{ pmol kg}^{-1}$ for both components.

As no CFC poor water is available in the western subpolar North Atlantic, the Niskin bottle blanks could not be checked directly. On our cruises in the Northern Indian Ocean and the Tropical Atlantic, where CFC free deep water is available, the blanks of the precleaned bottles were lower than $0.003 \text{ pmol kg}^{-1}$ for both components (CFC-12 and CFC-11).

The temporal evolution of the ECD efficiency is shown in Figure 2. During the cruise the efficiency decreased about 20%. Major changes occurred, when the drying agent (magnesium perchlorate) in the purge and trap unit was exchanged or the molsieves had to be baked and therefore exchanged.

To correct the temporal drift, a calibration curve with 4-6 different standard gas volumes was carried out before and after each station, the change between these curves is thought to occur linear with time. As a typical example, the two calibration curves for station 20 are presented in Figure 3. CFC concentrations are calculated by using the two neighbored calibration points, assuming that the calibration curve is linear between these points.

At first we used sample volumes, precalibrated by the company (Machery and Nagel, Germany) for the analysis of standard gas. It turned out that these volumes could be off by more than 5%, affecting the precision of the measured oceanic CFC concentrations by the same amount. Therefore, in 1998, the volumes for the gas standard measurements (nominal 2 mL and 5 mL) were calibrated against two 'master' volumes by D. Wallace's group, who had done this task also for the CO₂ community.

CFC measurements of the air inside the vessel and especially in the lab were carried out frequently in order to check for contamination. In general, the CFC concentrations in both places were only a few percent higher than in clean air. Clean air measurements were carried out occasionally by sampling air from the ship's compass bridge or forecastle.

