# Halogenated substances as marine tracers

*Toste Tanhua*

# Halogenated substances as marine tracers

by

## *Toste Tanhua*



## Akademisk avhandling

# Abstract

Tanhua, Toste. **Halogenated substances as marine tracers**.
*Department of Analytical and Marine Chemistry, Göteborg University, S-412 96 Göteborg, Sweden.*

Low molecular weight halogenated hydrocarbons, halocarbons, have been studied and used as marine tracers. Special interest has been focused on the chlorofluorocarbons (CFCs) CFC-11, CFC-12 and CFC-113 together with carbon tetrachloride ($CCl_4$) and methyl chloroform ($CH_3CCl_3$). These halocarbons are transferred from the atmosphere to seawater via the air-sea interface. The prerequisites for the use of them as tracers of water mass movement and mixing are examined. The distribution and surface saturation of the CFCs and $CCl_4$ in the Greenland Sea are discussed. Multivariate analysis is described and applied to tracer and hydrographical data from the Denmark Strait, and has proved to be a useful tool for demonstrating water mass variability in the strait. The sources and sinks of halocarbons in seawater are examined. In particular the removal of halocarbons by means of reduction in oxygen-depleted seawater is discussed. It is concluded that halocarbons, with the exception of CFC-12, are removed from anoxic seawater and cannot be used as tracers there.

The determination of halocarbons and sulphur hexafluoride is accomplished by purge and trap sample pre-treatment followed by gas chromatographic separation and electron capture detection. A description of the analytical techniques is provided together with a discussion of the capacity of the techniques.

The distribution of water masses over the continental shelf in the southern Weddell Sea is discussed in paper I, where residence times of water masses under the ice shelf in the Weddell Sea are estimated with the aid of CFC measurements. Some CFCs together with other halocarbons were used as marine tracers in the Bosphorus Strait, Turkey, paper II. Indications of the removal of carbon tetrachloride from the anoxic bottom waters in the Baltic Sea during an investigation in 1992 are presented in paper III. Further investigations into the fate of halocarbons under oxygen depleted conditions were conducted in the Black Sea. Removal of the halocarbons seemed to be correlated to the redox potential in the seawater, paper IV. Measurements of the CFCs were made during a field trip to the superanoxic fjord Framvaren, Norway. A model for the ventilation of the fjord, based on silicate, salinity and tritium profiles, was made and interpretations of the persistence of the CFCs could be made based on this model. It was found that CFC-12 was persistent whereas CFC-11, CFC-113, $CCl_4$ and $CH_3CCl_3$ were all removed from anoxic seawater with half-lives in the range of 2-14 years, paper V. Hydrographical and chemical data obtained within the Nordic WOCE programme during 1994 from the area between Scotland and Greenland were used to study the overflow from the Nordic Seas (Greenland Sea, Norwegian Sea and Iceland Sea) to the North Atlantic. Multivariate analysis was applied to the hydro-chemical data and mixing of the overflow water south of the ridge as well as the composition of the overflowing water could be estimated, paper VI.

**Key words**: gas chromatography, purge and trap, halocarbons, chlorofluorocarbons, sulphur hexafluoride, marine tracers, Weddell Sea, Black Sea, Baltic Sea, Denmark Strait, Greenland Sea, anoxic seawater, reduction, deliberately released tracers, multivariate analysis.

# Halogenated substances as marine tracers

by

*Toste Tanhua*

## Akademisk avhandling

# Abstract

Tanhua, Toste. **Halogenated substances as marine tracers**.
*Department of Analytical and Marine Chemistry, Göteborg University, S-412 96 Göteborg, Sweden.*

Low molecular weight halogenated hydrocarbons, halocarbons, have been studied and used as marine tracers. Special interest has been focused on the chlorofluorocarbons (CFCs) CFC-11, CFC-12 and CFC-113 together with carbon tetrachloride ($CCl_4$) and methyl chloroform ($CH_3CCl_3$). These halocarbons are transferred from the atmosphere to seawater via the air-sea interface. The prerequisites for the use of them as tracers of water mass movement and mixing are examined. The distribution and surface saturation of the CFCs and $CCl_4$ in the Greenland Sea are discussed. Multivariate analysis is described and applied to tracer and hydrographical data from the Denmark Strait, and has proved to be a useful tool for demonstrating water mass variability in the strait. The sources and sinks of halocarbons in seawater are examined. In particular the removal of halocarbons by means of reduction in oxygen-depleted seawater is discussed. It is concluded that halocarbons, with the exception of CFC-12, are removed from anoxic seawater and cannot be used as tracers there.

The determination of halocarbons and sulphur hexafluoride is accomplished by purge and trap sample pre-treatment followed by gas chromatographic separation and electron capture detection. A description of the analytical techniques is provided together with a discussion of the capacity of the techniques.

The distribution of water masses over the continental shelf in the southern Weddell Sea is discussed in paper I, where residence times of water masses under the ice shelf in the Weddell Sea are estimated with the aid of CFC measurements. Some CFCs together with other halocarbons were used as marine tracers in the Bosphorus Strait, Turkey, paper II. Indications of the removal of carbon tetrachloride from the anoxic bottom waters in the Baltic Sea during an investigation in 1992 are presented in paper III. Further investigations into the fate of halocarbons under oxygen depleted conditions were conducted in the Black Sea. Removal of the halocarbons seemed to be correlated to the redox potential in the seawater, paper IV. Measurements of the CFCs were made during a field trip to the superanoxic fjord Framvaren, Norway. A model for the ventilation of the fjord, based on silicate, salinity and tritium profiles, was made and interpretations of the persistence of the CFCs could be made based on this model. It was found that CFC-12 was persistent whereas CFC-11, CFC-113, $CCl_4$ and $CH_3CCl_3$ were all removed from anoxic seawater with half-lives in the range of 2-14 years, paper V. Hydrographical and chemical data obtained within the Nordic WOCE programme during 1994 from the area between Scotland and Greenland were used to study the overflow from the Nordic Seas (Greenland Sea, Norwegian Sea and Iceland Sea) to the North Atlantic. Multivariate analysis was applied to the hydro-chemical data and mixing of the overflow water south of the ridge as well as the composition of the overflowing water could be estimated, paper VI.

**Key words**: gas chromatography, purge and trap, halocarbons, chlorofluorocarbons, sulphur hexafluoride, marine tracers, Weddell Sea, Black Sea, Baltic Sea, Denmark Strait, Greenland Sea, anoxic seawater, reduction, deliberately released tracers, multivariate analysis.

# Table of contents

## Part A

# Part B

I     Gammelsrød, T., Foldvik, A., Nøst, O.A., Skagseth, Ø., Anderson,
      L.G., Fogelqvist, E., Tanhua, T., Jones, E.P. and Østerhus, S.,
      1994. Distribution of Water Masses on the Continental Shelf in the
      Southern Weddell Sea. In: *The Polar Oceans and Their Role in
      Shaping the Global Environment,* Eds. R. Muench, and O.M.
      Johannessen,  American Geophysical Union, Washington DC,
      USA. Geophysical Monograph 84, 159-176.

II    Fogelqvist, E., Tanhua, T., Bastürk, Ö. and Salihoglu, I. 1995. The
      distribution of some man-made and biologically produced
      halocarbons in a double layer flow strait system. *Continental Shelf
      Research.* **16(9),** 1185-1199.

III   Krysell, M., Fogelqvist, E. and Tanhua, T., 1994. Apparent
      removal of the transient tracer carbon tetrachloride from anoxic
      seawater. *Geophysical Research Letters.* **21(23),** 2511-2514.

IV    Tanhua, T., Fogelqvist, E. and Bastürk, Ö., 1996. Reduction of
      volatile halocarbons in anoxic seawater, results from a study in the
      Black Sea. *Marine Chemistry*, **54**, 159-170.

V     Fogelqvist, E., Tanhua, T. and Olsson K.A., 1997. Modelling
      ventilation of the anoxic fjord Framvaren for evaluation of
      halocarbon tracer persistence. Submitted to *Marine Chemistry*.

VI    Fogelqvist, E., Blindheim, J., Tanhua, T., Buch, B. and Österhus,
      S., 1997. Greenland-Scotland Overflow studied by hydro-chemical
      multivariate analysis. Manuscript.

# 1. Introduction

Low molecular weight halogenated hydrocarbons, here called halocarbons, are widespread compounds in the environment, including seawater. These compounds are either produced naturally by living organisms or they are of anthropogenic origin. Several of them will fall into both categories.

The anthropogenic halocarbons have different sources and pathways into seawater. A distinction can be made between the halocarbons that enter the seawater from the atmosphere via the sea surface and those entering via discharge of industrial waste water or artificially chlorinated water. A major interest of this thesis is the utilisation of the chlorofluorocarbons (CFCs), especially CFC-12 ($CCl_2F_2$), CFC-11 ($CCl_3F$), CFC-113 ($CCl_2FCClF_2$) and the chemically related compounds carbon tetrachloride ($CCl_4$) and methyl chloroform ($CH_3CCl_3$) as marine tracers. These compounds will be referred to as the halocarbon tracers. They are compounds that enter the seawater via the air-sea interface and have a time-dependent source function due to, until recently, increasing atmospheric concentrations. Their time-dependent source functions, together with negligible natural background levels, generally few sinks in seawater, and the relatively fast and inexpensive method for their determination, make these compounds suitable as transient marine tracers. With these tracers it is possible to determine residence times of water masses and their mixing with surrounding water.

In recent years a new transient tracer has been introduced, sulphur hexafluoride ($SF_6$), which is a gaseous halogenated compound that also has anthropogenic origin. Sulphur hexafluoride has an atmospheric source similar to the halocarbon tracers and can also be used as a transient tracer. Although sulphur hexafluoride may be used as a transient tracer, its major use has so far been as a deliberately released tracer to, for example, determine diapycnal diffusivity and air-sea transfer velocities.

In oceanographic studies generally, a wide range of chemical and hydrographical parameters are available for the interpretation of marine systems. Multivariate analysis is a statistical method for interpreting many variables simultaneously. These may, in oceanographic studies, include salinity, temperature, nutrients and halocarbon tracers. Multivariate techniques are especially useful for the study of mixing between different water masses.

A prerequisite for the use of halocarbons as transient tracers on oceanic scales is their persistence in seawater. The chemical and biological degradation of the halocarbon tracers is generally believed to be slow in comparison with the time scales of water mixing in the oceans. Different investigations have, however, shown evidence that the halocarbon tracers are unstable under certain conditions. Investigations in waters which are depleted in oxygen, such as the anoxic waters of the Black Sea and the Baltic Sea, and in the thermocline of the oceans point to a removal pathway for halocarbons controlled by redox reactions. Furthermore, in warm waters hydrolysis is an important removal pathway for both $CH_3CCl_3$ and $CCl_4$.

Concentrations of halocarbons in natural seawater are typically in the picomolar ($10^{-12}$ mol L$^{-1}$) range, and sulphur hexafluoride in the femtomolar ($10^{-15}$ mol L$^{-1}$) range, and their determination is not trivial. Measurements are usually performed by a "gas-solvent extraction" technique, the purge and trap technique, coupled to gas chromatography with electron capture detection. There are many advantages to the purge and trap technique over other extraction techniques. In the purge and trap technique the volatile compounds are transferred from the water phase to a gas phase by "bubbling" gas through the water sample. The volatiles are then trapped and concentrated onto a cold trap, from where they are desorbed by heat and injected into the gas chromatograph. After separation on a quartz capillary column the halogenated compounds can be detected by the highly sensitive and selective electron capture detector. A modified purge and trap technique is used for the determination of sulphur hexafluoride in seawater. The sample is injected into an evacuated purge chamber, promoting the transfer of $SF_6$ to the gas phase. The vacuum sparge method is also coupled to gas chromatography with electron capture detection.

Part A of this thesis discusses various aspects of halogenated marine tracers. The analytical technique is described and the sources and sinks of the halocarbons are examined. Emphasis is put on chemical degradation of halocarbons in seawater. Applications of halocarbons as marine tracers are illustarted in the Denmark Strait and the Greenland Sea. Part B of the thesis consists of six scientific papers. Results and interpretations from halocarbon measurements from various parts of the world are presented. Three of the papers deal with the removal of halocarbons in anoxic seawater. The halocarbons are used as tracers in oceanographic studies in two papers and a wider range of halocarbons is used in one paper to describe a double layer flow strait system.

# 2. Determination of halocarbons

The concentrations of halocarbons encountered in natural marine waters are low, usually up to a few picomoles per litre seawater. The low concentrations, together with the fact that seawater provides a complex matrix from an analytical point of view, necessitate the need for powerful sample pre-treatment. Isolation and concentration techniques for capillary column gas chromatography are reviewed by Poole and Schuette (1983). A useful sample work-up method for this kind of analytical problem is provided by headspace techniques. Headspace techniques are commonly used for the detection of volatile analytes with complex matrices, such as blood or soil, and/or with low concentrations of the analyte. The usefulness of headspace techniques for analysis of solid samples is discussed by Venama (1990). In headspace techniques, the volatile analytes are transferred from the actual sample to a gas phase, which is then injected into the analytical instrument, generally a Gas Chromatograph (GC). We may consider both static and dynamic head-space analyses.

In static headspace analysis the sample is allowed to equilibrate with a gas phase, the headspace gas, in a closed vessel. The headspace gas is then sampled and analysed. Usually, equilibrium is allowed to be established before the headspace gas is sampled. The sample can sometimes be heated to speed up equilibration. The advantages of this technique are its simplicity and ease of automation. All different kinds of samples, even solid samples, sediment etc., can be analysed and the measurements can be standardised either by the technique of standard additions or by standard mixtures in a similar matrix (at least for liquid samples). A drawback is the relatively high limit of detection for the method as a part of the sample is left in the non-gaseous phase and not all of the gas is sampled for analysis.

To overcome the higher limit of detection of static headspace analysis, dynamic headspace analysis can be applied. In this technique a flow of a pure gas (the purge gas) is passed over the sample which then releases its content of volatile substances. The volatiles are removed from the gas flow by a trap. There are numerous different designs of trap, depending on the nature of the analyte or separation method. The trap can be an open capillary cold trap (e.g. Graydon and Grob, 1983), a trap filled with some kind of adsorbent material (e.g. Grob et al., 1990), or a combination of both. To desorb the volatile analytes from the trap, the trap is usually heated and the GC carrier gas flows through the trap in the opposite

direction to the purge gas flow. Another technique to desorb the analytes is rinsing the trap with a solvent.

A larger part of the analyte is removed from the sample in dynamic headspace than in the static approach. This larger fraction is injected into the analytical instrument thus lowering the limit of detection. A drawback of dynamic headspace is that the time needed for total evaporation of the analytes to the gas flow may be quite long. This time can be shortened by heating the sample or by "salting out" the analyte, thus speeding up the equilibration process. A practical solution is to measure exactly the time during which gas flows over the sample and measure to what extent the analytes are evaporated. The purge efficiency is then accounted for in the calibration process.

Purge and trap is a special case of the dynamic headspace technique. In this technique a pure gas (the purge gas) is bubbled through a liquid sample instead of over it, thus decreasing the time needed for total evaporation of the volatiles from the sample. A recent overview of purge and trap sample work-up technique is provided by Scott et al. (1994). Voice and Kolb (1994) made a comparison between purge and trap and static headspace techniques in analysis of environmental samples and found better precision for the static headspace technique, concluding that this was the better approach, at least for soil analyses.

An alternative method to headspace analysis for halocarbon analysis in seawater is liquid-liquid extraction (Eklund et al., 1978; Fogelqvist et al., 1986). A major drawback of this method is that the most volatile halocarbons, i.e. the CFCs, are too volatile to be analysed this way since they will coelute with the solvent. Thus, purge and trap is the technique of choice for halocarbon analysis if one intends to measure the CFCs at the same time (Krysell and Nightingale, 1994). Purge and trap analytical methods for CFCs are described by e.g. Bullister and Weiss, (1988); Haine et al., (1995) and Happell et al., (1996). The Montreal Protocol from 1987 and its amendments put severe restrictions on the use of CFCs. This has caused an increase in the production of the CFC replacement compounds, hydrofluorocarbons (HFCs) and hydrochloro-fluorocarbons (HCFCs), with their subsequent release to the atmosphere. Analysis of these volatile chlorofluorocarbon replacement compounds by purge and trap is described by Sturrock et al., (1993), O´Doherty et al (1993) and Simmonds et al. (1995). A purge and trap system for the determination of halocarbons will be described in detail below, together

with discussions on sample treatment, calibration procedures and analytical difficulties.

## 2.1 Sampling and storage of samples.

Analysis of seawater for halocarbons has to be done shortly after sampling since halocarbons are volatile substances and are present at low concentrations in seawater. The sample may be affected by release to the atmosphere or may become contaminated by high atmospheric concentrations. Furthermore biological activity may also change the composition of the sample as some halocarbons are actually produced by algae living in seawater. It is therefore essential that the analysis takes place rapidly after sampling and that the samples are stored in an appropriate way during the storage time.

Sampling of water for analysis is, in most cases, performed on board a research vessel. The water is then collected with sampling bottles, usually mounted on a rosette with a CTD probe connected to it. Sampling takes place immediately once the water is on deck, and samples for CFCs and/or $SF_6$ are (usually) the first to be taken from the sampling bottle. The samples are drawn into 100 ml ground-glass syringes and flushed carefully without letting the water come in contact with the ambient air at any time. The syringes are equipped with luer-lock fittings on which a 3-way stainless steel stopcock is fitted. The syringes are stored in stainless steel buckets filled with cold seawater after sampling. This procedure is to prevent the water sample from being in contact with the atmosphere and to keep the samples cold. When a cold water sample is warmed up, small gas bubbles can form, which may lead to loss of volatiles from the water. To prevent this from happening the water samples are kept cold in the steel buckets either by constant flow of cold surface water or by adding ice-cubes to the steel buckets. In this way, the water samples are not affected by storage for up to 12 hours. Even so all analyses are made as rapidly as possible, usually within 6 hours, and seldom more than 12 hours after sampling.

## 2.2. Purge and trap

A purge and trap system for rapid shipboard analysis of halocarbons in seawater has been constructed and built. This system is a development of the purge and trap system described by Krysell and Nightingale (1994), which was used for the work presented in papers II and III. The requirements for the new analytical system were sufficiently high analysis capacity without any sacrifice of precision or accuracy. The purge and trap system is a dual line system with two parallel and identical lines connected to a GC equipped with two columns and two detectors. The two lines run simultaneously and in parallel, thus doubling the number of samples analysed per unit time. One of the parallel lines in the system is described schematically in Fig. 2.1.

The system has been built to be run in different modes; determination of halocarbon tracers where high precision and accuracy are needed together with high analysis capacity, or for the determination of a wider range of halocarbons where the need for precision and speed is reduced. Some minor changes in system configuration and technique have to be made depending on which mode the system is running in.

The halocarbon-system is built on an aluminium framework and all gas tubing is made of stainless steel. In the first part of the system, to the purge chamber, all tubing is of 1/8" ID and in the latter part all tubing is of 1/16" ID. The purge chamber, the sample loop and the dessicant tube are all made of glass. The valves 1 and 2 are made of hastelloy C-22 (a nickel-chromium-molybdenum alloy) to better withstand the corrosive seawater, the other valves are made of stainless steel (all valves from Valco). Valves 4 and 5 are thrown electrically, triggered by the GC programme, whereas the other valves are manual.

