

R/V Sonne 128

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Indian Ocean Chlorofluorocarbons

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- Region: Arabian Sea, 8°N – 21°N, 50°E – 70°E
- Date: January, 7 – January, 29, 1998
- Files: sonne128.sum, sonne128.sea

Sample collection and technique

All samples were collected from 10 L Niskin bottles. The bottles had been cleaned prior to the cruise using isopropanol. All 'O' rings, valves, and taps were removed, washed in isopropanol and baked in a vacuum oven for 24 hours. 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.

About 100 mL of water were taken from the water bottles with gastight glass syringes (Becton and Dickinson). Then 15-25 mL of the samples were transferred to a purge and trap unit and analyzed on board following the procedures described in *Bullister* and *Weiss* [1988]. The CFCs were separated on a packed stainless steel column filled with Porasil C and detected with an Electron Capture Detector (ECD). The carrier gas was ECD pure Nitrogen, which was additionally cleaned by molsieves (13X mesh 80/100). A standard gas 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).

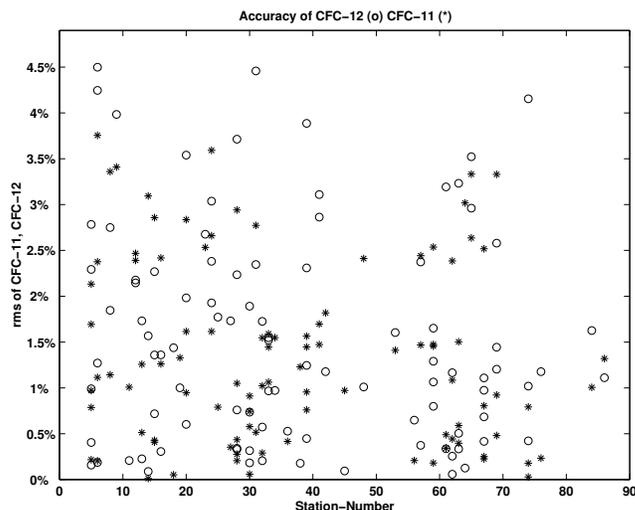


Figure 1: Accuracy of CFC-11 (*) and CFC-12 (o); replicate samples plotted vs station number.

Performance

During the cruise So128 the Kiel CFC system worked continuously. Both freon components CFC-11 and CFC-12 had been sampled on 75 CTD stations and 1210 water samples were analyzed. The accuracy was checked by measuring more than 10% of the water samples twice or more (Figure 1). It was found to be 1.4% or $0.007 \text{ pmol kg}^{-1}$ for CFC-12 and for CFC-11 1.3% or $0.006 \text{ pmol kg}^{-1}$. The mean blank of the sample transfer and the measurement procedure was determined by degasing 1–2 mL of CFC free deep water. During the cruise it was in the order of $0.008 \text{ pmol kg}^{-1}$ for CFC-11 and $0.006 \text{ pmol kg}^{-1}$ for CFC-12. Furthermore, CFC free water was created by degasing 5 L of seawater with ECD-pure nitrogen gas to determine blanks of the measurement system and the syringes. Analysis of 25 mL of blankwater resulted in concentrations below $0.007 \text{ pmol kg}^{-1}$ for both components. The efficiency of the ECD decreased from 100% at the beginning to about 65% for CFC-11 and to 45% for CFC-12 at the end of the cruise (Figure 2). To correct the temporal drift of the ECD, a calibration curve with seven different gas volumes was taken before and after each station. The temporal change of the efficiency between two calibration curves was assumed to be linear in time. CFC concentrations were calculated by using the two neighbored calibration points, supposing that the calibration curve is linear between these points.