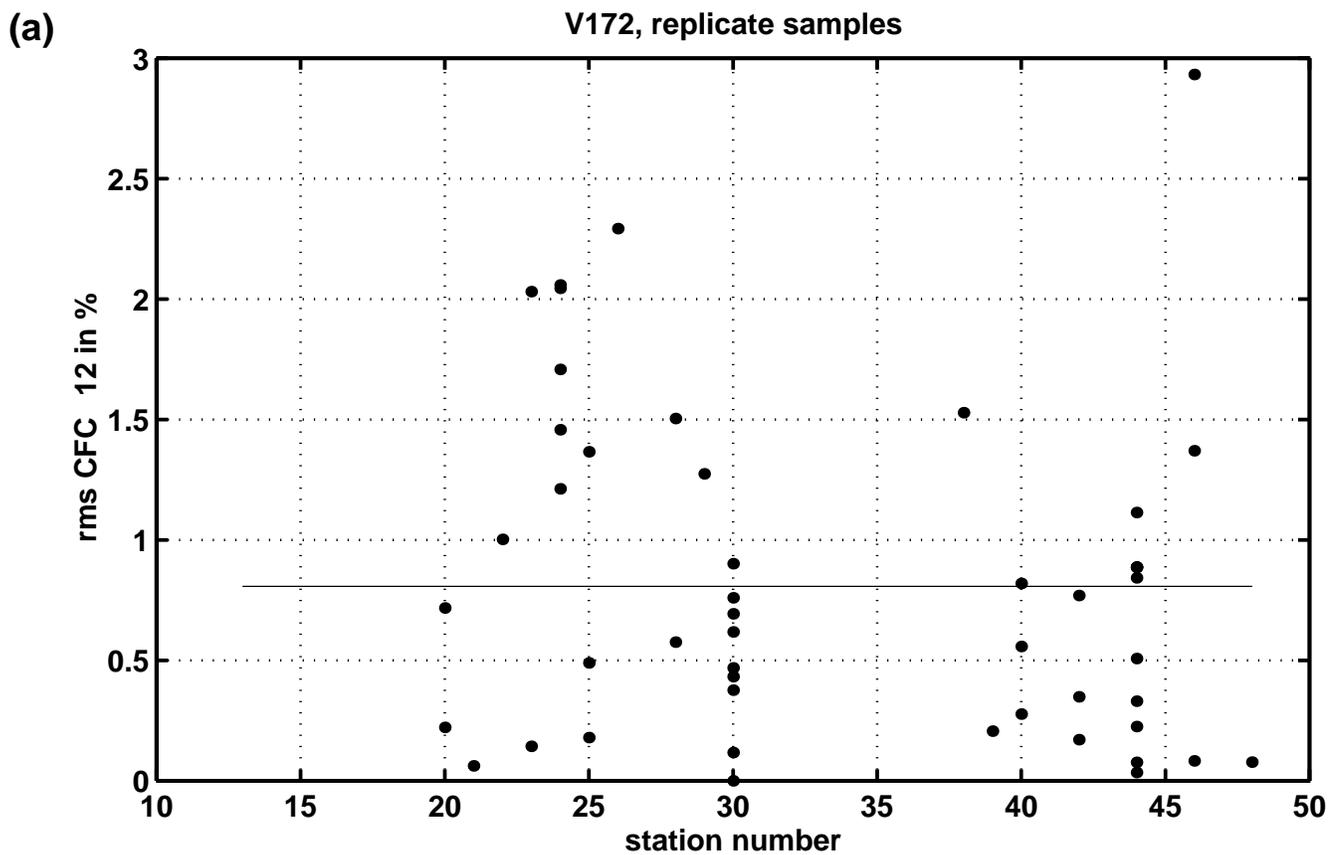
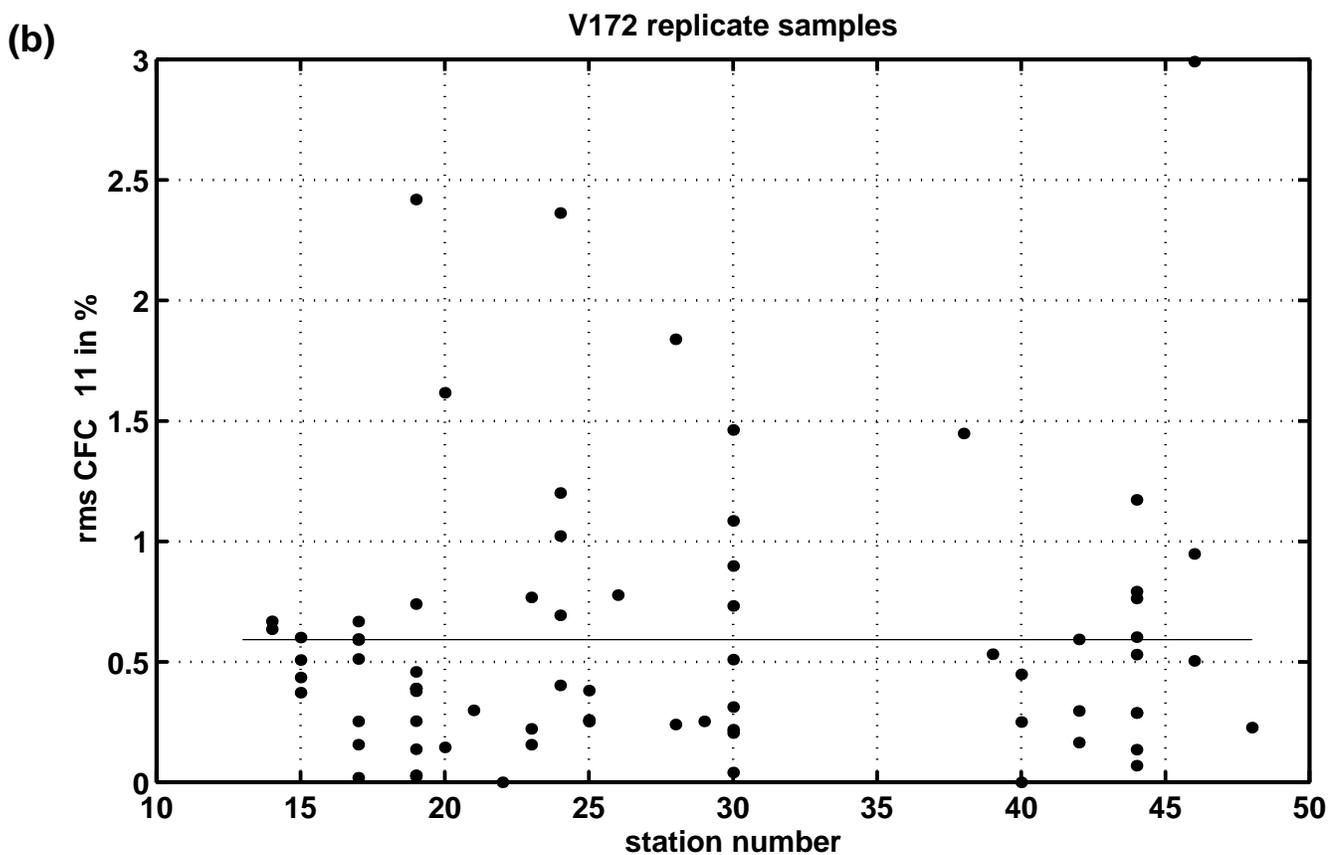