High quality nitrogen gas doped with 0.5 % hydrogen gas led over a heated palladium catalyst (which breaks down any traces of halocarbons) provides ultra-pure purge gas. The purge gas is regulated to a pressure of approximately 5 bar before it enters the system, where it is split into the two identical lines. A metal bellow flow controller (Porter Instruments, VCD-1000) followed by a toggle valve controls the flow of purge gas through the system.

Water is loaded on to the system through a glass loop, whose exact volume is gravimetrically determined (approximately 40 ml), and is injected into the purge chamber by the manual turn of the valve 1.
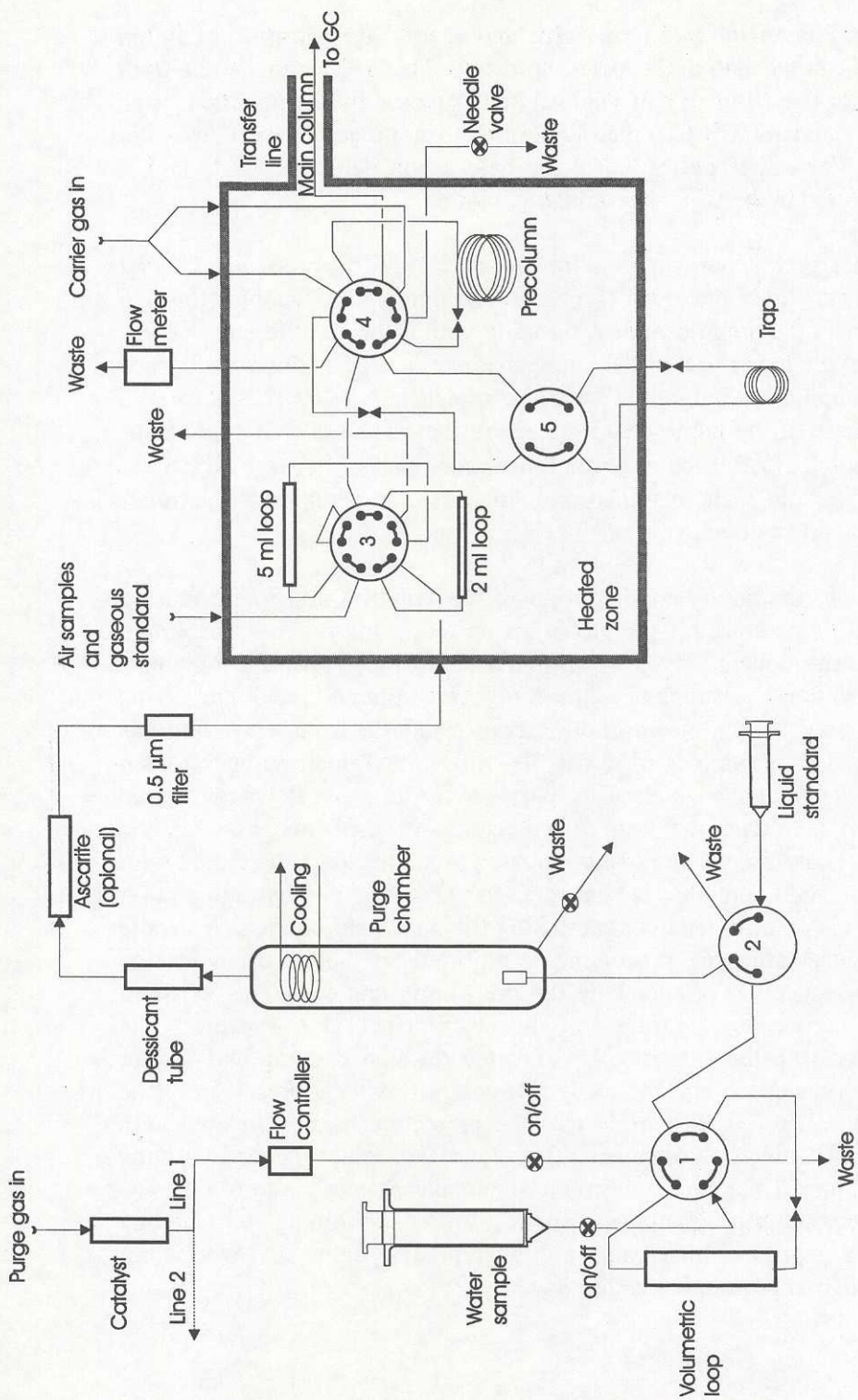
6

**Fig. 2.1.** *The purge and trap system for halocarbon analysis. The valves are in desorption mode, i.e. carrier gas flows to the trap before entering the GC and the purge gas is directed to the flow meter after the gas sampling loop. Only one of the two parallel lines is shown.*

7

Valve 2 is an internal loop valve and is used for injection of liquid standards, other than the halocarbon tracers. This valve can also be used to monitor the efficiency of the analytical process by the injection of an internal standard ($CBrCl_3$) dissolved in methanol together with the water sample. Valve 2 is only used in the halocarbon detection mode and is disconnected in the CFC determination mode.

The purge chamber is a glass tower with a glass frit (pore size 2) inlet in the lower end of the tower (Fig. 2.2). The purge gas is bubbled through the water in the purge chamber, bringing with it the volatile compounds. A vent in the lower part of the purge chamber is used to drain the purged water sample before the next sample is injected. A water trap is located downstream of the purge chamber. For further discussion of water traps see section 2.3. After the water trap, the purge gas is filtered by a 0.5 μm filter to avoid salt crystals and magnesium perchlorate particles damaging downstream valves.

To avoid premature condensation of the volatiles and to maintain a constant temperature for the gas injection loops and for the precolumn, the three subsequent valves are all in a heated zone. Valve 3 is a ten port valve with two gas sampling loops of different volume (2 and 5 ml). This valve is used for the injection of gaseous standards from a standard gas cylinder and air samples from dry 100 ml ground-glass syringes. A ten port valve (4) directs which of the purge or carrier gases flows to the trap valve (5) and onto the trap. A precolumn of the same kind as the analytical column, but only approximately 4 metres long, compared with 75 m. for main comumn, is connected to valve 4 to prevent late eluting compounds entering and contaminating the analytical column. A needle valve placed after the precolumn is adjusted so that it simulates the pressure restriction provided by the precolumn and maintains constant flow of carrier gas regardless of the position of valve 4. During the desorption step the carrier gas is directed through the trap and further onto the precolumn and the analytical column. After a preset time (see Fig 2.3) valve 4 is thrown so that the precolumn is backflushed with carrier gas. This way compounds that elute late are not injected onto the main column. This process, heart cutting, makes it possible to run the GC with temperature programmes without a final conditioning step, leading to better reproducibility, and the analytical column is saved from contamination prolonging its lifetime.

The purge gas flow is monitored by a flow meter (Sierra Instruments, Top Trak) before the gas is passed to waste. Valve 4 and 5 are driven by electric actuators and operated via the chromatographic software. Valve 5 is further controlled by a time-relay that is activated when a sample is injected into the system and closes the valve automatically after the predetermined purge time.

The trap consists of a 500 mm long open stainless steel capillary tube with internal diameter 0.75 mm (880 µl volume). The small volume of the trap makes it possible to get a sharp band of injection onto the column without any cryo-trapping device (see Section 2.4). The trap is kept at a temperature of about -150°C by immersion in the vapours over liquid nitrogen in a Dewar flask while a sample is being purged. This temperature is sufficient to trap most volatile halocarbons (CFC-12 is the most volatile of the halocarbons we measure with a boiling point of -29.8°C) without any of them breaking through the trap. This has been tested by comparing chromatograms of standard injections with various trapping times. The trap valve closes automatically after the predetermined purge time and is kept closed until desorption. For desorption the trap is heated by submersion in boiling water. The GC programme then triggers the opening of the trap valve and the halocarbons are transferred with the carrier gas flow to the precolumn and futher to the main column in the GC.

## 2.3 Drying the purge gas

The purge gas will be saturated with water vapour when it is passed through the water sample in the purge tower. Thus a 10 minute purge of a water sample with a purge gas flow of 80 ml/min will carry with it about 30 mg of water at normal laboratory temperatures. It is essential that the purge gas is dried before the trap. Water in the trap will reduce, or even completely block, the purge gas flow through the trap because of ice formation. It has been found that it is better to desorb the contents of a moist trap to waste rather than onto the column, even if a sample is lost. There are many good reasons for this. Firstly, the amount of purge gas that has passed the purge tower is likely to be less than the desired amount because of restricted flow, which may lead to insufficient extraction of halocarbons from the sample. Secondly, the water in the trap will cause distortion in the chromatogram if injected onto the column. Furthermore the electron capture detector will be damaged and the performance of the GC column will deteriorate with an excess of water. The chromatogram from an injection with water in the trap is thus

likely to produce erroneous results. Furthermore passage of a large quantity of water through the column will necessitate some conditioning of the column and detector before they regain their original performance. This will cause a break in the analytical scheme and a new calibration curve has to be made. There are, therefore, many good reasons for a reliable method of drying the purge gas.

There are different techniques available to dry the purge gas without removing any analytes at the same time. The use of condensers is one commonly used technique to remove water vapour. Pankow (1991) describes the use of a short column of glass beads at low temperature as water trap. Another approach is to use tubing made from semipermeable Nafion membranes. The membrane can be surrounded by a resin which absorbs water such as molecular sieve 5A or by a counter flow of a dry gas. The Nafion membrane has the drawback that certain polar compounds are removed together with the water. The Nafion drying method have been tried and evaluated, and the method does dry the purge gas effectively. Experiments confirm that the halocarbons are not polar enough to pass through the nafion tubing, but remain in the purge gas flow. The molecular sieve has only to be replaced and reconditioned weekly when analysing continuously. Despite this, the Nafion tubing was occasionally severely contaminated with CFCs, and could not be sufficiently cleaned. The Nafion drying method has been abandoned in favour of other methods in order to avoid such events. The principle of a counter gas flow over a semipermeable membrane for drying the purge gas has been tried on a vacuum sparge system for analysis of $SF_6$ in seawater (see section 3.1). In this system the moist purge gas is passed through a Nafion tube, which is coiled into a plexi glass tube (internal diameter 25 mm). Around the Nafion tube and counter to the moist purge gas flow is a flow of a dry gas.

Chemisorption of water vapour on hygroscopic salts such as magnesium perchlorate ($Mg(ClO_4)_2$) or potassium carbonate ($K_2CO_3$) is a widely used technique for drying the purge gas. Kolb et al. (1996) describe a method that utilises lithium chloride on a porous support as a water trap. Drying the purge gas by the use of the hygroscopic salt $Mg(ClO_4)_2$ placed in 1/4" x 10 cm glass tubes has been tried as a drying method in halocarbon analysis. The purge gas is dried, but a major drawback is that the desiccant tube has to be replaced about 3 times a day. A tube with magnesium perchlorate is however placed downstream of the main drier in both the halocarbon and the $SF_6$ systems as extra

security if the drying should fail and in order to check that the purge gas is dry.

Another way to dry the purge gas in halocarbon analysis was needed to overcome the shortcomings of the Nafion and the $Mg(ClO_4)_2$ drying methods. The solution was a modified purge chamber with a cooling spiral in its top part (Fig. 2.2). Virtually all the water vapour is condensed and removed from the gas flow when a cooling medium (water/ethylene glycol) at a temperature a few degrees below $0^\circ C$ flows through the cooling spiral. This method of drying the purge gas has proved successful.
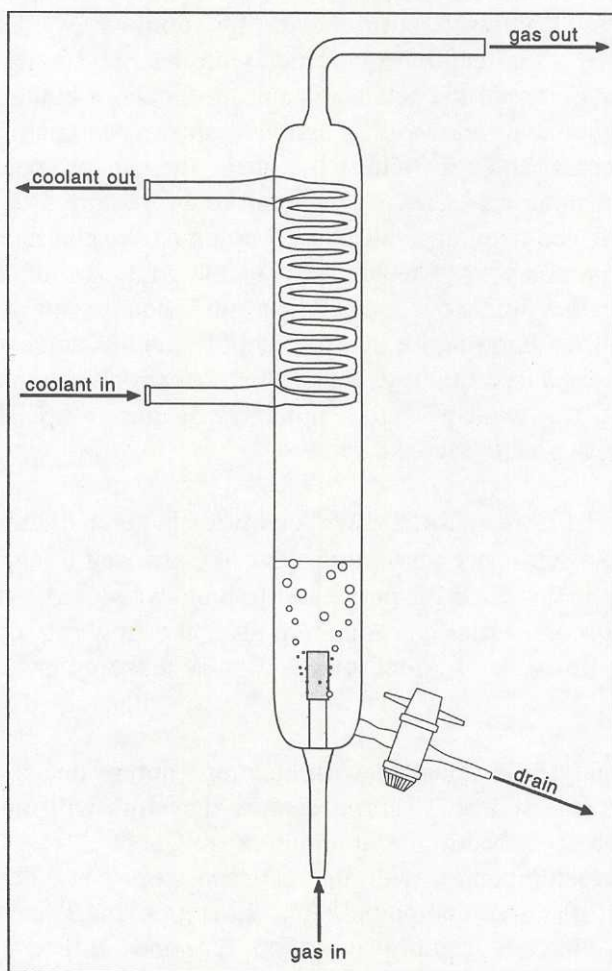


**Fig. 2.2.** *The purge chamber with the cooling spiral in the top part that removes water vapour from the purge gas by condensation.*

## 2.4 Gas chromatography and detection

A Varian 3400 GC (Gas Chromatograph) is used for the chromatographic separation and detection. The GC is equipped with two Electron Capture Detectors (ECDs) and two GC columns for simultaneous separation and detection of the samples from the parallel lines in the purge and trap system. Data handling is achieved with the aid of a PC and Varian's chromatographic software, Star.

The injection of the trap content onto the column is critical when working with purge and trap techniques. The large volumes of gas injected from the trap have to be considered. This is not a major problem when packed GC columns are used, but it may be for capillary GC. This can be partly solved by using capillary columns with a large diameter, i.e. megabore columns (internal diameter 0.53 mm). Megabore columns have large enough volume to allow for a sample capacity comparable with a packed column and, in addition, offer the sharp peaks characteristic of open columns. They may therefore be regarded as a good compromise between capillary and packed columns. Furthermore, cryo-trapping is a commonly used technique, i.e. the first part of the column is cooled at the beginning of the analytical run. Thus the analytes are recondensed on the column and a sharp injection band is achieved when the temperature is raised quickly. The volume of the trap is also important. By using a trap with a small volume, i.e. a micro-trap, the need for cryo-trapping is greatly reduced.

The columns used (DB624 from J&W Scientific) have an internal diameter of 0.53 mm, a stationary phase thickness of 3 $\mu$m and a length of 75 m. This column is designed for purge and trap analysis of volatile halogenated substances. As carrier gas is helium used at a flow rate of 8 ml/min. Nitrogen at a flow rate of 20 ml /min is used as make-up gas for the detector.

Detection of the analytes is achieved with electron capture detection whith $^{63}$Ni as the electron source. Electron capture detectors with non-radioactive sources are described in the litterature, e.g.. Cai et al. (1996). The ECD is selective to compounds with high electron affinity and has a low limit of detection for these compounds (e.g. Lovelock and Watson, 1978). This makes electron capture detection a good choise for halocarbon analysis, althogh the use of mass spectrometric detection is an interesting option, especially for low halogenated compounds where the ECD is less sensitive.

## Time axes showing time events for two sets of samples
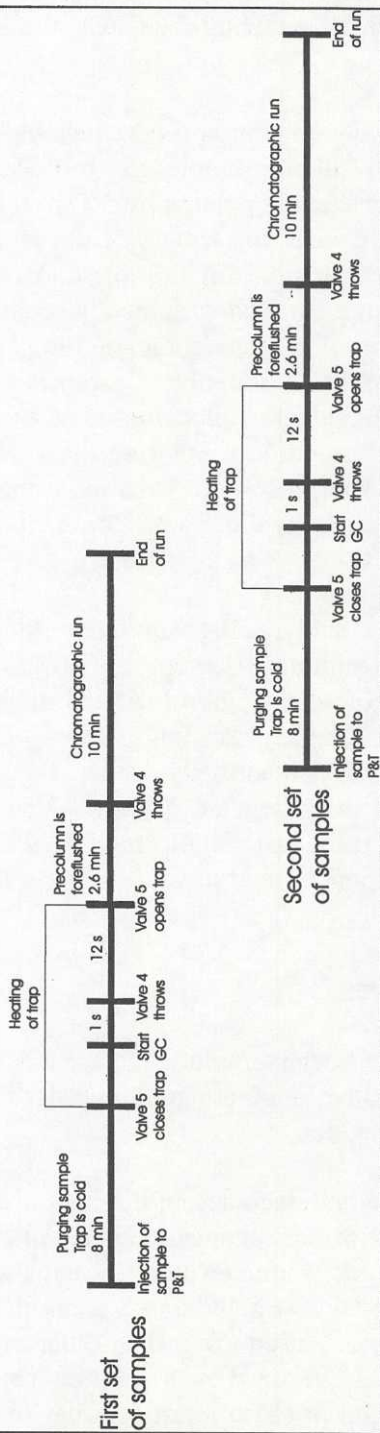


**Fig. 2.3.** *Two overlapping time axes showing events during analysis in CFC-determination mode and how one set of samples is being purged while the other set is injected into the GC. The halocarbon determination mode is essentially similar, except that the times for purging, foreflushing of the precolumn and for the chromatographic runs are longer. The precolumn is being backflushed at all times except during the first part of the chromatographic run. Observe that the scale of the time axis is not constant.*

13

In our work, two different methods have been developed for the chromatographic separation of the halocarbons. One method is used for analysis of the most volatile compounds, including the CFCs, the other one for a wider range of halocarbons.

A temperature programme for the GC column is used when analysing in halocarbon determination mode. A typical programme is as follows; starting with 2 minutes at $70^\circ$C and increasing the temperature by $5^\circ$C/min to $140^\circ$C followed by a $10^\circ$/min temperature rise to $180^\circ$C. This temperature programme takes 20 minutes. The purge time for this method is also 20 minutes, so while two samples are being chromatographically separated two new samples are treated in the purge and trap (compare Fig. 2.3). This means that the capacity of the system is roughly 4 samples per hour (allowing some time for loading the samples). A precolumn is used to avoid compounds that elute late, i.e. after bromoform, entering the column and possibly degrading its performance. The precolumn is of the same kind as the analytical column, but only approximately 4 metres long. The precolumn is located in a valve oven kept at $130^\circ$C.

Some modifications are made to the analytical system when running it in CFC determination mode. The precolumn is kept at $50^\circ$C and the chromatograms are cut after the elution of the carbon tetrachloride peak. It was found that a better sample to sample precision (table 2) could be achieved when the GC was running isothermally rather than with a temperature programme. The GC oven is kept at $70^\circ$C and the time for chromatographic separation is then 12 minutes with this method. This makes it possible to analyse 8 samples per hour since the water sample is purged for only 8 minutes.

## 2.5 Standardisation procedures

When CFCs are used as tracers in oceanographic studies, it is of great importance that both the accuracy and precision are good in order to resolve complicated circulation and mixing patterns.