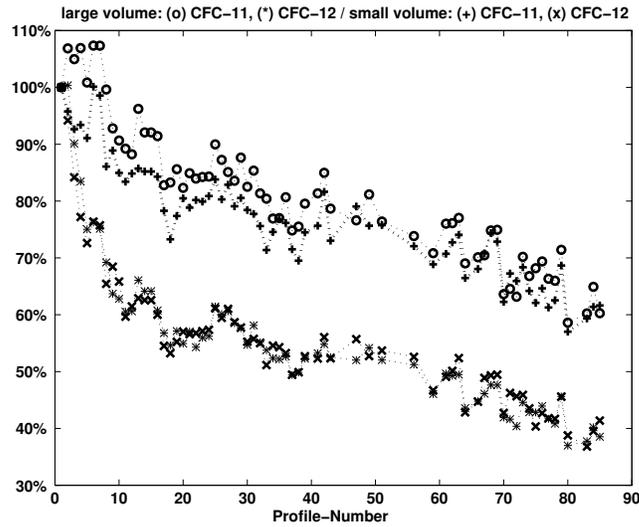


Figure 2: *Temporal evolution of the ECD-efficiency for the small sample volume (0.5 mL) and the large volume (2 mL).*

Contamination

At the beginning of the cruise, some samples indicated higher freon concentration within the deep water. However, detail analysis show that these signals were made by five syringes, which were taken away and these data were removed.

On some stations, the CFC-12 peaks were disturbed by the high N_2O levels, these data were removed.

Comments

As we know from previous WOCE cruises in the Arabian Sea, the freon concentrations decrease exponentially from the surface to about 1000 *m* depth. During this cruise many water samples were collected at larger depth, to confirm this result or to find a new signal in the deep water. The detection limit decreased to larger depth, but below about 1400 *m* depth no significant CFC signal could be found (Figure 3). Thus no ventilated deep or bottom water reached the Arabian Sea north of 8°N until January 1998.

South of Oman at about 60°E (profiles 83-86) the CFC-12 concentrations in the density range of the PGW (Persian Gulf Water, $26.3 < \sigma_\theta < 26.8$) were much higher than in other region, whereas the CFC-11 concentrations remained unaffected. Thus the CFC-11/CFC-12 ratio was extremely low with values of less than 1.1 [Plähn et al., 1999], which is usually not observed in the ocean (Figure 5). East of Socotra this feature was observed, too, with a ratio of 1.3.

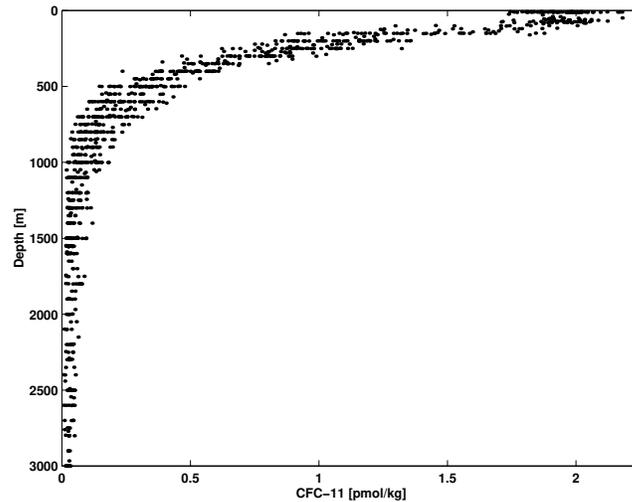


Figure 3: All CFC-11 concentration [pmol kg^{-1}] versus depth measured during the cruise So128.

These high CFC-12 concentrations were not caused by contamination of the Niskin bottles, syringes, or of the CFC purge and trap system. The same signal was observed in the Gulf of Oman during the Knorr cruise 145, in August 1995 (R. Fine, RSMAS Miami, USA) and during the Meteor cruise 32/1, in April 1995 [Rhein et al., 1997]. Until 1998, the feature spread southward and was measured during the So128 cruise south of Oman and east of Socotra. The PGW was probably contaminated in the northern Persian Gulf, as the signal was restricted to the density level of the PGW [Plähn et al., 1999].

The surface saturation was between 105% and 115%, with mean values of 111% for CFC-11 and 109% for CFC-12 (Figure 4). The reason for these supersaturations is unknown. In January, the SST was higher than measured in summer 1995 (cruise Meteor 32), presumably caused by the different time scales of heating and air-sea gas exchange.