Figure 1: Accuracy (%) of the CFC-12 (a) and CFC-11 replicate samples (b) against station number. The lines represent the mean accuracy of the CFC-12 and CFC-11 samples, respectively.



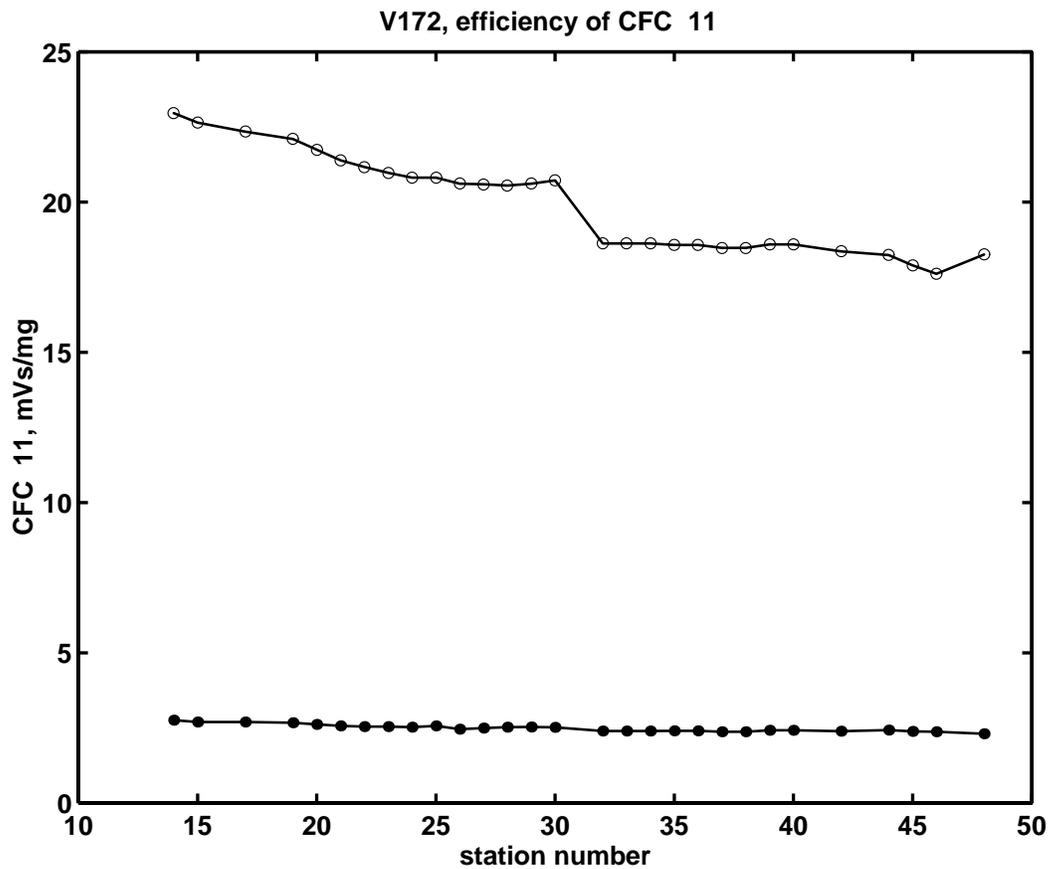


Figure 2: Temporal evolution of the efficiency of the ECD (mVs/mg standard) for the 5 mL sample volume.