Calibration of standards to obtain good accuracy in the measurements is essential for comparability between data sets obtained at different times and by different laboratories. For the work presented here gaseous standards have been used for the calibration of CFCs (including $CCl_4$ and $CH_3CCl_3$), whereas liquid standards have been used for the other measured halocarbons. The gaseous standard is prepared in a dilution chamber in which the halocarbon tracers are mixed in air to a ratio similar to the ratio

found in surface waters. Some air from the dilution chamber is sucked into an evacuated stainless steel gas cylinder, which is then pressurised to approximately 30 bar with nitrogen gas. After checking that the ratio between the halocarbon tracers is right, the gas standard is diluted to a concentration where approximately 12 ml standard gas gives the same signal as a natural surface water. The concentrations of the constituents of this standard gas will, however, change during the first time of storage, probably due to adsorption onto the walls of the gas cylinder. This is especially true for $CCl_4$ and for $CH_3CCl_3$. After a few months, when the gas is believed to have stabilised in the cylinder, this gas standard is calibrated against a primary gas standard, with concentrations determined on internationally used scales (for CFC-11 and 12; Scripps Institute of Oceanography, USA and for CFC-113; Plymouth Marine Laboratory, England). A set of calibrations of the gas standard is made before an experiment as well as after. When offshore, during a cruise, measurements are made on marine air, which has well known concentrations of halocarbon tracers. In cases where large deviations between expected and measured concentrations in marine air occurred, this was taken as an indication of badly calibrated standard. In the case of carbon tetrachloride and methyl chloroform marine air was often the best source for calibrating the gas standard, because these compounds are unstable in the gas cylinder. The gaseous standard is transferred from the cylinder to a dry ground glass syringe, from where it is injected into the purge and trap system.

The liquid standard solutions are gravimetrically prepared. Two or three different standard mixtures containing different sets of halocarbons are prepared to avoid interference between closly eluting compounds. A stock solution is prepared in pentane, with both the halocarbons and the pentane kept cold to avoid evaporation of the standard compounds. The stock solutions are then diluted in acetone to a standard of the concentration suitable for injection onto the purge and trap system.

Every calibration of a standard, no matter how carefully executed, will introduce an increased uncertainty to the determined concentration. It is therefore important to reduce the number of calibrations and handling procedures of a standard to reduce this uncertainty. We have felt that the procedure of producing secondary standards may introduce uncertainties and systematic errors in our measurements. We have therefore purchased a 40 litre tank of calibrated CFC standard gas from Brookhaven National Laboratory, Upton, New York. This standard gas contains halocarbon tracers in ratios similar to the ratios found in natural seawater. It is no longer necessary to make secondary standards, because there is a sufficiently large

volume of the primary standard to last until it is too old to use, which will take a few years. The stability of the standard gas is controlled on a regular basis through calibrations against well calibrated air samples from Nivot Ridge, Colorado. The standard gas is connected through the pressure regulator on the gas cylinder directly to the gas sampling loop via stainless steel tubing, a needle valve and a ball valve.

For the standardisation of the halocarbon tracers, a calibration curve is made daily (at least) by the injection of various volumes of gaseous standard (typically a six point calibration with volumes 0-19 ml). The gas sampling loops are placed in a temperature controlled area with a constant and well known temperature. The volumes of gas standard are chosen so that all water measurements fall within the standard curve. The calibration curves are best fitted to a polynomial function of the third degree since the electron capture detector is not perfectly linear in response to the halocarbons. Blank signals are monitored regularly, and zero blank signals for the halocarbon tracers, as well as for other halocarbons, are normally achieved.

## 2.6 Precision and limits of detection.

The requirements to meet the regulations of the World Ocean Circulation Experiment (WOCE) are a sample to sample precision of 1% and a total intralaboratory standard deviation of a series of measurements of 1-2 % for the CFCs. For all halocarbon tracers, this target is aimed for.

Sample to sample precision and limits of detection for different halocarbons are presented in Tables 2.1 and 2.2. The limits of detection are based on the noise level. If there are blank peaks, the limits of detection are calculated as twice the standard deviation of the blank signals obtained over an entire experiment. The sample to sample precisions are derived from analysis of a set of samples (usually 5-7) taken from the same water sample, and calculated as the standard deviation divided by the average value for the set, i.e. the coefficient of variation. The purge efficiency is the relative fraction of analyte that is removed from the water to the gas phase, and is determined from repeated purge cycles of the same water. Table 2.1 presents data when the system is running in halocarbon determination mode and Table 2.2 presents data from CFC determination mode. The reason for the lower precision for CFC-113 is the low concentration of this compound in seawater. In fact concentrations under the limit of detection are often encountered in deep or bottom waters of the oceans.

The chromatographic peaks are measured as areas, when the system is run in CFC determination mode, since this gives slightly better precision than measuring as heights. On the other hand the peaks are measured as heights when the system is running in halocarbon determination mode because of the greater risk of having peaks without perfect baseline separation. In this case a better precision was achieved by measuring heights rather than area.

| Compound | Precision (%) | Limit of detection (pmol L$^{-1}$) | Purge efficiency (%) |
|---|---|---|---|
| CFC-12 | 3.0 | 0.16 | 100 |
| CFC-11 | 8.8 | 0.01 | 100 |
| CFC-113 | 3.0 | 0.09 | 100 |
| CCl$_4$ | 2.6 | 0.04 | 100 |
| CH$_3$CCl$_3$ | 4.1 | 0.6 | 66 |
| CHCl$_3$ | 3.5 | 0.8 | 92 |
| C$_2$HCl$_3$ | 6.4 | 1.3 | 71 |
| C$_2$Cl$_4$ | 3.5 | 0.02 | 97 |
| CH$_3$I | 7.7 | 0.1 | 84 |
| CH$_2$ClI | 6.3 | 0.03 | 60 |
| CH$_2$Br$_2$ | 6.4 | 0.2 | 56 |
| CHBrCl$_2$ | 4.7 | 0.06 | 77 |
| CHBr$_2$Cl | 6.6 | 0.5 | 55 |
| CHBr$_3$ | 10.0 | 5 | 43 |

**Table 2.1.**. *Precisions, limits of detection and purge efficiency for the analytical system in halocarbon detection mode. The gas chromatographic runs started with 2 min at 70°C and increased to 140°C at 5°C/min. followed by a 10°/min temperature rise to 180°C. The detector temperature was set to 250°C and the chromatographic peaks were measured as heights.*

| Compound | Precision (%) | Limit of detection (pmol L$^{-1}$) | Purge efficiency (%) |
|---|---|---|---|
| CFC-12 | 1.5 % | 0.04 | 100 |
| CFC-11 | 1.0 % | 0.02 | 100 |
| CFC-113 | 2.4 % | 0.06 | 100 |
| CCl$_4$ | 1.1 % | 0.02 | 100 |

**Table 2.2.** *Precision, limits of detection and purge efficiency for the analytical system during the cruise with R/V Johan Hjort in the Norwegian Sea and the North Atlantic, 1994. The gas chromatographic runs were isothermal at 70°C and a precolumn was used to cut the chromatogram after the CCl$_4$ peak. The chromatographic peaks were measured as areas.*
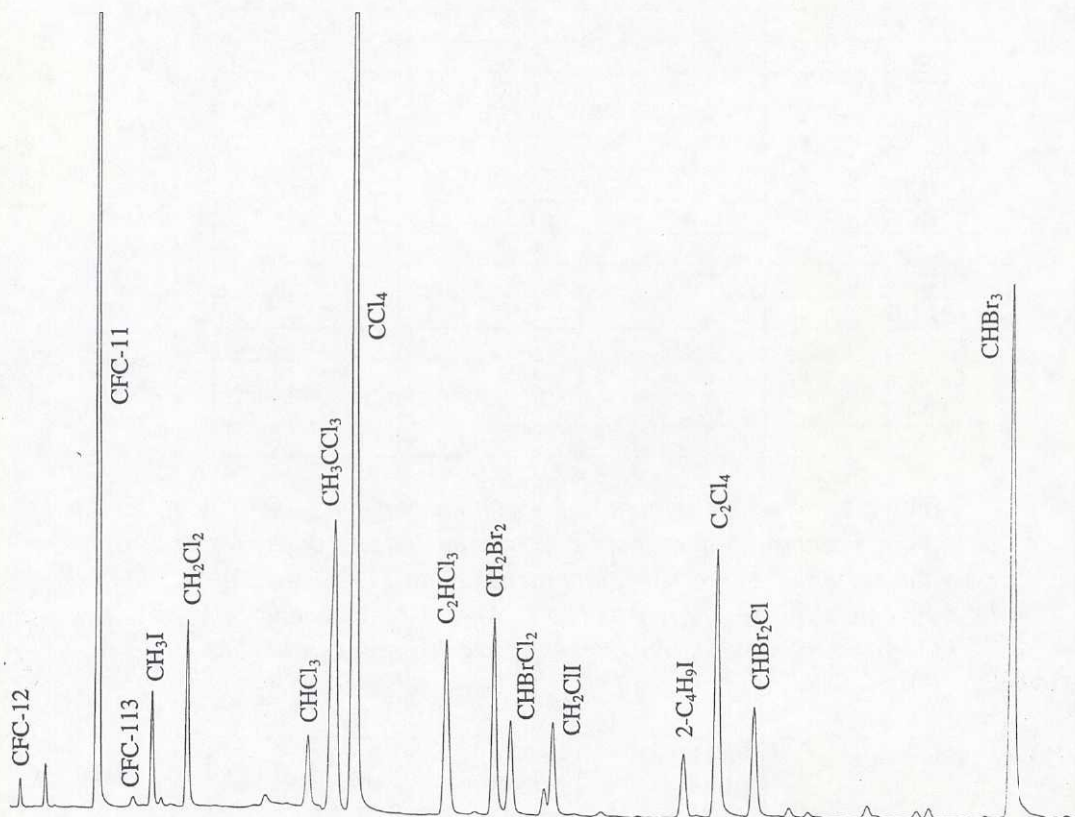
**Fig 2.3.** *A chromatogram of surface seawater in the Baltic Sea. The chromatographic run started with 2 minutes at 70°C and increased by 5°C/min to 140°C followed by a 10°/min temperature rise to 180°C. The last peak, CHBr₃ is eluting after 18 minutes.*

18

**Fig. 2.4.** *A chromatogram from the Greenland Sea obtained 1996. The gas chromatographic run was isothermal at 70°C and a precolumn was used to cut the chromatogram after the CCl₄ peak. The last peak, CCl₄, is eluting after 10 minutes.*
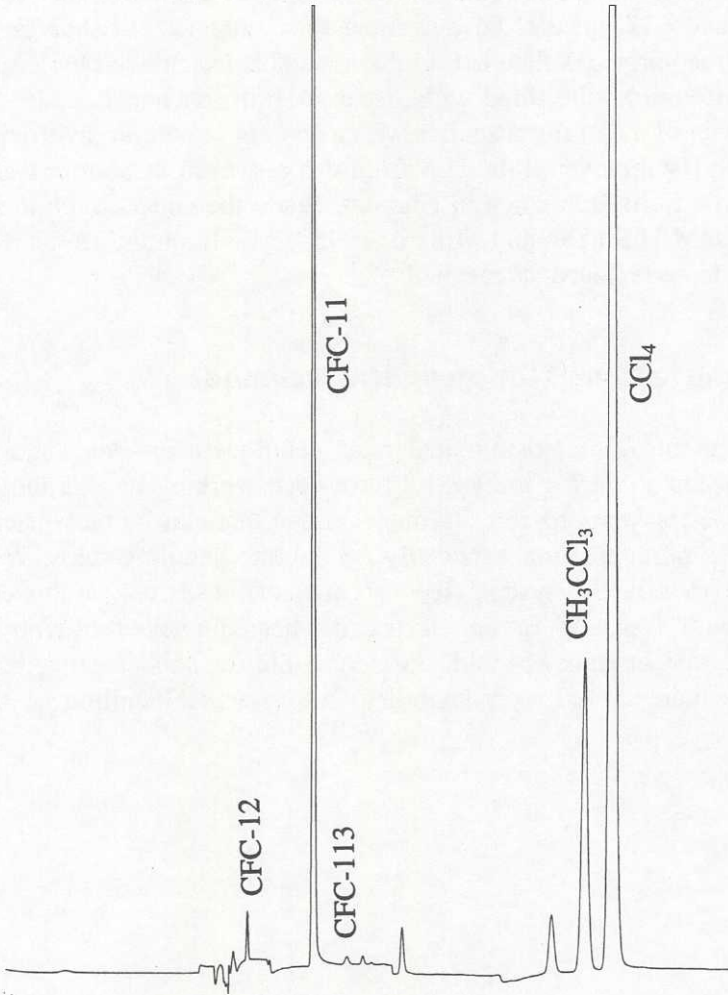
## 2.7 Determination of halocarbons in anoxic seawater

The presence of hydrogen sulphide ($H_2S$) in anoxic seawater causes problems in the determination of halocarbons due to the high response to $H_2S$ in the electron capture detector. A large peak of $H_2S$ will overlap and mask the CFC-12 peak, and at higher concentrations of $H_2S$, also the CFC-11, CFC-113 and $CH_3I$ peaks. To overcome this problem, $H_2S$ has to be removed from the purge gas flow before the trap. This is achieved by letting the gas flow through a tube filled with Ascarite (Bullister and Lee, 1995). Ascarite is a resin of a non fibrous silica with a coating of sodium hydroxide and will effectively remove all the $H_2S$ from the gas, even in bottom water samples from the fjord Framvaren in Norway, where the concentrations are as high as 6-8 mM $H_2S$ (Yao and Millero, 1995; Dyrssen et al., 1997). The Ascarite needs to be replaced at least daily.

## 2.8 Future ideas about the analytical technique

The improvements of an existing analytical technique is an ever ongoing project. It has been so during the years I have been working on this thesis, and it will be so for years to come. Among things that can be better is an increased degree of automation, especially for the trap handling steps. With the experience from the $SF_6$ system (see next chapter), it seems that this can be achieved with the help of an electrically heated packed microtrap, surrounded by, for instance, a cold aluminium block. This improvement could possibly increase the reproducibility and ease the handling of the system.

# 3.   Determination of sulphur hexafluoride.

As for the halocarbons, the determination of $SF_6$ is complicated by its low concentration in seawater. The surface water concentration of $SF_6$ is actually about 3 orders of magnitude lower than that of CFCs and is today about 2 fmol $L^{-1}$ (fmol=$10^{-15}$ mole). It is however still possible to determine such low concentrations thanks to the very high response to $SF_6$ by the electron capture detector (ECD). Analysis of $SF_6$ in seawater is described by Law et al, (1994) and by Wanninkhof et al. (1991). A continuous underway analysis system for $SF_6$ is described by Upstill-Goddard et al. (1991).

An analytical system for the determination of $SF_6$ in seawater was built during 1996 for a special purpose; deliberate release of $SF_6$ in the Greenland Sea. The requirements for the system were that it should be automated to a large extent, fast, precise and able to handle samples over a wide concentration range. The method chosen was a vacuum sparge system similar to a system described by Law et al., 1994.   The vacuum sparge system is really a purge and trap system in which the sample is sprayed into an evacuated purge chamber, promoting the transfer of $SF_6$ to the gas phase.

## 3.1 The analytical system

The $SF_6$ system is, in contrast to the CFC system, a single channel system (see Fig 3.1). It is built on a plexiglass framework and all tubing is made of stainless steel. The purge chamber and the dessicant tube are made of glass. Two solenoid valves (ASCO) and one electrically actuated ball valve (Whitey) control the injection and drainage of sample to the purge chamber. There are 5 multiport valves (Valco) in the system, of which only the gas sampling valve is manually operated. Valve 1 is made of hastelloy C-22 while the other valves are made of stainless steel.
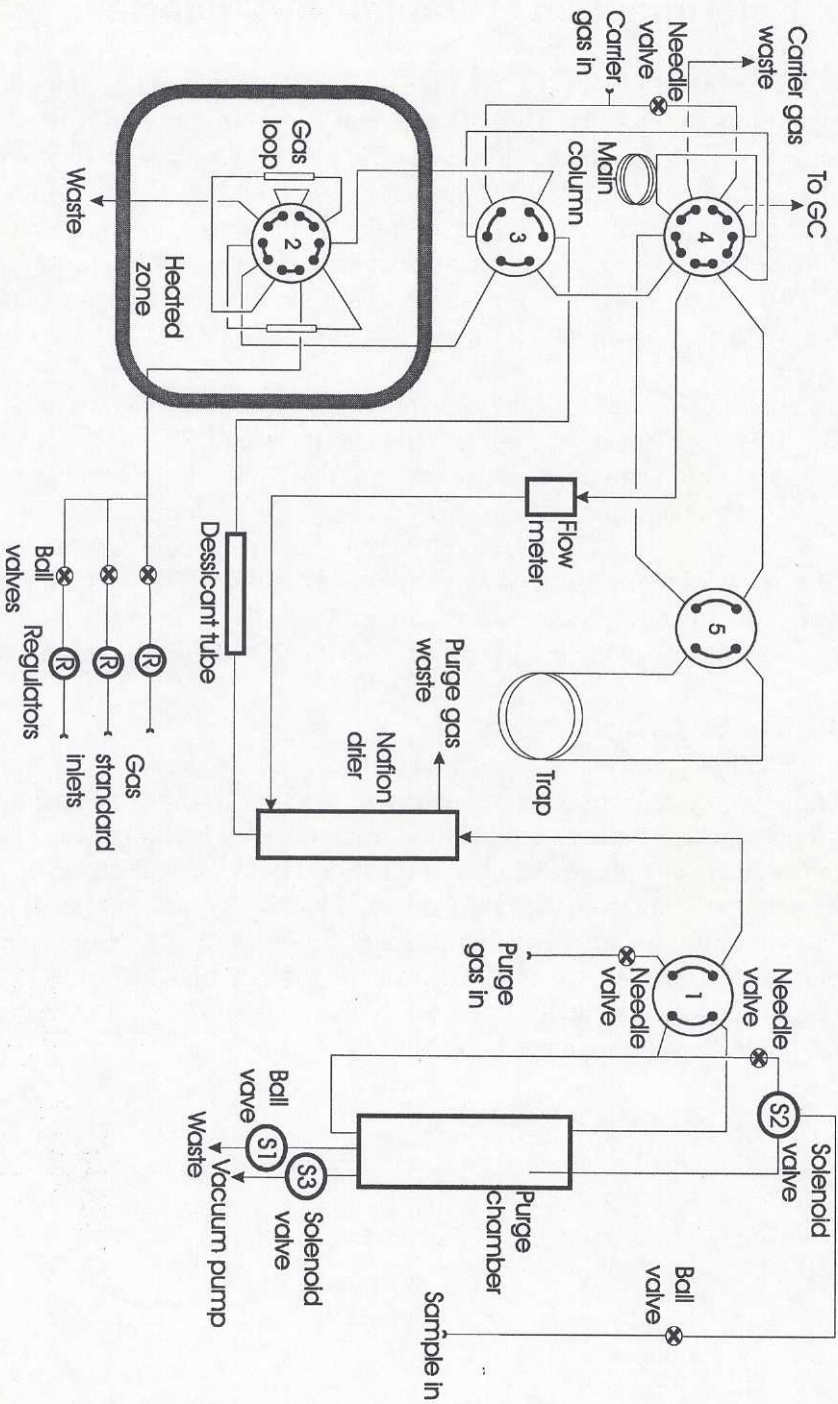
**Fig 3.1.** *Schematic picture of the analytical system for the determination of SF$_6$ in seawater.*

22

Water samples are introduced into the system by means of a vacuum created in the purge chamber. The sample inlet is manually placed into the water bottle and the purge chamber is isolated from the purge gas flow by valve 1. A vacuum pump (Divac 1.2, Leybold) then creates negative pressure in the purge chamber when solenoid S3 opens. A three way solenoid valve (S2) is thrown so that the sample inlet is connected to the top of the purge chamber at the same time as solenoid S3 closes and a small volume of water is drawn from the sampling bottle into the purge chamber. A positive pressure is then created in the purge tower by throwing solenoid S2 so that the sample inlet is isolated, and by throwing valve 1. The water used for rinsing the lines is then expelled to waste by opening valve S1. The cycle is then repeated but this time the purge chamber is filled up with the desired amount of water. Solenoid S2 isolates the sample inlet when two platinum electrodes in the purge chamber are submerged and the resistance between the electrodes changes. The low pressure in the purge chamber during the sample introduction forces the water to spray through four orifices in the top part of the purge chamber thereby promoting the transfer of $SF_6$ to the gaseous phase. Valve 1 is once again thrown when the water is introduced into the system and purge gas enters the purge chamber through a stainless steel frit in the lower part of the purge chamber.