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, S. 839–853.
- Plähn, O., M. Rhein, R.A. Fine, and K.F. Sullivan (1999). Pollutants from the Gulf War serve as water mass tracer in the Arabian Sea. *Geophys. Res. Lett.*, 26, S. 71–74.
- Rhein, M., L. Stramma, and O. Plähn (1997). Tracer signals of the intermediate layer of the Arabian Sea. *Geophys. Res. Lett.*, 24, S. 2561–2564.

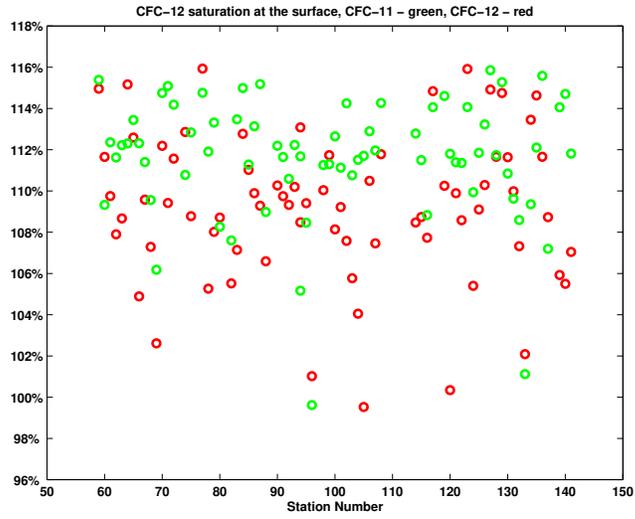


Figure 4: *CFC-11 (green) and CFC-12 (red) saturation at the surface*

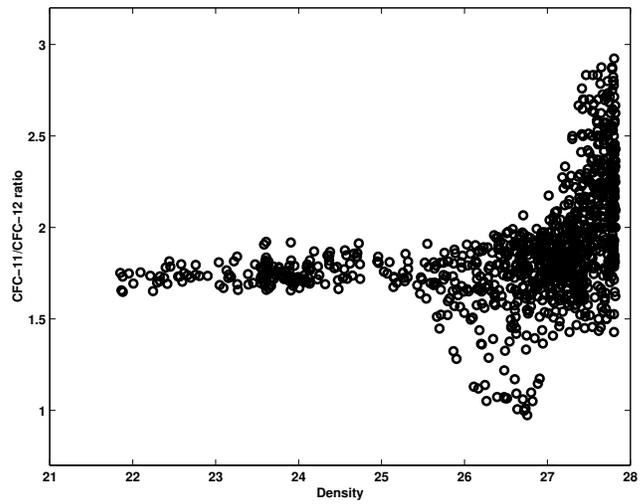


Figure 5: *CFC-11/CFC-12 ratio versus density*

Appendix

- the station file 'sonne128.sum' includes:

- 1 station number
- 2 year
- 3 month
- 4 day
- 5 hour: minutes in decimal system
- 6 latitude: minutes in decimals
- 7 longitude: minutes in decimals
- 8 water depth (*m*)
- 9 depth of CTD profile (*m*)

- the bottle file 'sonne128.sea' includes:

- 1 station number
- 2 bottle number
- 3 depth (*dbar*)
- 4 in-situ temperature ($^{\circ}\text{C}$)
- 5 salinity (psu)
- 6 CFC-12 (*pmol kg⁻¹*)
- 7 CFC-11 (*pmol kg⁻¹*)
- 8 WOCE quality flag for CFC-12 and CFC-11

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 $^{\circ}\text{C}$, 100 $^{\circ}\text{C}$
Column temperature	70 $^{\circ}\text{C}$, isothermal
ECD temperature	300 $^{\circ}\text{C}$
Electron capture detector	Shimadzu
Software for chromatogram analysis	Shimadzu CLASS LC 10 (1.63)
Standard gas	ALM 064824, D. Wallace, PMEL

Accuracy	CFC-11: 1.3%, CFC-12: 1.4%
Blanks	CFC-11: 0.008 <i>pmol kg⁻¹</i> , CFC-12: 0.006 <i>pmol kg⁻¹</i>