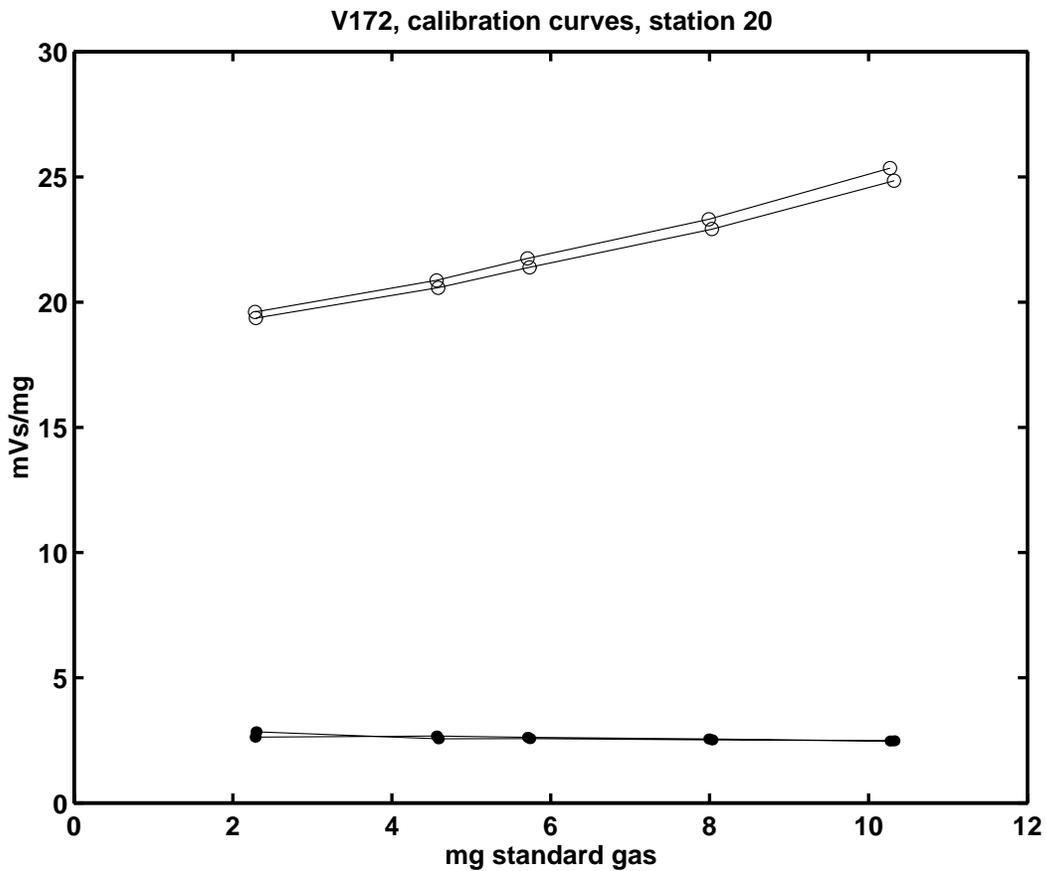


Figure 3: Examples for calibration curves of CFC-12 and CFC-11, station 20.

Problems

From CTD profiles 14 to 21 the CFC-12 data could not be processed because of an unknown substance with a similar retention time than CFC-12.

On the third leg, the CFC system malfunctioned and it was later found out, that the connection between the gas chromatographic column and the ECD was broken.

Comments

The CFC-11 surface saturation relative to the atmospheric value of 266 ppt varied from 104-125% (Figure 4). The largest supersaturations were found off the shelf near Flemish Cap, they are correlated with a low salinity (Figure 5). These supersaturations are presumably caused by recent mixing of cold, fresh, and CFC rich water with warmer water from the south, while the air sea gas exchange had not enough time to equilibrate with the atmosphere. Such extreme values are observed in summer 1997, too [Körtzinger et al., 1999].