The purge chamber consists of a top and a bottom part made of stainless steel. The water inlet and the purge gas outlet are situated in the top part whereas the purge gas inlet, the drain and outlet to the vacuum pump are situated in the lower part. Glass chambers of different volumes are then glued to the steel end fittings with Araldite. The exact volume of a purge chamber is determined by the position of the platinum electrodes. During a tracer release experiment concentrations over many orders of magnitude will be encountered. Purge chambers of different nominal volumes (50 ml, 150 ml and 350 ml) were therefore prepared.

A water trap is located after valve 1 and consists of nafion tubing coiled in a plexiglass tube with a counterflow of dry gas surrounding it. A dessicant tube with magnesium perchlorate after the nafion tubing dries the purge gas from any remaining water vapour. See section 2.3 for further discussions on water traps.

A six-port valve (valve 3) directs either the purge gas or the carrier gas through the gas sampling valve (valve 2). It is thus possible to inject gas standard with the purge gas onto the trap, or to make direct injections of the content in a gas loop onto the column with the carrier gas. The gas sampling valve is located in an oven so that the temperature of the gas loops is constant and only adjustments for fluctuations in air pressure have to be made in the standardisation procedure. Two loops with nominal volumes of 250 µl and 1000 µl connected to valve 2 facilitate the injection of different volumes of standard. The standard gas inlet in valve 2 is connected to three regulators (BSI1, Air Liquide) each connected to a standard gas cylinder. With this arrangement it is easy to vary the volume of injected gas and to change between standards of different concentrations.

Valve 4 is a ten port valve which directs either purge or carrier gas to the trap valve. The carrier gas, when routed to the trap valve, passes through both the main column and the postcolumn to the detector. After desorption of the trap content to the column, valve 4 throws and the main column is backflushed with carrier gas. Purge gas is then directed to the trap valve. The purge gas is passed to a flow meter (GMF17, Aalborg) that continuously monitors the purge gas flow after valve 4. The waste gas from the flow meter is used as the dry gas in the water trap, see section 2.3.

The trap valve (valve 5) isolates the trap from the gas flow at all times except while a sample is being purged or when the trap is being desorbed. The trap is a 35 cm long 1/16" stainless steel filled with an adsorbent (Carboxen 1000 45/60 mesh, Supelco). Carboxen 1000 is pyrolised polymers with an active surface area of 1200 $m^2$/g. O'Doherty et al. (1993a, 1993b) describe the use of Carboxen for trapping the volatile CFC replacement compounds, hydrofluorocarbons and hydro-chlorofluorocarbons. Eight different packing materials were tested by us for their retention power towards $SF_6$ at different temperatures. It was found that Carboxen 1000 was the only packing material (of those tested by us) that could retain $SF_6$ at temperatures above -30°C. Carboxen 1000 did in fact retain $SF_6$ at temperatures as as high +5°C. The trap is contained in an aluminium block and is electrically isolated from the block by Teflon tubing. The trap is cooled to -10°C by a flow of cooling media (water/ethylene glycol mixture) around the aluminium block, which is immersed in a dewar bottle. The trap is rapidly heated to about 250°C during desorption by applying a power of 300 VA at 6 VAC across the trap. After desorption the trap is cooled down sufficiently

quickly to allow a new sample to be introduced as soon as the previous sample is analysed.

The purge efficiency is the amount of $SF_6$ removed from the water to the gas phase during a purge cycle. The purge efficiency is determined from repeated purge cycles of the same water sample. In fig. 3.2 the purge efficiency is plotted vs. the purge time for seawater samples in the 350 ml purge chamber. A purge time of 300 seconds and a purge gas flow of 240 ml/min were used during subsequent experiments.
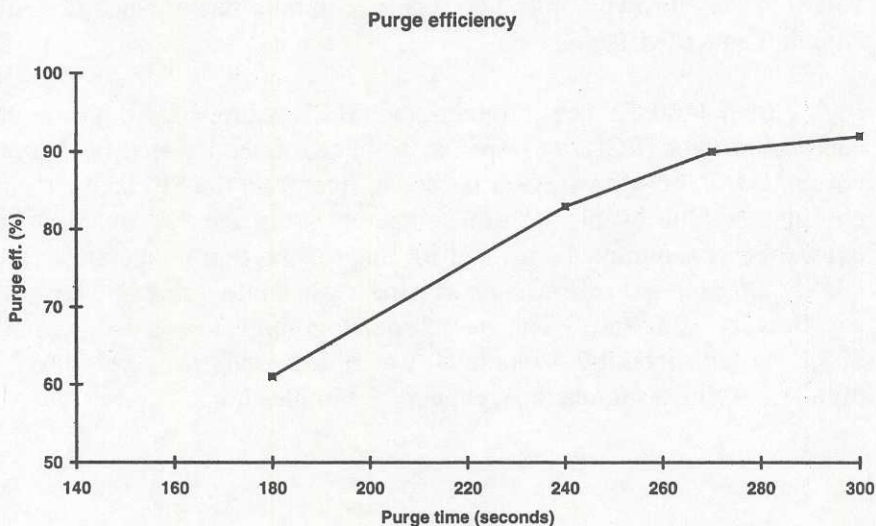
**Purge efficiency**



**Fig 3.2.** *The purge efficiency in percent for the 350 ml purge chamber. The purge gas flow was 240 ml/min and seawater spiked with $SF_6$ was used for the experiment.*

A PC operated relay card with 16 relay outputs is used to control all events in the purge and trap system, such as throwing valves, closing solenoids, starting heating the trap and starting data acquisition. The system is thus fully automated and a single command on the PC starts the whole analytical process.

## 3.2 Gas chromatography and detection

The main column is an approximately 3 metres long 1/8" stainless steel tube packed with molecular sieve 5A (80/100 mesh, Supelco). The post column is of the same kind as the main column but only about 30 cm long and is used as a pressure buffer. Both the main column and the post column are located in the GC oven, which is kept at 30°C. The $SF_6$ passes the columns without much retention whereas all other compounds are retained with oxygen eluting as a large peak shortly after the $SF_6$ peak. After about 2 minutes, when the $SF_6$ has passed the main column, valve 4 is thrown and the main column backflushed, venting contaminants to waste.

A Varian 3400 CX gas chromatograph (GC) equipped with an electron capture detector (ECD) is responsible for the detection of $SF_6$. Varian's chromatographic software Star is used to intergrate the $SF_6$ peak, control chromatographic events, control temperatures in the GC oven and the oven for gas sampling loops, and to monitor the trap temperature. High quality nitrogen gas is used both as carrier gas and purge gas. The carrier gas flow is 35 ml/min. The gas chromatographic run is isothermal at 30°C and takes about 2.5 minutes. A complete analytical cycle takes 12 minutes, giving a sample throughput of 5 samples/hour.
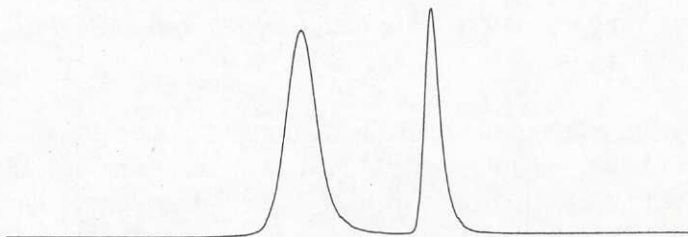
Fig 3.3. *A gas chromatogram of seawater with elevated concentrations of $SF_6$. $SF_6$ elutes after 1.7 minutes and shortly after elutes a $O_2$ peak.*

## 3.3 Standardisation and precision

The standardisation of SF$_6$ is achieved by injections of standard gas through one of two gas sampling loops. Three, of in total six, cylinders with gas standards are connected to the purge and trap system via three regulators and ball valves in such a way that any one of the standards can be readily injected. The gas cylinders are readily exchangeable, if another concentration range is to be calibrated. The gas standards are prepared by sucking air into an evacuated gas standard cylinder from a dilution chamber with high SF$_6$ concentrations. This gas cylinder is then pressurised with nitrogen gas to 45 bar. This gas cylinder is the high concentration standard. Low concentration standards are prepared by the transfer of gas to other gas cylinders followed by dilution with nitrogen gas. Four of the gas standards whose concentrations range from 10 to 5000 ppt were calibrated against SF$_6$ standards prepared by Plymouth Marine Laboratory (PML), England.
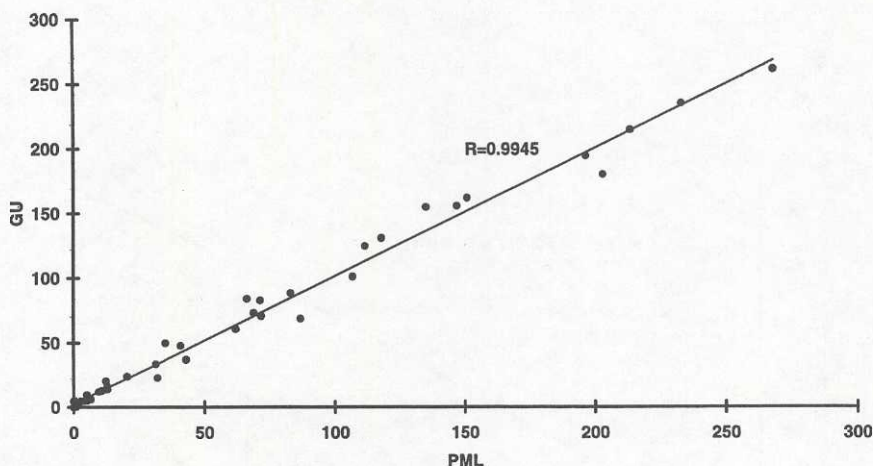


**Fig. 3.4.** *Intercomparison of seawater samples over a wide range of concentrations between a SF$_6$ system from Plymouth Marine Laboratory (PML) and that from University of Göteborg (GU). The scales on the axes are in fmol L$^{-1}$.*

Presented in Fig. 3.4 is an intercomparasion of seawater measurements made on our instrument (GU) and on the $SF_6$ system of PML during mapping of the $SF_6$ patch released during the tracer release experiment in the Greenland Sea (European Subpolar Ocean Programme, ESOP) 1996. Which was also the first time the instrument was used in field work. The figure shows results from samples analysed over a wide range of concentrations. It is clear that there is no systematic difference between the two analytical systems, other than in the background concentration range, where the GU instrument suffered from a background signal during this cruise, due to a leaking solenoid valve.

A calibration curve was made from duplicate injections of all four standards at various volumes in the beginning of an experiment. The standard curve was fitted to a polynomial function of the third order with peak size on the X-axis and the amount of $SF_6$ on the Y-axis. Standard runs were performed at regular intervals during an experiment and any deviation of detector response from the standard curve was applied as a factor in the calibration. This factor was usually only a few percent of the curve. The calibration curve is not linear in any range, not even for a calibration curve in the background concentration range .



The equation shown on the plot:

$$y = -6E\text{-}15x^3 + 3E\text{-}09x^2 + 0.0016x - 0.3176$$
$$R^2 = 0.9994$$
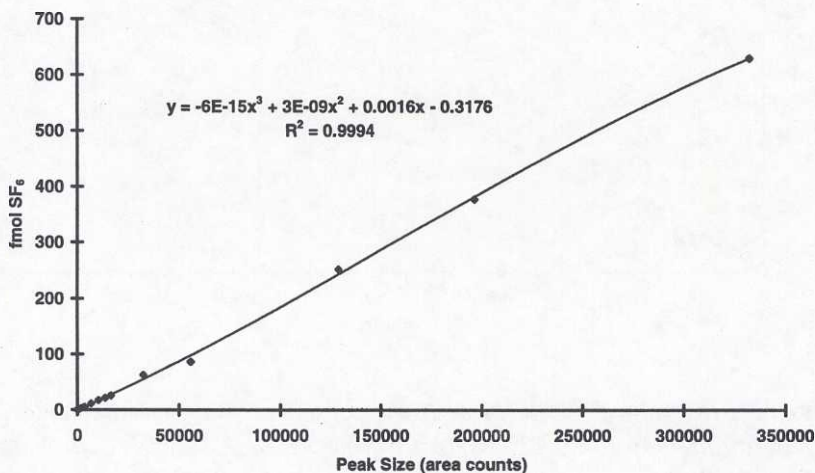
**Fig. 3.5.** *A standard curve from duplicate injections of several volumes of four different standards ranging in concentration from 10 to 5000 ppt $SF_6$.*

Several series of analyses to determine the precision of the method have been performed as 5-8 measurements of the same sample. The precision is measured as the standard deviation of the results. The following precisions have been measured in the laboratory: natural seawater 0.03 fmol $SF_6$ (1.5%) and 1 ml of 50 ppt standard gas injections 0.007 fmol $SF_6$ (0.34%). Duplicates of standard gas measurements during a cruise in the Greenland Sea, on 52 occasions, covering the concentration range 10 - 6000 ppt showed a mean coefficient of variation of 0.72%.

# 4. Halogenated marine tracers

A marine tracer is a compound used to study the processes such as formation, circulation and mixing in the oceans and in coastal areas. A lot of information can be collected from a good selection of tracers. An ideal marine tracer should have a well established source function, be persistent, not adsorb onto particles, have low or at least well known natural background, be rapid and inexpensive to determine. Few substances exhibit all these properties. I will discuss below to what extent these criteria are fulfilled for some halogenated compounds.

Many halogenated substances are used as marine tracers. Some of the chlorofluorocarbons (CFCs), for instance, have properties that are close to ideal. A range of halogenated compounds other than the CFCs are also useful as marine tracers, although for many of these compounds their sources and sinks are less well known. The use of CFCs and the chemically related carbon tetrachloride ($CCl_4$) and methyl chloroform ($CH_3CCl_3$) as marine tracers will be discussed in section 4.1. The halogenated tracer sulphur hexafluoride ($SF_6$) as a transient tracer will be discussed in section 4.2, and as a deliberately released tracer in section 4.4. Halocarbons other than the halocarbon tracers will be treated in section 4.3.

## 4.1 Halocarbon tracers

The chlorofluorocarbons (CFCs) are entirely man-made compounds and did not occur in the environment in preindustrial times. The CFCs are compounds used in refrigerators and cooling systems, for foam blowing, as aerosol propellants and as industrial solvents. A large fraction of the CFCs produced is subsequently released to the atmosphere, and they are stable compounds with residence times of the order of a hundred years. The atmospheric residence times for the CFCs are 74 years for CFC-11 and 111 years for CFC-12 (Cunnold et al., 1986). The life-time for CFC-113 is estimated to be 136 or 195 years by Golombek and Prinn (1989) depending on model parameters. Fisher and Midgley (1993) use a lifetime of 90 years ( WMO, 1989) for CFC-113 to calculate expected atmospheric mixing ratios.

The CFCs and other man-made halocarbons such as carbon tetrachloride and methyl chloroform have been targeted in the Montreal Protocol because of their negative effect on the Earth's ozone layer. The

date for the cessation of production and consumption of CFCs in the industrialised countries was January 1, 1996. The effect of the Montreal Protocol is already evident. The atmospheric concentrations are levelling out, and even decreasing for all but CFC-12 (See Fig. 4.1). Other halogenated substances are produced as replacement compounds for the CFCs, such as the hydrohalocarbons (HHCs). These include the hydrochlorofluorocarbons (HCFCs) and the hydrofluorocarbons (HFCs). The presence of hydrogen atoms in these compounds makes them subject to a faster degradation, compared with the CFCs, through photochemical reactions or by hydroxyl radicals in the atmosphere, reducing their lifetimes (Prather and Spivaskovsky, 1990; Wine and Chameides, 1989). Thus, the amount of these compounds that reaches the ozone layer is considerably less. Further, chlorine is much more aggressive to ozone than fluorine, and the HFCs do not contain any chlorine atoms. Therefore they have no or little impact on the stratospheric ozone. The use of the CFC replacement compounds as marine tracers will, however, not be discussed here, since these have not been included in our measurements. However, some of these compounds have potential as marine tracers, especially HCFC-22 (chloro-difluoromethane).

The naming of CFCs is in accordance with The American Society of Refrigerating Engineers (ASRE) numerical coding system, which says that the last digit is the number of fluorine atoms in the compound, the next to last digit is one more than the number of hydrogen atoms in the compound, and the third digit from the right is one less than the number of carbons in the compound (when this digit is zero, it is omitted). The remaining binding sites to the carbon molecules are occupied by chlorine atoms. The three CFCs that have been used in this work are trichlorofluoromethane ($CCl_3F$, CFC-11), dichlorodifluoromethane ($CCl_2F_2$, CFC-12) and 1,1,2-trichloro-1,2,2-trifluoroethane ($CCl_2FCClF_2$, CFC-113).

In addition to CFC -11, -12 and -113, two further transient tracers are included in this work. They are tetrachloromethane ($CCl_4$, carbon tetrachloride) and 1,1,1-trichloroethane ($CH_3CCl_3$, methyl chloroform). In this section, methyl chloroform and carbon tetrachloride will be treated together with the CFCs, since their sources to the ocean (from the atmosphere) and their use as transient tracers are similar. These five compounds as a group will be referred to as the halocarbon tracers. Like the CFCs, $CCl_4$ and $CH_3CCl_3$ enter the atmosphere from industrial release. Their atmospheric lifetimes are, however, a bit shorter than for the CFCs, only 6.3 years for methyl chloroform (Prinn et al. 1987) and

40 years for carbon tetrachloride (Simmonds et al., 1988). As can be seen in Fig. 4.1, carbon tetrachloride has the longest atmospheric history of the five halocarbon tracers treated here, stretching back to the 1910s, and have low or no natural background (Krysell and Wallace, 1988; Krysell, 1992, Wallace et al., 1994). Due to their long residence time in the atmosphere, the CFCs are globally well mixed, with only a small concentration gradient between the northern and southern hemispheres, the northern hemisphere having the higher concentration since the majority of the release of CFCs is concentrated there. The atmospheric concentrations of CFCs are time dependent and well known since they were first measured in the 1970s, see Fig. 4.1. Concentrations before 1970 are estimates, based on production data and release estimates (Cunnold et al. 1986 for CFCs 11 and 12, Fisher and Midgley 1993 for CFC-113, Simmonds et al. 1983 for carbon tetrachloride, Prinn et al. 1987 for methyl chloroform).