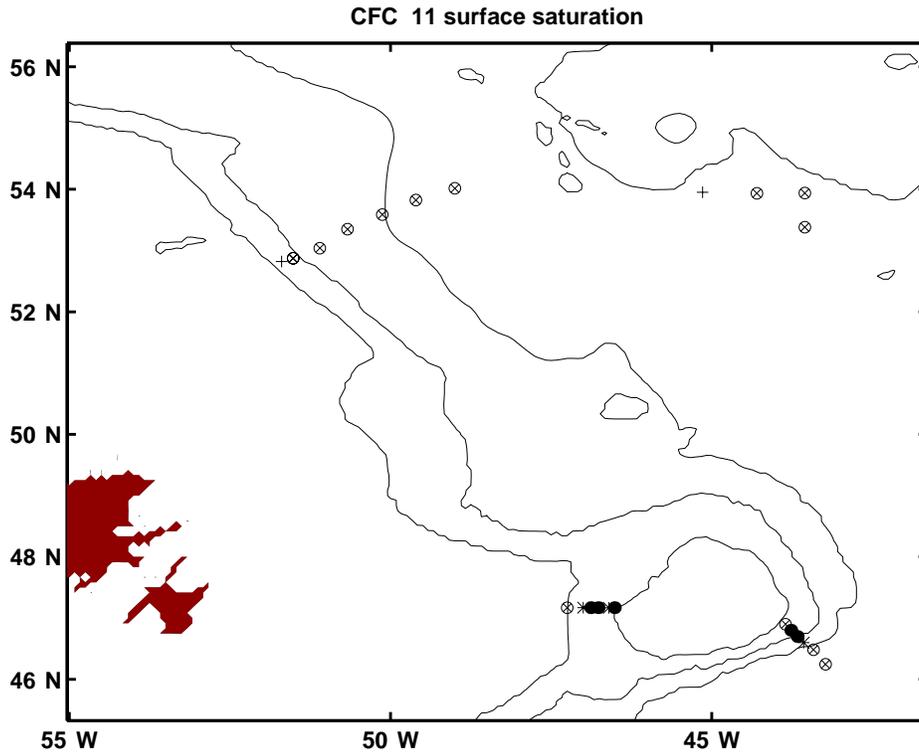


Figure 4: CFC-11 surface saturation relative to 266 ppt CFC-11, black dot: 120-125%, star: 120-115%, circle with cross: 115-105%, and cross: 105-104%.

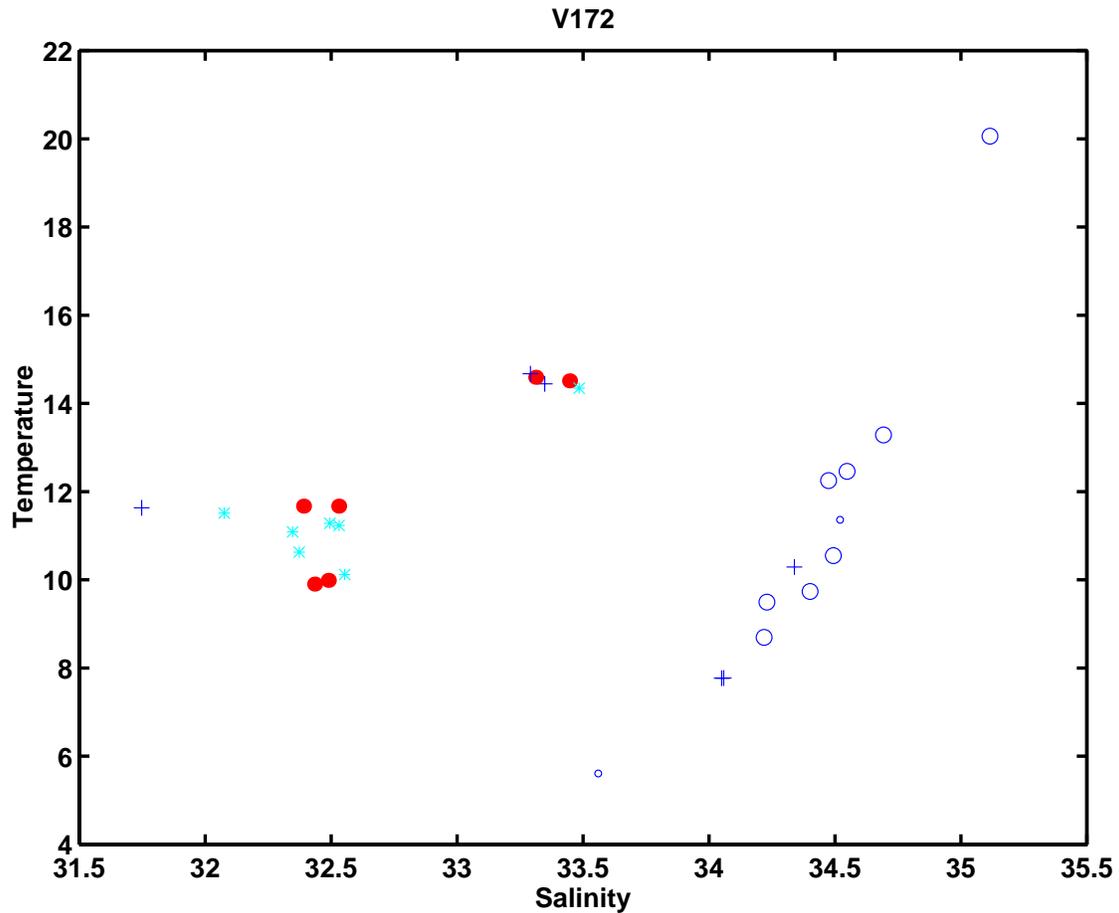


Figure 5: Theta-S diagram for surface water; black dots: CFC-11 saturation (relative to 266 ppt) 120-124%, star: 120-115%, plus: 115-110%, open circles: 110-105%, small circles: 105-103%.

The CFC-11/CFC-12 ratio below 1000 m depth is 2.05 in the mean (**Figure 6**), which is similar to the observation made in summer 1997 during the Meteor 39 cruise.

In **Figure 7** all CFC-11 concentrations measured during the cruise Valdivia 172 are shown. In the upper 2000 m (the lower limit of the LSW) the values are about 4 pmol kg^{-1} . At larger depth (within the GFZW) the concentrations decreased to less than 2 pmol kg^{-1} and increased again near the bottom caused by CFC-rich DSOW.

References

Bullister, J.L. and R.F. Weiss (1988). Determination of CCl_3F and CCl_2F_2 in seawater and air. *Deep-Sea Res.*, 35, p. 839-853.

Körtzinger, A., M. Rhein, and L. Mintrop (1999). Anthropogenic CO_2 and CFCs in the North Atlantic Ocean – A comparison of man-made tracer. *Geophys. Res. Lett.*, 26, p. 2065-2068.