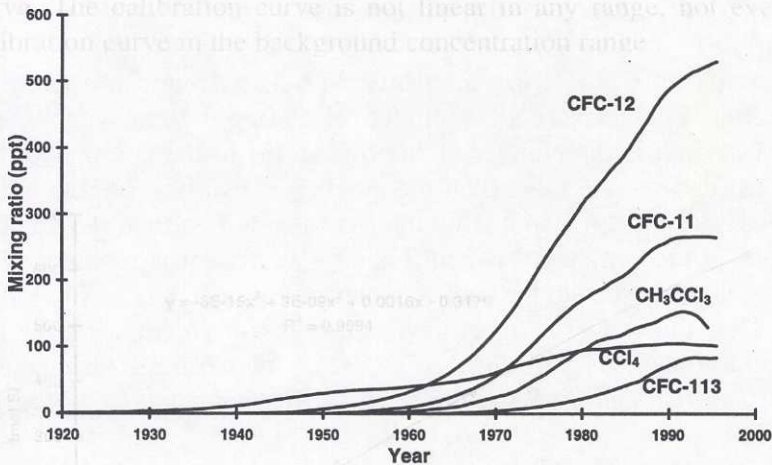**Fig. 4.1.** *Atmospheric mixing ratios for some transient tracers, based on data from SIO (R.F. Weiss, personal communication) for CFC-11, -12, -113 and CCl₄, Prinn et al. (1987) and Prinn et al. (1995) for CH₃CCl₃.*

The CFCs enter the seawater through equilibriation with the atmosphere. The equilibrium is salinity and temperature dependent (see Fig. 4.2 for illustration of the temperature dependence of CFC-12). The

equilibrium between the atmosphere and seawater, the Henry´s Law constants, at different temperatures and salinities, are well documented for CFC-12, CFC-11 (Warner and Weiss, 1985) and for CFC-113 (Bu and Warner, 1995). For carbon tetrachloride and methyl chloroform the Henry´s Law constants are reported by Hunter-Smith et al. (1983). However, the measured surface concentrations of carbon tetrachloride are at times not consistent with the expected concentrations derived from Hunter-Smith et al. or in comparison with the saturation of the other CFCs. In a work by Fogelqvist and Johansson (1997) new solubility data for carbon tetrachloride in natural waters are presented, based on recent work in our laboratory in Göteborg. The new solubility equation yields lower saturation levels in cold seawater compared to the levels calculated from Hunter-Smith et al., which are in better accordance with field observations.
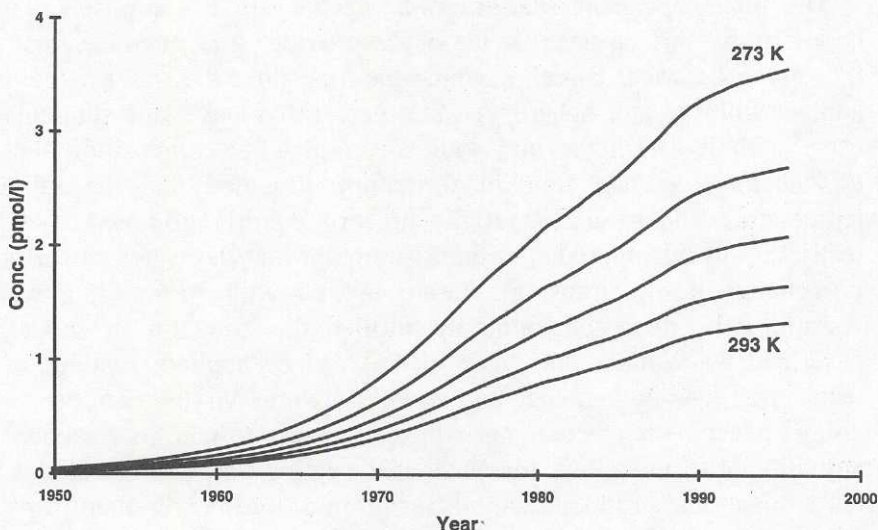


**Fig. 4.2.** *Concentrations in seawater of CFC-12 at equilibrium with the atmosphere for five different temperatures (5 Kelvin between each line) versus year of equilibration. The salinity is 35.*

The time-dependent concentration of CFCs in the atmosphere and the well known equilibrium constants mean that the CFCs have a well established source function as an oceanic tracer. One very important obstacle is the saturation level for the CFCs in the surface waters. Deviations from 100 % saturation are often found in field measurements. Oversaturation is not at all uncommon in the surface water layer.

Similarly it is not unusual to find undersaturated waters, particularly in polar areas where the surface is partially ice covered. Saturation levels for CFCs in the Pacific Ocean are reported and discussed by Lobert and Baring (1993). Wallace and Lazier (1988) report, from measurements made in 1986, that Labrador Sea Water is significantly undersaturated (60% saturation) with respect to CFCs. This is likely to be variable from year to year. The depth and the seasonal variations of the surface mixed layer will also influence the saturation of CFCs as discussed by Haine and Richards (1995). Saturation of CFCs in the Greenland Sea is further discussed below.

The sources and sinks of the halocarbons in seawater are discussed more thoroughly in chapter 6, in particular the persistence of the halocarbon tracers is discussed in section 6.5.

The time dependent concentration of CFCs in the atmosphere and hence in the surface layer of the ocean provides a means of estimating the "age" of a water parcel, meaning the time since the water parcel lost contact with the atmosphere. A water parcel that leaves the surafce will carry with it a "fingerprint" with a certain CFC composition that is typical for a certain time of formation, provided that the salinity, temperature and saturation at the time of equilibration is known. A restriction to this approach is the assumption that the water parcel does not change during transport due to mixing with surrounding water. Assuming that these constraints are fulfilled, the "freight train" model, as described by Wallace and More (1985) can be applied. Evaluation of residence times is then easy and straightforward. Mixing can, however, almost never be neglected and is thus necessary to take into account in any attempt to use CFCs for water mass dating purposes. A model for entrainment and turbulent eddy diffusion in a fjord is presented in paper VI. The magnitude of entrainment and mixing with other water masses is, generally, not known and the use of the concentration of a single halocarbon tracer is thus of limited use. Another approach is then to use the ratio between two halocarbon tracers, see Fig. 4.3. This ratio will not be affected by dilution as long as the entraining water has no CFC content. This is usually not the case, and the CFC content of the entrained water has to be taken into account, as for instance in the model proposed by Jenkins (1980). The derived ventilation time of a given water mass can be thought of as a water mass age. Even though an exact dating of a water mass may be difficult, the CFC content does reveal information on the age of a water mass in relation to a nearby water mass, i.e. a "younger" or "older" water mass. The fact that the

concentrations of the halocarbon tracers in the atmosphere are levelling out or decreasing also complicates "water mass dating" for recently ventilated waters.

The CFCs 11 and 12, and the ratio between them, have been used for some time as transient tracers (see for example, Bullister and Weiss 1983, Weiss et al., 1985). The ratio of CFC-11/CFC-12 has, however, ceased to increase since the mid seventies, so this ratio is of limited use for more recently ventilated waters. In these waters, other ratios must be used, for example ratios including CFC-113 since this is a tracer with a short atmospheric history and the ratio has increased so rapidly, until very recently, that it is possible to estimate ventilation times with a resolution of about a year (e.g. paper II). The ratio CFC-113/CFC-11 is plotted together with the ratios CFC-11/CFC-12 and CFC-11/CCl$_4$ in Fig. 4.3. One further advantage when using CFC ratios for "age" determinations of water masses is that the ratio is less sensitive to deviations from saturation of the surface water than the use of single CFCs. If two CFCs are saturated to the same degree, the "ratio-age" will not be affected by any deviations from 100% saturation, whereas any attempt to use the concentration of a single CFC to determine the age of a water mass will be affected.
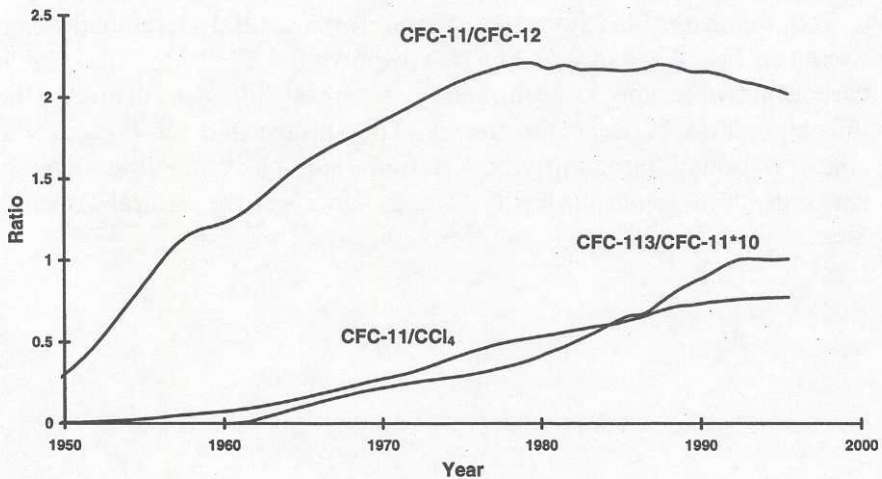


**Fig. 4.3.** *The ratios of some halocarbon tracers that are saturated to equilibrium with atmosphere in seawater with salinity 35 and temperature 2°C versus year of equilibration.*

As an example of the use of the halocarbon tracers as indicators of the age of water masses I will discuss CFC data from the Greenland Sea obtained during a cruise with M/S Håkon Mosby in February/March 1995.

Deep water formation takes place during the winter in the Nordic Seas (Norwegian Sea, Greenland Sea and Iceland Sea). The water formed in the Nordic Seas during the winter is one of the most dense water masses in the oceans. The dense water mixes with other water masses when it flows over the Greenland-Scotland ridge, forming North Atlantic Deep Water, which is an important component in the global circulation in the oceans. The most important area for deep water formation is the Greenland Sea gyre. In the cyclonically circulating gyre the density surfaces are doming upwards, and dense water is forced close to the surface. During the cold and stormy winter months the surface water gets colder and denser, and deep convection may take place. Temperature loss to the atmosphere of high saline water and ice formation in the area may further be important mechanisms for deep water convection in the Greenland Sea. The mechanisms of these processes are poorly known, mainly because of the difficulties in operating in the area during winter and because deep convection is probably a local and episodic event as discussed by Johanessen et al. (1991).

Two depth profiles from one station in the central Greenland Sea are shown in Fig. 4.4 and 4.5. Fig. 4.4 displays the CFC-11, -12, -113 and carbon tetrachloride concentrations, whereas Fig. 4.5 displays three different ratios between the tracers. The surface and the bottom water concentrations found at this station are close to the averaged concentrations found during the whole survey in the central Greenland Sea.

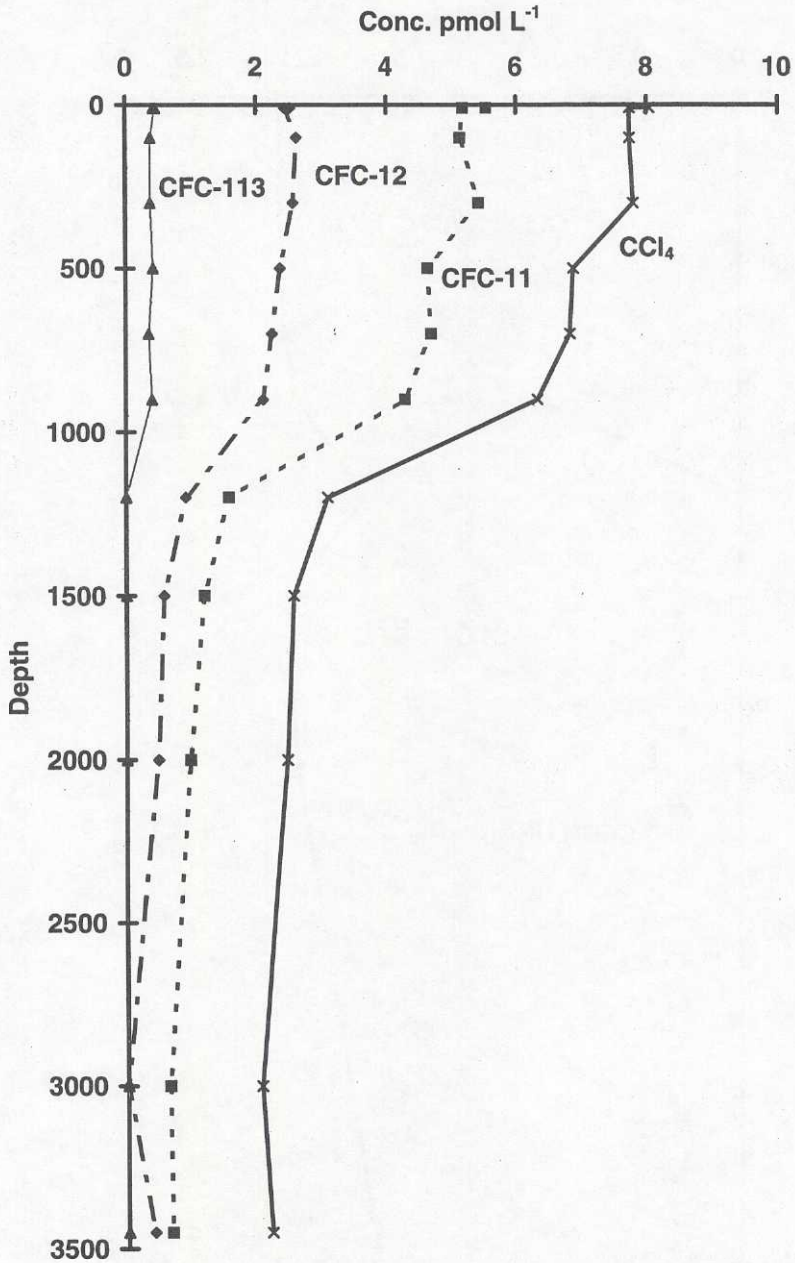**Fig 4.4.** *Depth profile of the halocarbon tracers from a station in the centre of the Greenland Sea at position 75º45´N 3º39´W.*
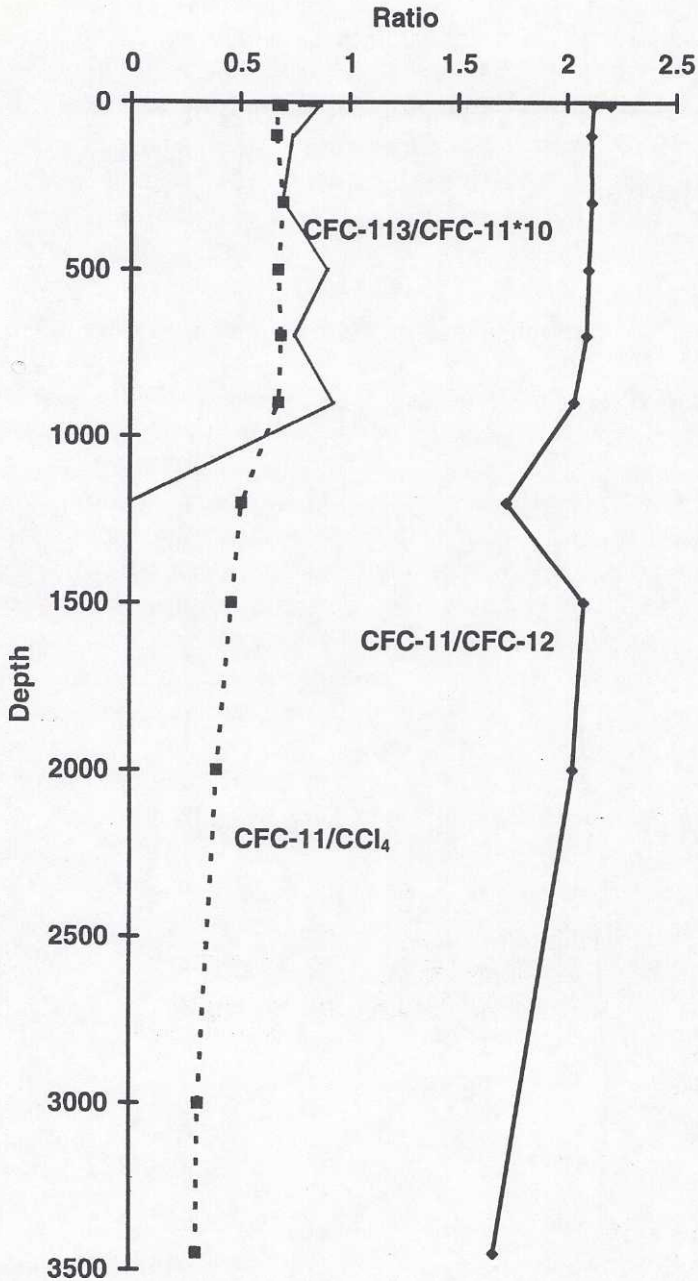
**Fig 4.5.** *Depth profiles of some halocarbon tracer ratios from the same station in the Greenland Sea as in Fig. 4.4.*

Listed in Table 4.1 are the averaged concentrations and the saturation anomalies calculated from expected saturations at salinity 34.86 and a temperature of -0.92°C. Furthermore, the saturation in the central Greenland Sea is a function of salinity, as shown in Fig. 4.6. Here the CFC-11 saturation from samples collected at 10 metres depth are plotted versus salinity. The higher the salinity, the more the influence of Atlantic Water and hence deeper convection depth (as discussed by Rhein, 1996) and thereby lower surface saturation levels as discussed by Haine and Richards (1995). Two points in Fig. 4.6 do not follow the general trend. These points are from the westernmost stations in the section. It seems as if this water has a different history compared to the surface water in the rest of the section, possibly a longer time as surface water and hence higher saturation levels. Carbon tetrachloride shows a similar pattern, but for CFC-113 and CFC-12 there is no obvious relationship between salinity and saturation. Also listed in Table 4.1 are the apparent ages of the Greenland Sea Deep Water (GSDW) calculated from the use of single halocarbon tracers, assuming the saturation was the same during the year of formation as during the winter 1995. The apparent ages for CFC-11 and CFC-12 are roughly the same, 32-33 years, whereas carbon tetrachloride indicates a much older water. This discrepancy can possibly be due to carbon tetrachloride not being stable even in the cold and well oxygenated waters of the Greenland Sea, and is a further indication that carbon tetrachloride data should be used with caution for age determination purposes. Another explanation could be that the atmospheric concentrations of carbon tetrachloride are incorrectly estimated before the 1970s.

| Tracer | Surface water konc. | Bottom water konc. | Surface saturation | Apparent age of bottom water |
|--------|---------------------|--------------------|--------------------|------------------------------|
| CFC-11  | 5.41 | 0.70 | 75 % | 32 |
| CFC-12  | 2.70 | 0.45 | 72 % | 33 |
| CFC-113 | 0.40 | 0.00 | 53 % | - |
| CCl$_4$ | 8.34 | 2.40 | 83 % | 51 |

**Table 4.1.** *Tracer concentration, surface saturation and apparent age found in the central Greenland Sea during February/March 1995. Concentrations are given in pmol kg$^{-1}$.*
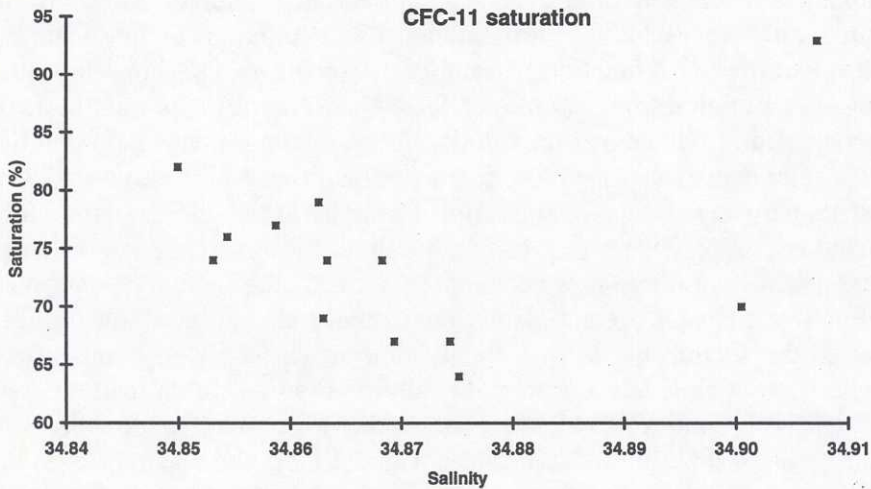
**Fig 4.6.** *The saturation of CFC-11 versus salinity in samples from 10 metres depth in the central Greenland Sea. The two samples with high salinity are from the two westernmost stations, see text.*