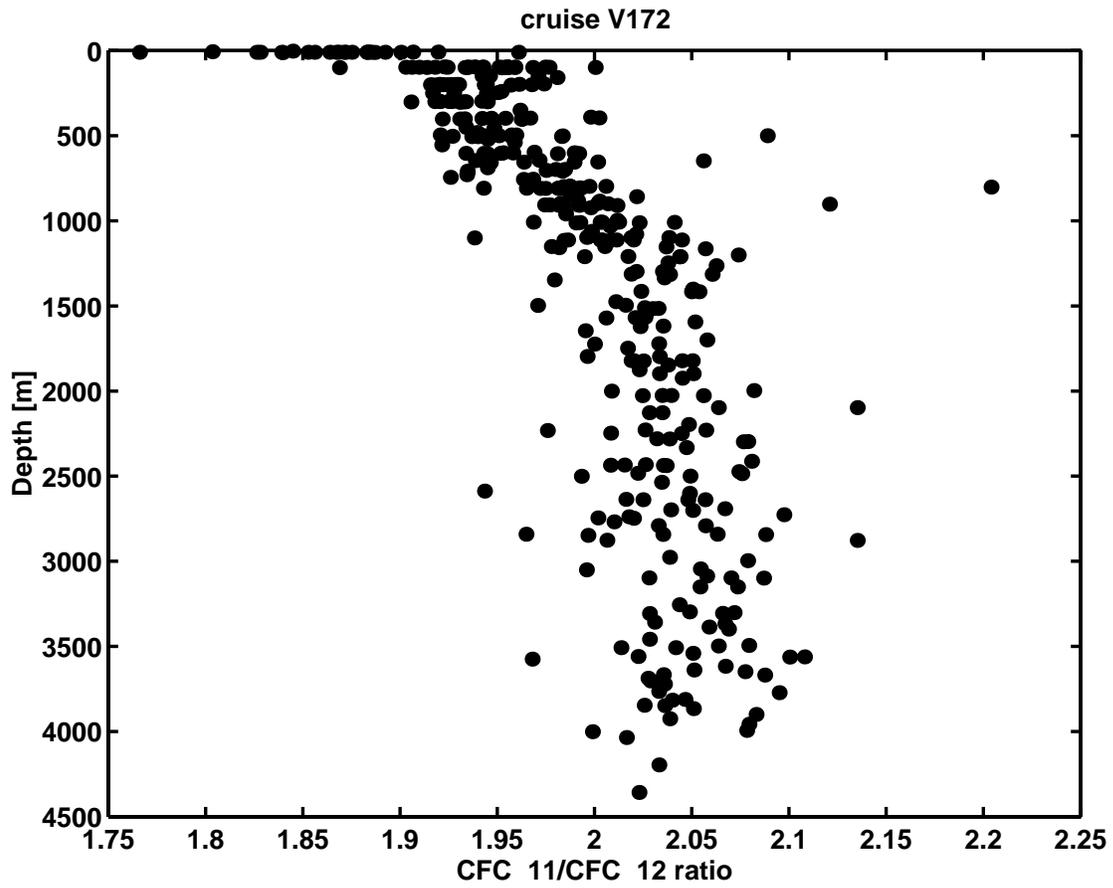


Figure 6: Cruise V172, all CFC-11/CFC-12 ratios versus depth.

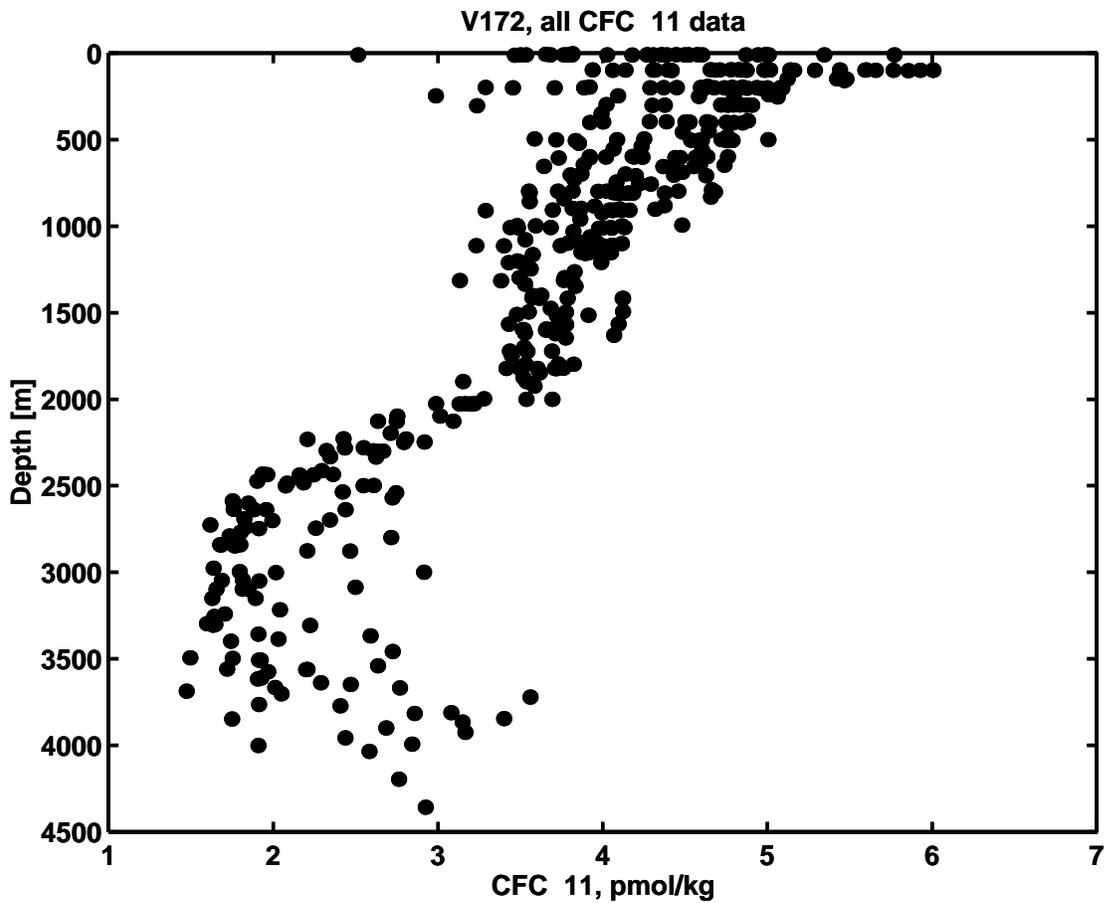


Figure 7: Cruise V172, all CFC-11 [pmol kg⁻¹] data versus depth.