In Table 4.2 the ratios CFC-11/CCl$_4$, CFC-11/CFC-113 and CFC-11/CFC-12 in surface and bottom waters in the central Greenland Sea are listed together with estimates of their ratio age. The ratio age is compensated for differences in saturation levels as indicated in Table 4.1. The ratio age CFC-11/CFC-12 indicates an apparent age of just over 30 years just like the single CFC-11 and -12 values. The ratio CFC-11/CCl$_4$ indicates a younger age because of the low carbon tetrachloride values. In waters as old as the GSDW the CFC-113 concentrations are under the detection limit and of little use.

| Tracer ratio | Ratio in bottom water | Ratio in surface water | Ratio age of bottom water |
|:---:|:---:|:---:|:---:|
| **CFC-11/CFC-12** | 1.62 | 2.08 | 31 |
| **CFC-113/CFC-11** | - | 0.10 | - |
| **CFC-11/CCl$_4$** | 0.26 | 0.75 | 26 |

**Table 4.2.** *Ratios found in the central Greenland Sea during February/March 1995. The ratios are compensated for saturations given in table 4.1.*

In Figure 4.7 a CFC-11 section across the central Greenland Sea from west to east along 75°N is displayed. East of 8°E, towards Bear Island, the section was sampled along 74.5°N. The section was sampled in February and March 1995. A seven day long stop in the sampling was encountered due to bad weather after the station at 0°E. The sections for CFC-12 and $CCl_4$ show very similar appearances to the CFC-11 section. CFC-113 has too short an atmospheric history to be used in the deep waters. The water masses down to about 1000 metres depth are recently ventilated, and there is a sharp gradient in halocarbon tracer concentrations at that depth. The Greenland Sea Deep Water (GSDW) below 1500 metres has small gradients in halocarbon tracer concentrations. The isolines for CFC-11 are curved downwards in the central Greenland Sea below 1500 metres because of more rapid ventilation in the area. The lowest concentrations in the section are found in the deep water at 5°E (0.23 pmol $kg^{-1}$ CFC-11) on the slope of Mohns Ridge and connected to the Boreas Plain in the north. Low concentrations (0.47 pmol $kg^{-1}$ CFC-11) are also found on the slope towards Bear Island at longitude 10-15°E at the eastern end of the section. These stations are actually situated in the northern part of the Norwegian Sea. This is an indication of older deep water in the Norwegian Sea. Further evidence for this is found from CFC data collected further south in the Norwegian Sea, at 67°N where the CFC-11 was 0.30 pmol $kg^{-1}$. The data presented here give only an indication of relative age, or the CFC-age. No effort to model mixing and entrainment has been made, which would be necessary in order to obtain figures for the ventilation rate for these basins. Modelling efforts based on halocarbon tracers in the Greenland Sea are presented by other authors, e.g. Bullister and Weiss (1983); Bullister (1984); Rhein (1991); Schlosser et al. (1991); Bönish and Schlosser (1995) and Rhein (1996). The use of other transient tracers (tritium, $^3$He, $^{14}$C, $^{85}$Kr and $^{39}$Ar) to study the ventilation of the Greenland Sea is reported by e.g. Smethie et al. (1986) and by Schlosser et al. (1995).
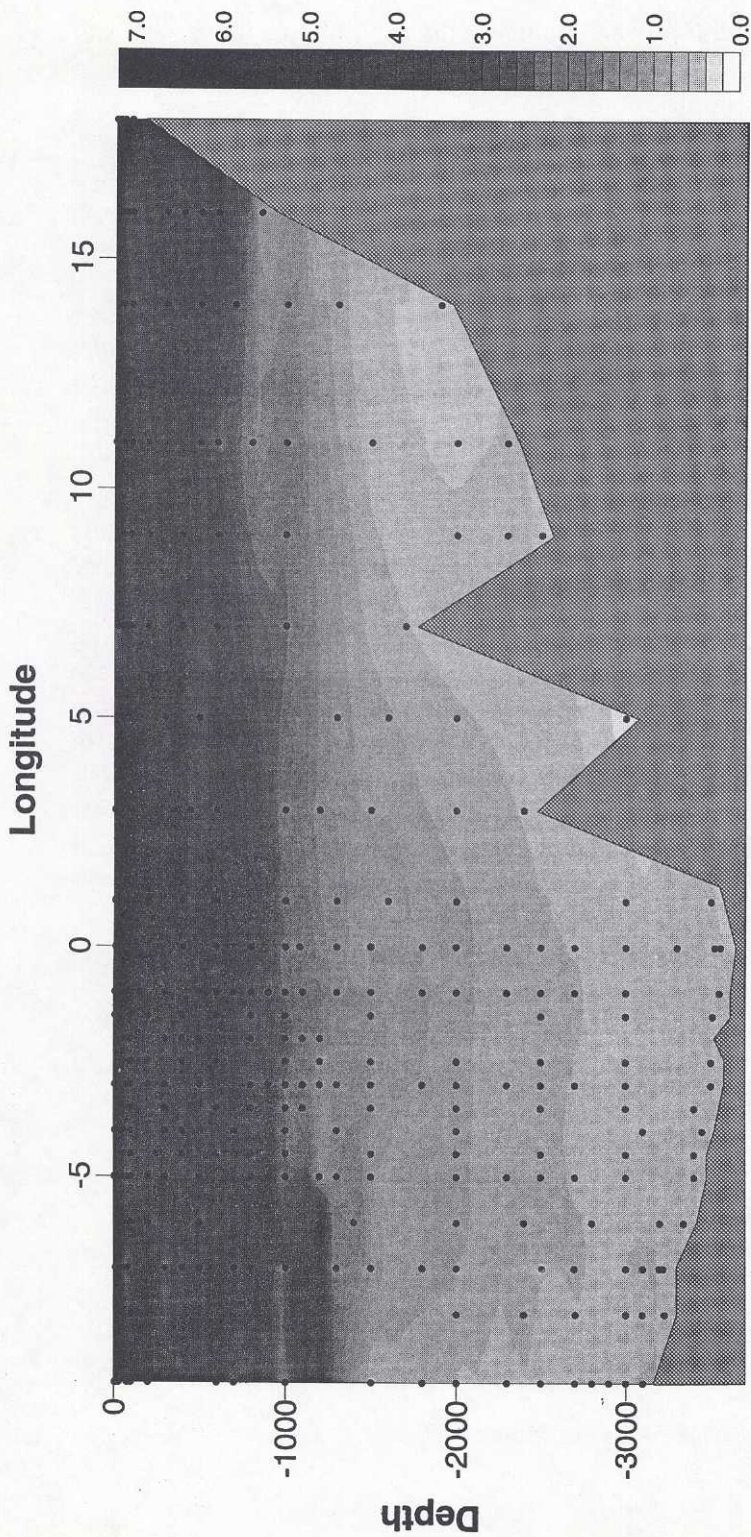
**Fig. 4.7.** *A section of CFC-11 across the Greenland Sea from west to east mainly along 75°N obtained during February and March 1995. The units are pmol kg$^{-1}$, depths are in metres.*

42

## 4.2 Sulphur hexafluoride

Sulphur hexafluoride ($SF_6$) is a compound that is mainly used as a gaseous electrical insulator. There are no natural sources for $SF_6$ and hence no natural background of the compound in the environment. The early atmospheric history of $SF_6$ is modelled by Watson and Liddicoat (1985) from comparisons between CFC-11 and $SF_6$ profiles in the North Atlantic. More recent trends in atmospheric concentrations are reported by Law et al. (1994). These data and more recent observations made by Watson and Messias (personal communication) are plotted in Figure 4.8. The concentration of $SF_6$ in the atmosphere is at present only about 4 ppt and it is rising rapidly. The low solubility of $SF_6$ in seawater results in very low present background concentrations of about 2 fmol $L^{-1}$. (fmol=$10^{-15}$ mole) in seawater. The high sensitivity of the electron capture detector to $SF_6$ makes it possible to detect even these minute quantities of $SF_6$ in seawater. For a discussion on analytical techniques, limits of detection etc. see chapter 3. Experiments suggest that $SF_6$ does not adsorb onto particles and is nonreactive in, at least, oxygenated waters (Ledwell and Watson, 1991). The solubility for $SF_6$ in seawater is discussed by Wanninkhof et al. (1991) and Wanninkhof (1992).
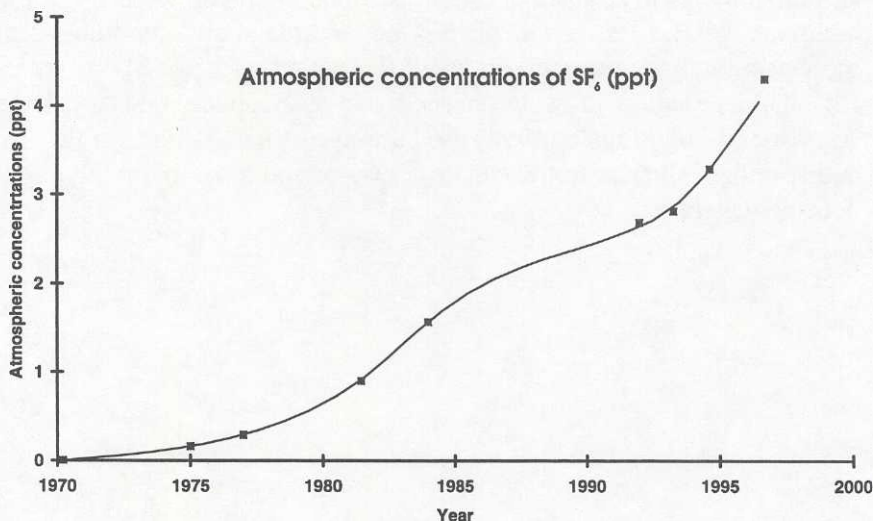


**Fig 4.8.** *Atmospheric history of $SF_6$ in the northern hemisphere. Data from Law et al. (1994) and references therein, and from measurements by Watson and Messias (personal communication). The trend line is our own estimate.*

Sulphur hexafluoride fulfils many demands that can be put on a marine tracer. Until recently, however, not many studies have been published where $SF_6$ is used as a transient tracer in oceanographic studies. Law and Watson (1997) studied the ventilation in the Arabian Sea with the aid of $SF_6$ as a transient tracer. The utilisation of $SF_6$ as a transient tracer in the oceans is likely to increase in the future, especially since the atmospheric concentrations of CFCs are levelling off whereas the $SF_6$ concentration is rapidly raising. $SF_6$ as a transient tracer can be treated in very much the same way as the halocarbon tracers are treated and the same limitations are valid, see previous sections for further discussion.

## 4.3 Other halogenated tracers

It is possible to use halogenated substances other than the halocarbon tracers or $SF_6$ as marine tracers, even though they have less well established source functions. A variety of different compounds will give a more complex "fingerprint" of a given water mass, and hence additional parameters for evaluation of water mass mixing. For a discussion on the use of multiple tracers with multivariate analysis, see chapter 5. The use of halocarbons others than the halocarbon tracers is especially useful when investigating short term processes, e.g. mixing and movements in straits and estuaries, since the possible decay of tracer compounds has a less pronounced effect and the source functions can be more accurately determined. In paper II a variety of halocarbons are used for characterisation of water masses in the Bosphorus Strait, Turkey. Krysell and Nightingale (1994) used a range of halocarbons in the Rhine and Humber estuaries to trace the river water and to study its mixing with oceanic waters.

## 4.4 Deliberately released tracers

Deliberate release of tracers is a useful method for studies of properties that otherwise are difficult to determine. One example is determination of diapycnal mixing in the oceans, where an injection of a tracer at known density level is essential. A tracer that reaches the ocean through the air-sea interface, a CFC for example, will be introduced at all density surfaces, since the surface of the ocean covers a wide range of density intervals. These tracers may then be transported via isopycnal processes, that are much faster than the diapycnal. It is then difficult to distinguish between the two processes. Other examples of the use of deliberately released tracers are studies of gas transfer over the air-sea interface and coastal discharge dispersal studies.

A deliberately released tracer should ideally have no natural background, be detectable in minute concentrations, be inexpensive and easy to handle and should not be harmful to the environment. A commonly used group of tracers is fluorescent dyes, like for instance Rhodamine. They have many attractive properties. Firstly, they can easily be detected in low concentrations with *in-situ* fluorimeters, there is no need to take discrete water samples and instant results can be presented. They can further be detected over a wide range of concentrations. There is however a background fluorescence signal in natural waters containing organics such as humic acids, that can make fluorescent dye measurement difficult. Another drawback is scavenging onto suspended particles, which can account for a high loss rate, especially in turbid waters (e.g. Özoy et al., 1995). Rhodamine is not conservative in natural waters, photo-degradation destroys the dye in sunlit water, and further, some degradation products can be toxic. Rhodamine itself is not highly toxic but there are aesthetic considerations in using rhodamine since higher concentrations visibly colour the water. Further, fluorescent dyes are rather expensive. Other deliberately released tracers are being sought. Perfluoromethyldecalin is a compound that has been used as a deliberately released tracer, e.g. Watson and Ledwell (1988).

$SF_6$ is an inexpensive, nontoxic and easy to handle chemical, in addition to the properties mentioned in section 4.2, and it makes a very good candidate for a deliberately released tracer. In contrast to the fluorescent dyes, $SF_6$ is a gas. This makes it more difficult to inject into the water and eventual loss to the surface must be considered. This may however be an advantage in experiments in shallow waters like estuaries, where new measurements can be conducted with short intervals without interferences from previous experiments. An article by Watson and Ledwell (1988) discusses purposefully released tracers for the determination of the rate of mixing over the main thermocline in the oceans. They investigate the use of a Rhodamine dye, perfluordecaline and sulphur hexafluoride as potential tracer substances. A tracer-release experiment in the Santa Monica Basin utilised $SF_6$ to study isopycnal and diapycnal ocean mixing, Ledwell and Watson (1991). An open ocean tracer-release off the Canary Islands in May 1992 used $SF_6$ as a tracer to determine the diapycnal diffusivity coefficient in the thermocline, Ledwell et al. (1993). Sulphur hexafluoride has also been used in in-situ experiments to study air-water gas exchange, both in freshwater (e.g. Wanninkhof et al., 1985) and marine systems (e.g. Watson et al., 1991). Sulphur hexafluoride can also be used to trace other substances released into water, such as pollution from river run off (Clark et al., 1996). Sulphur hexafluoride was used to trace a patch of iron-enriched water in an experiment off the Galapagos designed to test the hypothesis that iron is a limiting element for phytoplankton growth in the oceans, Martin et al. (1994). A tracer release experiment design to study the thermohaline circulation in the Greenland Sea is using $SF_6$ as tracer. An analytical instrument for $SF_6$ measurements in seawater was constructed for this purpose, see chapter 3.

# 5. Application of multivariate analysis in chemical oceanography, example from the Denmark Strait.

Denmark Strait is the strait between Greenland and Iceland. With a sill depth of some 650 metres, it is the second deepest passage (Faroe Bank Channel being slightly deeper) between the Nordic Seas (Greenland Sea, Norwegian Sea and Iceland Sea) and the North Atlantic. Denmark Strait is of importance for the transport of deep water from the Nordic Seas to the North Atlantic, where the Denmark Strait Overflow Water (DSOW) mixes with other water masses and forms North Atlantic Deep Water (NADW) (Dickson et al. 1990, Swift et al. 1980).

The area is dominated by four water masses. These are Iceland Sea Arctic Intermediate Water (ISAIW), Polar Intermediate Water (PIW), Polar Water (PW) and Atlantic Water (AW). The classification and naming of water masses follows mainly that from Swift (1986), but names are in some instances adjusted in accordance with those used in paper V. The overflow water through Denmark Strait is mainly a mixture of Iceland Sea Deep Water (ISDW) and ISAIW. Estimates derived from multivariate analysis that are presented in paper V show that DSOW is a mixture of about 70 % ISAIW and 30 % ISDW, from a survey made in 1994. Swift et al. (1980) conclude that the main component of the Denmark Strait overflow is an intermediate water of Arctic origin, and that Norwegian Sea Deep Water (NSDW) contributes to less than 10 % of the overflow. Another water mass found in the strait is the PIW, which typically has temperatures below $0^{\circ}$ C and salinities between 34.4 and 34.7 and is traditionally distinguished from the upper AIW by geographical observations together with S and T characteristics (Swift, 1986; Malmberg, 1972). The surface water masses are dominated by PW and AW, also known as Irminger Sea Water (ISW). The PW, with an origin in the East Greenland Current, is characterised by temperatures below $0^{\circ}$ C and salinities below 34, whereas the AW is characterised by high temperatures ($>5^{\circ}$ C) and high salinities ($>35$).

An intensive study in the Denmark Strait was carried out during a Nordic WOCE (The Nordic countries contribution to the World Ocean Circulation Experiment) cruise in 1993 with the Finnish research vessel Aranda. One objective for the survey was to study the variability of the overflow water through the Denmark Strait. In order to achieve this five sections across the deep channel in the strait were sampled repeatedly

over several weeks. Water samples for CFC tracer analysis were taken during the first three weeks of the survey from August 24th to September 10th, a total of 62 stations. One of the sections was sampled for CFC tracers during all three weeks (on August 26th and 31st and on September 10th), the S-section, which is therefore chosen for this presentation. The S-section is located just to the North of the sill between positions N 66° 23.0′ W 25° 42.1′ and N 66° 48.3′ W 27° 21.7′ (see Fig 5.1). Heavy ice conditions in the Denmark Strait prevented an extension of the section towards Greenland, which was originally planned.
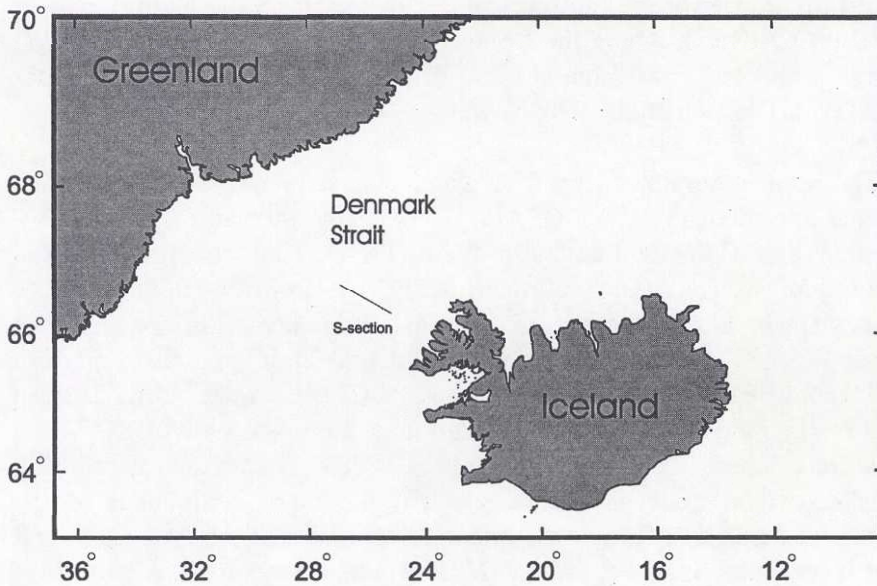


**Fig. 5.1.** *Location of the S-section in the Denmark Strait.*

## 5.1 Multivariate analysis

As the number of parameters in oceanographic studies is becoming larger (salinity, temperature, oxygen, nutrients, tracers, etc.), new methods of treating data are needed. Multivariate analysis is a set of statistical methods for handling large numbers of variables simultaneously. The use of multivariate analysis is a technique that is becoming more and more important in many fields. Multivariate analysis of oceanographic data is not a new feature, although not so commonly used. Mackas et al. (1987) used least squares regression of six variables to distinguish between five different water masses off Vancouver Island. Preisendorfer (1988) describes the use of Principal Component Analysis

(PCA) in meteorological and oceanographic applications. Multivariate analysis has been used in Paper V to determine the water mass composition in the Norwegian Sea, the Faroe Bank Channel and in the Iceland Sea. In this study multivariate analysis is used to interpret the mixing of different water masses and the variability of water mass distribution in the Denmark Strait. Principal Component Analysis (PCA) is used to identify samples from typical water masses and to detect outliers in the data set. Partial Least Square calibration (PLS) is then used to assign a certain mix of water masses to each data point. I will describe some basic ideas about the way we have treated data in this study. For practical instructions and for underlying principles, see Esbensen et al (1994), Martens and Naes (1989) and references therein.
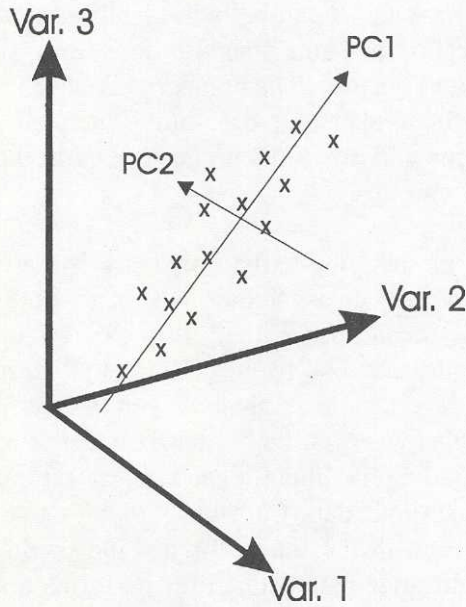


**Fig. 5.2.** *The two first principal components in a three dimensional data set. PC1 is perpendicular to PC2.*

Principal Component Analysis (PCA) is a method in which a data set is mathematically transformed into orthogonal base vectors (Principal Components, PCs). In the context of statistical treatment of the data in this study, a variable means a measured parameter and anobject is a water sample. PCA decomposes a data set into a structure part and a noise part. The first PC is the line that minimises the squared projection distances from the data points to the line. The first PC contains most information, or rather the most variance, of the PCs of a data set. To calculate the PCs,

as a first step the data are usually centred by subtracting the mean value from each variable. The data matrix, X, can then be split in two terms, a matrix product, $TP^T$, plus a residual, E. $TP^T$ is the product of the score matrix, T, and the loading matrix, $P^T$. The PCs are calculated one at a time in a stepwise manner until most of the variance is explained, see equation below. The first two PCs in a three dimensional X matrix are illustrated in Fig. 5.2. The maximum number of PCs that can theoretically be obtained is seldom optimal, rather it is the decomposition of data into as few dimensions as possible that is the aim.

$$X = t_1 p_1^T + t_2 p_2^T + \cdots + t_A p_A^T + E$$

The variables in a data set can be individually scaled in the model. A commonly used scaling is 1/(the standard deviation), so that parameters measured on different scales can be compared. With PCA it is possible to find the most influential variables, study the characteristics of the objects, find patterns and any hidden phenomena in the data set, and to classify objects into groups.

A second step in the multivariate analysis is Partial Least Square (PLS) calibration. Partial Least Square (PLS), or Projections on Latent Structures as it is sometimes called, is a powerful tool for making predictions and interpretations from a data set. It always involves two sets of data, one X- and one Y-matrix. The X-matrix consists of the independent variables whereas the Y -matrix consists of dependent data. There is a corresponding Y-value for each object in the X-matrix. The X-matrix contains measured data from the variables that are available or which may be to used in the future for making predictions and the Y-matrix is the sought after parameter. PLS performs a simultaneous and interdependent decomposition of both X- and Y- matrices in order to obtain a model. This is done in such a way that the information in the Y-matrix is used directly as a guide for optimal decomposition of the X-matrix. PLS can be regarded as an extension of PCA with the difference that in PLS the criteria for significance is the model´s ability to predict the Y-matrix. The PLS model can then be applied to a data set to perform classifications and predictions. In this work, the X-matrix consists of salinity, temperature, CFC-11 and -12 data, and the Y-matrix is the proportions of the four source waters. The calibration data set which is used to make the PLS model is the choice of samples that are characteristic of, or rather define, the different water masses, the source waters. The X-matrix is then the measured data and the Y-matrix is used

to define which mixture of source waters the sample contains; in the calibration data set this value is 100 % for the individual source water samples.

Important tools for interpreting the PCA results are the score plot and the loading plots (Fig. 5.3-5.5). The score plot is a graphical presentation for studying variations and similarities between objects in a data set, where it is easy to detect patterns and formations. In the score plot in Fig. 5.3 the principal component 1 (PC1) is plotted versus PC2. In this model 59% of the variance in the data set is explained by PC1, and 22% is explained by PC2. Thus 81 % of the variance is explained by the two PCs visualised in Fig. 5.3. It is possible to identify at least four different endpoints (groups) in the pattern. Clearly these endpoints represent four different water masses, and the mixing lines between some of the water masses can be visualised. In Fig. 5.4 only those samples that were selected to represent the four water masses (AW, PIW, ISAIW and PW) are plotted. Note that they are plotted from a model with only these objects so that the scales of the figures are not quite the same. These samples were selected from careful studies of the score plot in Fig. 5.3, and are used in making the PLS model. A score plot is furthermore a good way of detecting outliers in the data set.
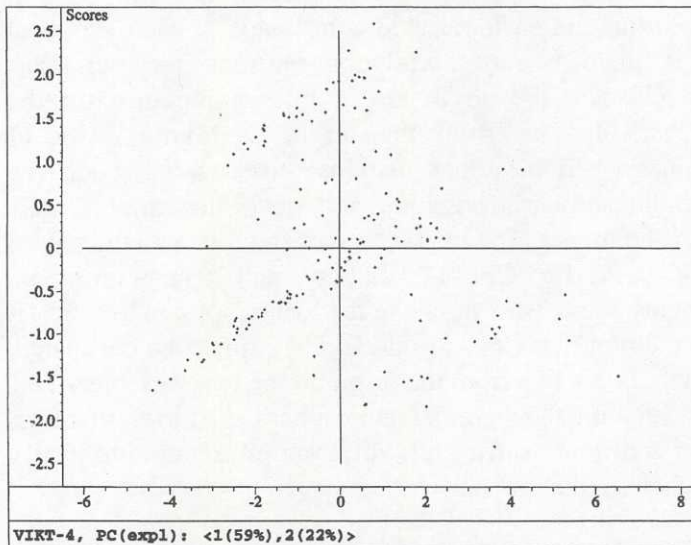


**Fig 5.3.** *Score plot with all samples from section S. Four parameters were used: CFC-11, CFC-12, Salinity and Temperature.*
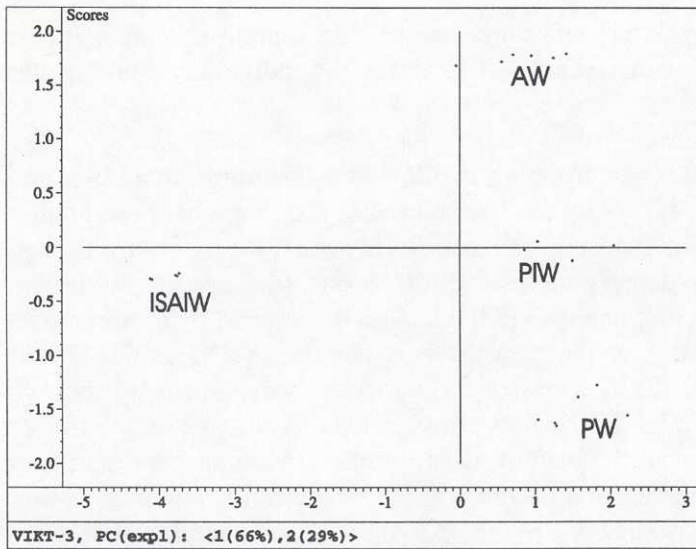
**Fig 5.4.** *A score plot with only the representative samples from the four different water masses in Denmark Strait: Atlantic Water (AW), Polar Water (PW), Polar Intermediate Water (PIW) and Iceland Sea Arctic Intermediate Water (ISAIW).*

The loading plot is another useful tool for interpreting the PCA. It tells how much information each variable contributes to each principal component and if there is any correlation between the variables. Variables that lie close to the origin are of little importance for the model, whereas variables far from the origin contribute a lot of information. Similarly variables that lie close to each other on the loading plot contribute similar information, and one of the variables may be unnecessary for the model. The importance of the four variables used in the modelling (CFC-12, CFC-11, salinity and temperature) on Principal Components 1 and 2 are shown in the loading plot in Fig. 5.5. It can be seen from the plot that CFC-11 and CFC-12 might be correlated, since they roughly fall on a line from the origin to the two variables. This is not surprising, keeping their similar atmospheric histories in mind. They do, however, contribute sufficiently different information to justify including both of them in the model.
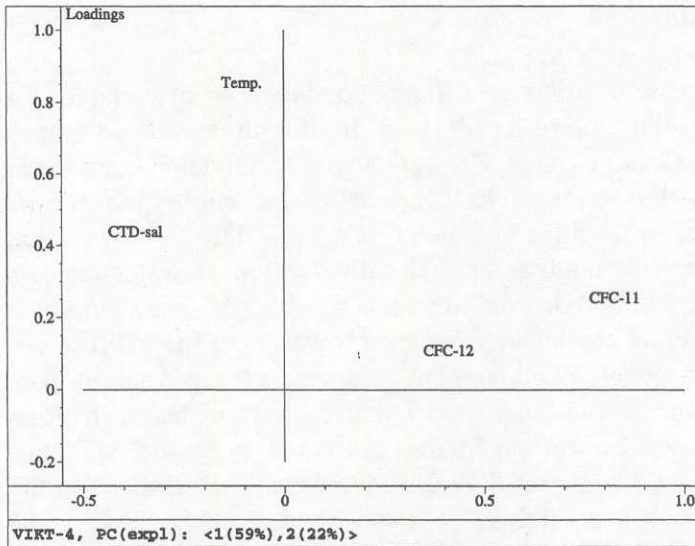
52

**Fig. 5.5.** *A loading plot of the variables in the model. The loading plot gives information on the relative importance of the variables for each Principal Component.*

The influence plot and the variance plot are two other important visualising tools for interpreting the model. The variance plot is useful when determining how many PCs are to be used in the model. The first PCs will contain the structure part of the data, the latter PCs will contain mainly noise and will therefore not contribute any information to the model, but will rather tend to overfit the model and should not be included. A reduction of dimensions is achieved by discarding the "noise" PCs. Similarly the use of too few PCs will produce a model that is underfitted, and relevant information may be lost. The variance plot is thus a tool that tells us where the structure part of the decomposed data ends and where the noise starts. The influence plot is a tool for detecting outliers, objects or variables that may bias the model. It is also a help in finding the most important object or variable for the total model.

The visualising tools that these plots provide are an aid in constructing a model that best describes the data set.

## 5.2 This model

It is possible to use a variety of different combinations of variables for the multivariate calibration of this data set. In this survey, in addition to CFC-11 and -12, CFC-113 and $CCl_4$ were also measured and could have been included in the model. The outcome of the calibration seems, however, not to be so sensitive to which CFCs are included in the model, since they covary to a large extent. The distribution of water masses, determined from PLS prediction, remains roughly the same in most attempts with different combinations of CFC tracers. The main difference between different models is the amount of noise in the prediction. It is therefore important to choose a model that uses variables with good analytical precision. In the prediction presented here the variables salinity, temperature, CFC-11 and CFC-12 are used. The salinity and the temperature are scaled to 1/SDev, i.e. the variables are divided by the standard deviation, whereas no scaling has been used for the CFCs. The reason for not using CFC-113 is that concentrations close to the detection limit are encountered in some of these waters and that these data therefore have a low relative precision. $CCl_4$, on the other hand, had too high a concentration in the cold polar water and was out of our calibration range. Other potentially powerful, routinely measured parameters that can be included in a model, are for example oxygen and nutrients, but those were unfortunately not measured during all three weeks of the survey.

Selecting the appropriate water samples to represent a given water mass, the "source waters", is a crucial step where some familiarity with the oceanography in the region has to be applied in the selection process. The score plot is the most important tool in this process. The choice of objects for the source waters is made from the endpoints in the score plot, provided their salinity, temperature and tracer content are realistic for that water mass. In this case it turned out that the choice of source waters was important for the prediction results, possibly even more important than the choice of variables, i.e. which of the CFC tracers were used in the model. Salinity and temperature were always important to include in the model. Different choices of variables gave roughly the same water mass distribution, but with different uncertainties in the prediction, while different selection of source waters gave a different water mass distribution. It is therefore important to select the source water samples with great care. Furthermore, it is important to include more than one sample from each source water in order to capture the natural variances

that exist within the source waters in the model. In this model there are 4 to 6 samples representing each source water.

It should be noted that the selected, representative, water samples represent the most typical samples of a given water mass found during this investigation. This means that the properties of the water masses in this work may differ from the properties, for the same water masses, found in the literature. This only reflects the fact that this investigation was carried out in an area of intense mixing and that the selected representative water samples may not be the pure water masses, but rather water masses that are already mixed to a certain extent. Source waters with properties similar to those found in the literature are to be found further away from the studied area. In Table 5.1. the selected source water samples are listed, together with data on the variables used for the modelling.

| Station | Depth m | CFC-12 pmol kg$^{-1}$ | CFC-11 pmol kg$^{-1}$ | Temp. $\Theta$ | Salinity | Water mass |
|---------|---------|------------------------|------------------------|-------|----------|------------|
| S5a | 100 | 3.01 | 5.95 | -1.758 | 32.948 | PW |
| S6 | 100 | 3.44 | 6.84 | -1.758 | 32.940 | PW |
| S6 | 150 | 3.30 | 6.56 | -1.757 | 33.339 | PW |
| S7a | 100 | 2.69 | 6.14 | -1.758 | 32.939 | PW |
| S7a | 140 | 3.30 | 6.24 | -1.777 | 33.223 | PW |
| R3 | 100 | 2.99 | 5.73 | -1.760 | 33.008 | PW |
| E3a | 200 | 3.25 | 5.89 | 6.491 | 35.080 | ISW |
| L1 | 200 | 3.09 | 5.69 | 6.601 | 35.089 | ISW |
| L1 | 300 | 2.70 | 5.02 | 6.439 | 35.087 | ISW |
| L3 | 150 | 2.86 | 5.63 | 6.505 | 35.058 | ISW |
| S4 | 100 | 3.36 | 6.35 | 6.633 | 35.022 | ISW |
| S2 | 100 | 3.18 | 6.25 | 6.553 | 35.019 | ISW |
| R3 | 1010 | 0.99 | 1.76 | -0.501 | 34.891 | ISAIW |
| R4 | 945 | 0.62 | 1.51 | -0.539 | 34.890 | ISAIW |
| H6a | 1000 | 0.91 | 1.75 | -0.586 | 34.899 | ISAIW |
| H6a | 1080 | 0.75 | 1.48 | -0.644 | 34.897 | ISAIW |
| H5a | 905 | 0.88 | 1.79 | -0.599 | 34.893 | ISAIW |
| S5 | 300 | 2.60 | 6.13 | -0.017 | 34.597 | PIW |
| S4 | 400 | 3.88 | 8.14 | 0.247 | 34.783 | PIW |
| L4 | 250 | 3.85 | 7.18 | -0.353 | 34.305 | PIW |
| L4 | 310 | 3.76 | 6.87 | 0.036 | 34.466 | PIW |

**Table 5.1**. *The water samples, and their properties, that represent the four water masses used for the PLS calibration in the Denmark Strait. The water masses are: Polar Water (PW), Atlantic Water (AW), Iceland Sea Arctic Intermediate Water (ISAIW) and Polar Intermediate Water (PIW). The depths were not included as a variable in the models.*

The percentages of the four different water masses are determined in each sample by PLS calibration. One obvious physical constraint in this process is that the percentage of a water mass in one sample cannot be more than 100 % or less than 0 %. The model will give an answer where the sum of water masses is 100 %. The model cannot, however, be constrained so that no samples have more than 100 % or less than 0 % of any water mass. Inevitably, some samples will fall outside the frame. This is especially true for water samples in the top 100 metres of the water column, where the model works less well due to the influence of summer heating and Icelandic river run-off. Few water samples with predicted water mass composition outside the constraints is an indication of a good selection of source waters and variables. Shown in Fig. 5.6 is the result from a prediction of the fraction of Atlantic Water in the samples from the S-section on September 10th, 1993. There are some samples with large error bars. These are surface water samples where the uncertainty of the model is large, but there are only a few samples that fall completely outside the model constraints. Samples above 100 meteres depth can be totally excluded from a model like this, but they are included in this work to illustrate the limitations of this approach.

The uncertainty of the prediction depends both on the error in the model itself and on the measurement errors of the variables (the sample to sample precision). One way of estimating the model error is by the Root Mean Square Error of Prediction (RMSEP). RMSEP is the square root of the average of the squared differences between predicted and measured Y-values of the validation objects and is a direct measure of the prediction error given in the original measurement units. It means in this case that the RMSEP values are given as the percentage of a given water mass. The validation objects are the calibration data set and cross validation of randomly selected calibration samples was used. A list of RMSEP values is found in Table 5.2. High RMSEP for PIW reflects the variability of that water mass.

| Water mass | RMSEP |
|------------|-------|
| PW | 8.0 |
| AW | 3.3 |
| PIW | 18.0 |
| ISAIW | 8.5 |

**Table 5.2.** *Root Mean Square Error of Prediction (RMSEP) for the water masses in the model. The RMSEP values are percentages, the unit used in the distribution plots for the water masses.*

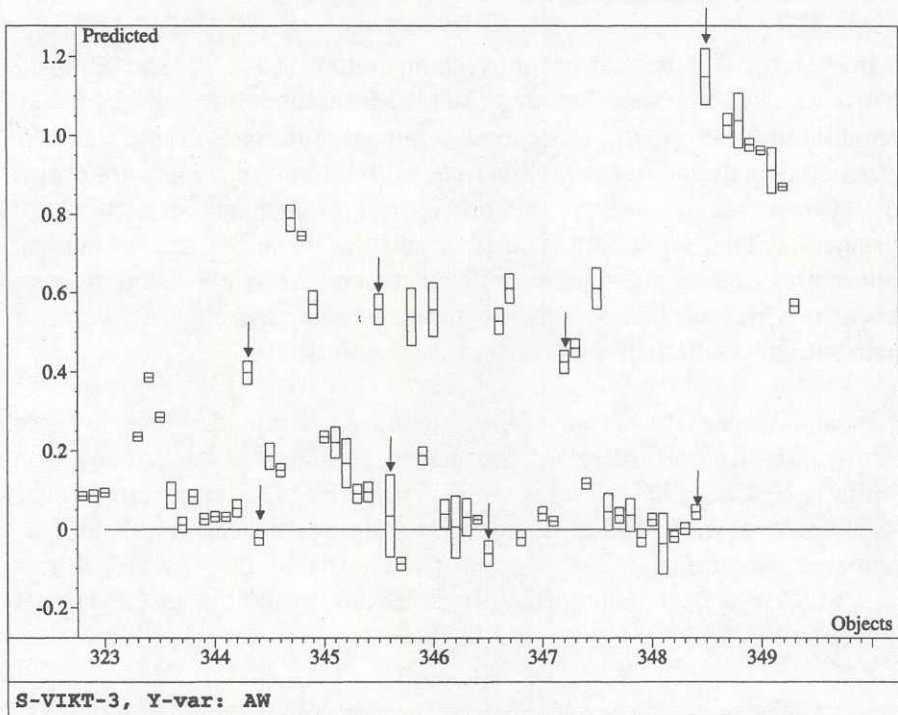**Fig. 5.6.** *Plot of the prediction result of the fraction of Atlantic Water in the S-section on 930910. The centres of the columns are the predicted fraction, and the total heights of the columns represent the uncertainty of the prediction. Marked columns are surface samples above 100 metres.*

The multivariate analysis was performed with the software "Unscrambler" Version 5.5, COMO AS, Trondheim.