Appendix

| The station file 'valdivia172.sum' includes: | The bottle file 'valdivia172.sea' includes: |
|---|--|
| 1 station number | 1 station number |
| 2 year | 2 bottle number |
| 3 month | 3 depth (dbar) |
| 4 day | 4 in-situ temperature (°C) |
| 5 hour: decimal minutes | 5 salinity (psu) |
| 6 latitude: decimal minutes | 6 CFC-12 (pmol kg ⁻¹) |
| 7 longitude: decimal minutes | 7 CFC-11 (pmol kg ⁻¹) |
| 8 water depth (m) | 8 WOCE quality flag for CFC-12 and CFC-11 |
| 9 depth of CTD profile (m) | |

Technical information

| | |
|------------------------------------|--|
| Gas chromatograph | Shimadzu GC 14 |
| GC column | stainless steel, packed with Porasil C |
| Cooling trap | with Porapak T and Porasil C |
| Trap temperatures | -30°C, 100°C |
| Column temperature | 70°C, isothermal |
| ECD temperature | 300°C |
| Electron capture detector | Shimadzu |
| Software for chromatogram analysis | Shimadzu CLASS LC 10 (1.63) |
| Standard gas | ALM 066676, D. Wallace, IfM Kiel |
| Precision | CFC-11: 3%, CFC-12: 5% |
| Accuracy | CFC-11: 0.6%, CFC-12: 0.8% |
| Blanks | negligible |

WHPO Data Processing Notes

| Date | Contact | Data Type | Data Status Summary |
|----------|---------|-------------|---|
| 02/14/00 | Uribe | BTL | Submitted temp, salinity, CFC11 and CFC12 |
| | | | <p>Files from directory valdivia172 were moved from ftp-incoming.2000.02.14/ This cruise took place July 14th - July 30th 1998. The data provided was temperature, salinity, CFC11 and CFC12. The expocode is 06AZ172. The doc file contained is M. Rhein's CFC report. All of the files are unformatted. Files were sent by Monica Rhein. Directory ar13_e/ar27 was created for this data. We have no records about who the Chi Sci for this cruise was.</p> |
| 12/22/00 | Uribe | CFCs | Data Encrypted; until released by Monica Rhein |
| 12/27/00 | Buck | BTL/SUM/DOC | Submitted; sum/btl/doc unformatted; btl encrypted |
| | | | <p>WHPO now has an unformatted sumfile, encrypted and unformatted BOT file, and unformatted DOC file. No PIs known for this cruise... This data is nonpublic.</p> |
| 04/23/02 | Lebel | CFCs | Final Data Submitted; still not public |
| | | | <p>Regarding line: AR13 ExpoCode: 06AZ172 Cruise Date: 1998/07/14 - 1998/07/26 From: LEBEL, DEBORAH Email address: lebel@ldeo.columbia.edu Institution: LDEO Country: US The file: valdivia172.dat - 78048 bytes has been saved as: 20020423.111843_LEBEL_AR13_valdivia172.dat in the directory: 20020423.111843_LEBEL_AR13</p> <p>The data disposition is: Non-Public To Go Public?</p> <p>The file format is: Plain Text (ASCII)</p> <p>The archive type is: NONE-Individual File</p> <p>The data type(s) is: Other-final CFC data</p> <p>The file contains these water sample identifiers: Station Number (STATNO) Bottle Number (BTLNBR)</p> <p>LEBEL, DEBORAH would like the following action(s) taken on the data: Merge Data Place Data Online Update Parameters</p> <p>Any additional notes are: These are the finalized CFC data for Valdivia 172 (06AZ172), including the QUALT2 word. Scale is SIO98, units are pmol/kg. Data have yet to be made public by PI, Monika Rhein.</p> |

WHPO Data Processing Notes

| | | | |
|----------|---|-------------|--------------------------------|
| 05/01/02 | Bartolacci | BTL/SUM/DOC | Reformatting Needed |
| | btl: cfc only; doc: pdf; SUM needs reformatting. BOT only contains CFCs & needs reformatting. No CTD. DOC not ascii/r | | |
| 04/03/03 | Kappa | DOC | Final PDF/TXT Reports Compiled |
| | Previous online doc was a text version of the PI's pdf file. New pdf includes figs & whpo-generated cruise track. Both new reports (text and pdf) include M. Rhein's cfc report (reformatted), whpo summary page, and these data processing notes. | | |