## 5.3 Result and discussion

In Figures 5.7 to 5.10 salinity, temperature, CFC-11 and CFC-12 distributions in the S-section are presented from three different days. The temperatures are given as potential temperature ($\Theta$). These are the parameters included in the multivariate calibration. All figures are drawn on the same scale with the station closest to Iceland (station S2) at distance 0. The depths are in metres and the distances are in nautical miles. The dots in the figures indicate where the water samples were taken for CFC tracer analysis. The salinity, temperature and CFC tracer distributions are derived from data in these points.

Polar Water (PW) can easily be traced from the salinity and temperature minima close to the surface. Atlantic Water (AW) can similarly be traced by salinities above 35 and by high temperatures. The distribution of ISAIW can be seen by salinities around 34.89 and by temperatures around -0.5° C, but most obviously by the low CFC tracer content. PIW is best distinguished from ISAIW by the higher CFC tracer concentrations in PIW.

**Fig. 5.7.** *Salinity during three consecutive weeks in the Denmark Strait. Depth in metres and distance from SE in nautical miles.*

**Fig. 5.8.** *Potential temperature for three consecutive weeks in the Denmark Strait. Depth in metres and distance from SE in nautical miles.*
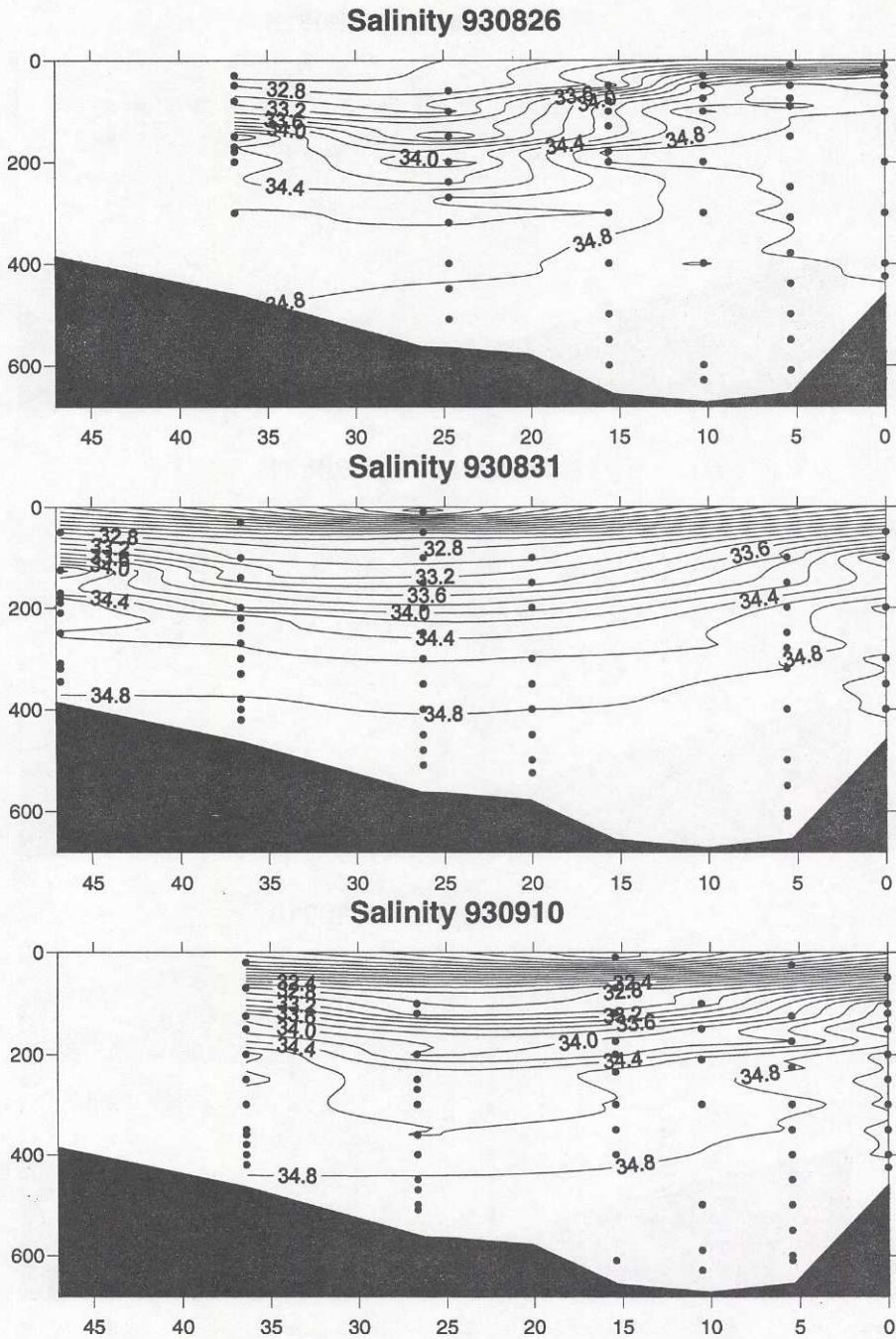
**Fig. 5.9.** *CFC-11 concentration during three consecutive weeks in the Denmark Strait. Depth in metres and distance from SE in nautical miles.*

**Fig 5.10.** *CFC-12 concentrations during three consecutive weeks in the Denmark Strait. Depth in metres and distance from SE in nautical miles.*

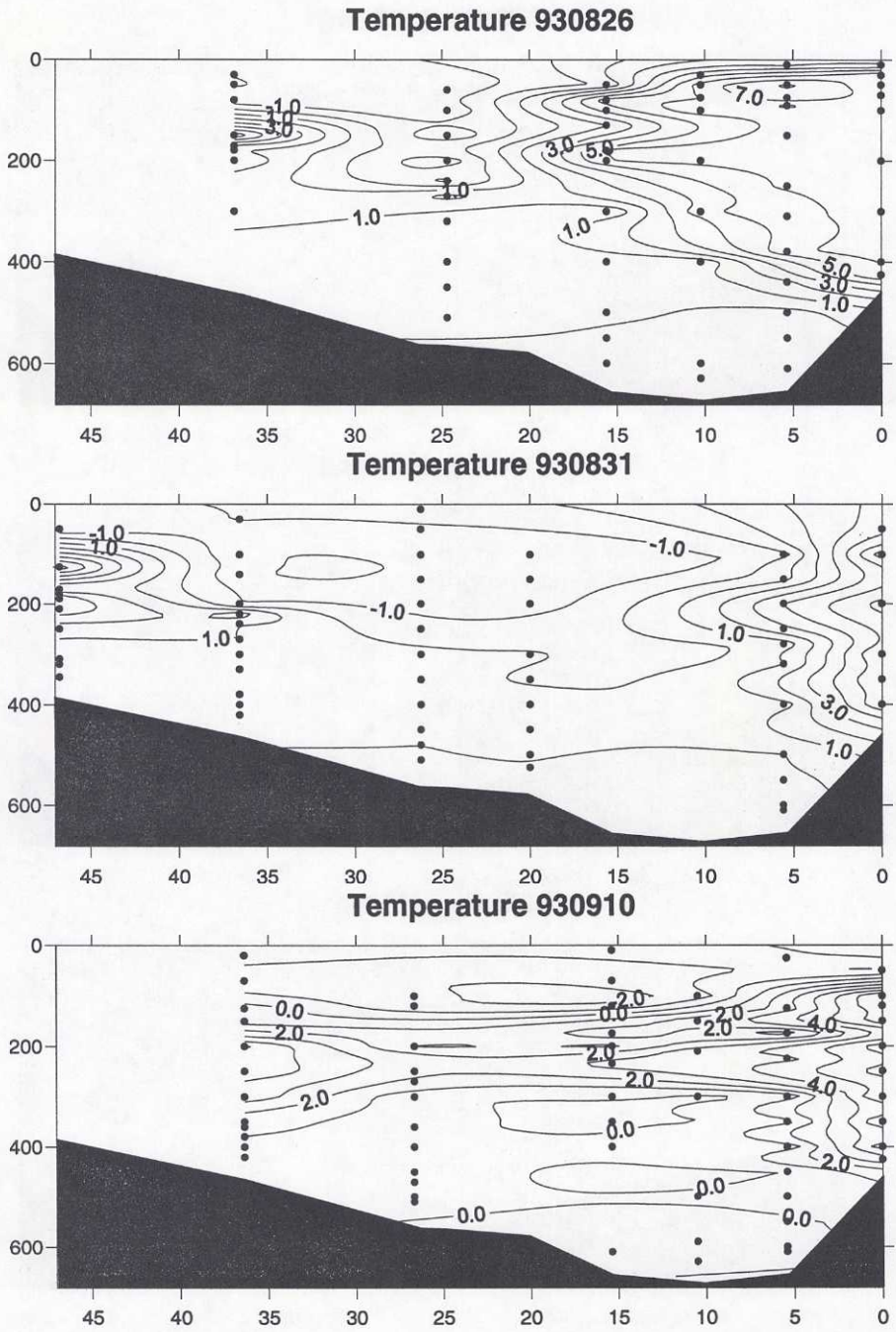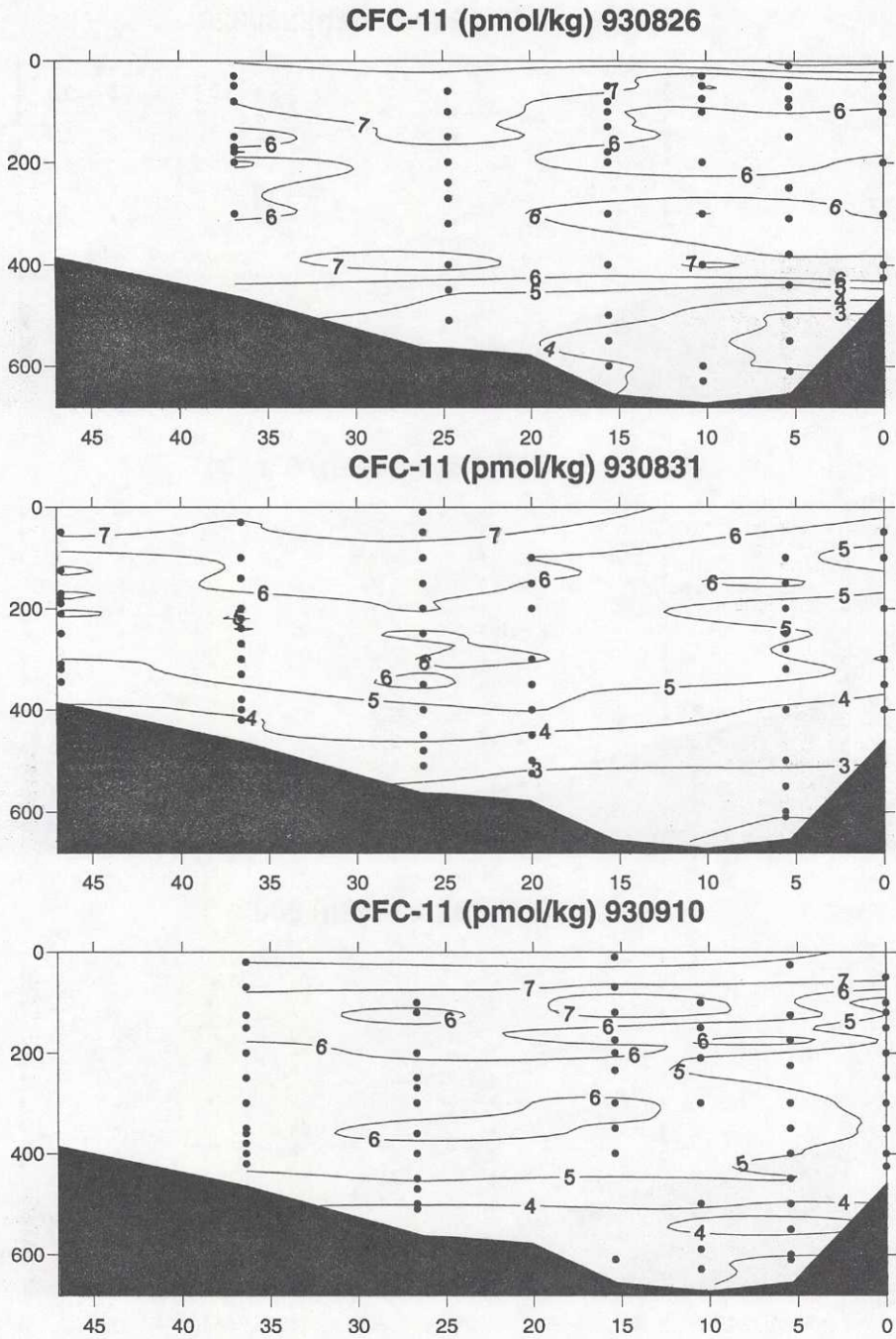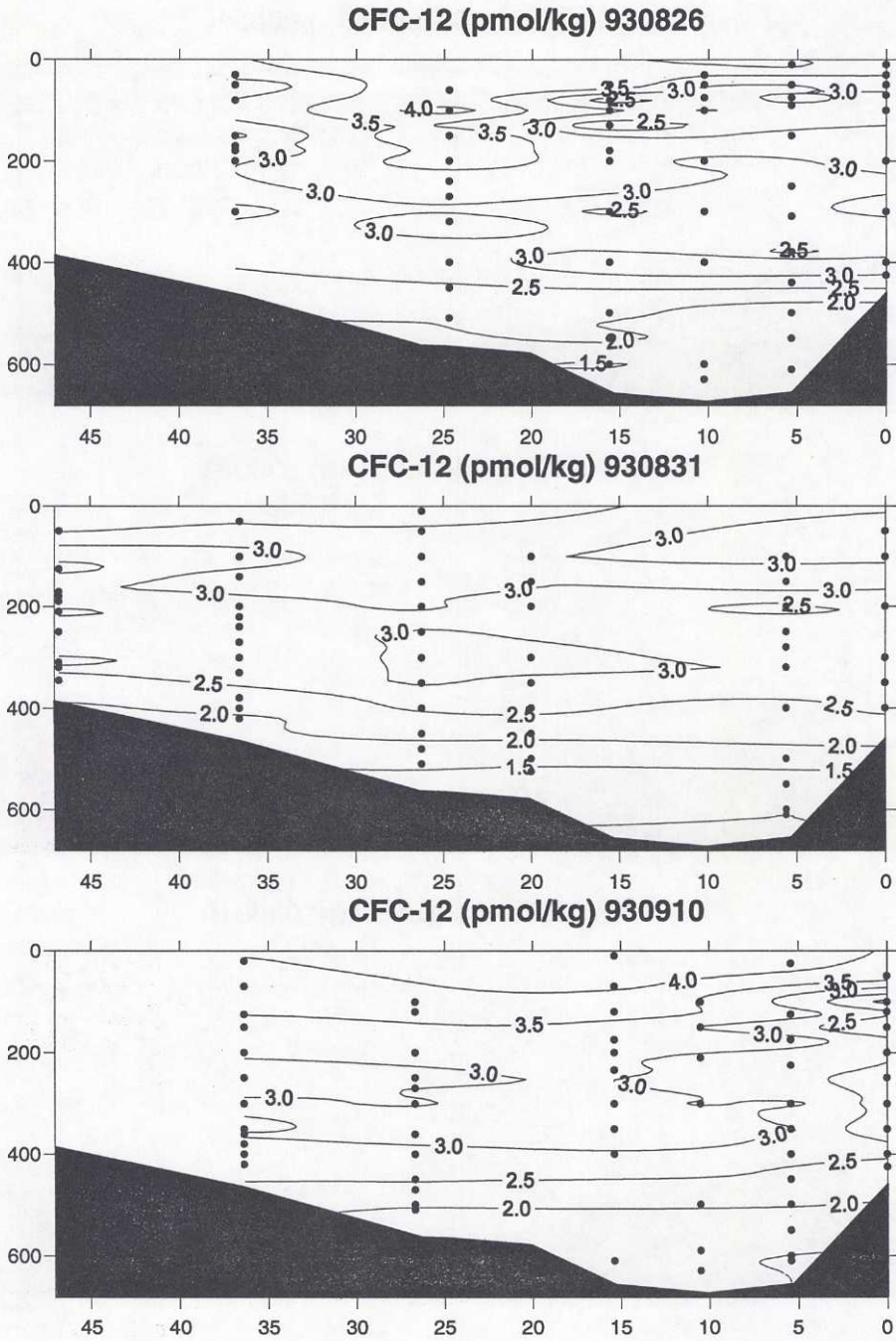Multivariate calibration of hydrographical and tracer data in the Denmark Strait proved to be a useful tool to distinguish between different water masses. The method was especially useful for distinguishing between PIW and ISAIW. Salinity and temperature data cannot separate sufficiently well between them, but the high CFC tracer concentration in PIW in relation to ISAIW will.

The PLS model does not work very well in waters above 100 m depth, where factors like summer warming and input of tracers from the atmosphere give water characteristics outside the tolerable range of the model. Furthermore the model is somewhat unreliable in the south-eastern part of the section, probably due to influence from Icelandic coastal waters, a water mass that is not included in the model. The model is, however, realistic and robust in waters below 100 meteres depth.

The relative distribution of the four water masses, PW, PIW, ISAIW and AW is presented in figures 5.11 to 5.14 for the three days. From the distribution of PW (Fig. 5.11) it is clear that PW dominates the upper part of the water column during the entire survey, but to a lesser extent in the first week. It is worth keeping in mind that the prediction in the top 100 metmes of the water column may give misleading conclusions, but is nevertheless included in this study to illustrate the advantages and shortcomings of this way of treating tracer data.

The distribution of AW is presented in Fig. 5.12. The Atlantic dominance is clear in the south-eastern part of the section, where this water mass is carried north by the East Icelandic Irminger Current. A water mass which is a mixture of AW and PIW is present in the north west part of the section This water is probably AW recirculated to the south in the Denmark Strait.

**Fig. 5.11.** *The distribution of Polar Water (PW) during three consecutive weeks in the Denmark Strait. Depth in metres and distance from SE in nautical miles.*

**Fig. 5.12.** *The distribution of Atlantic Water (AW) during three consecutive weeks in the Denmark Strait. Depth in metres and distance from SE in nautical miles.*
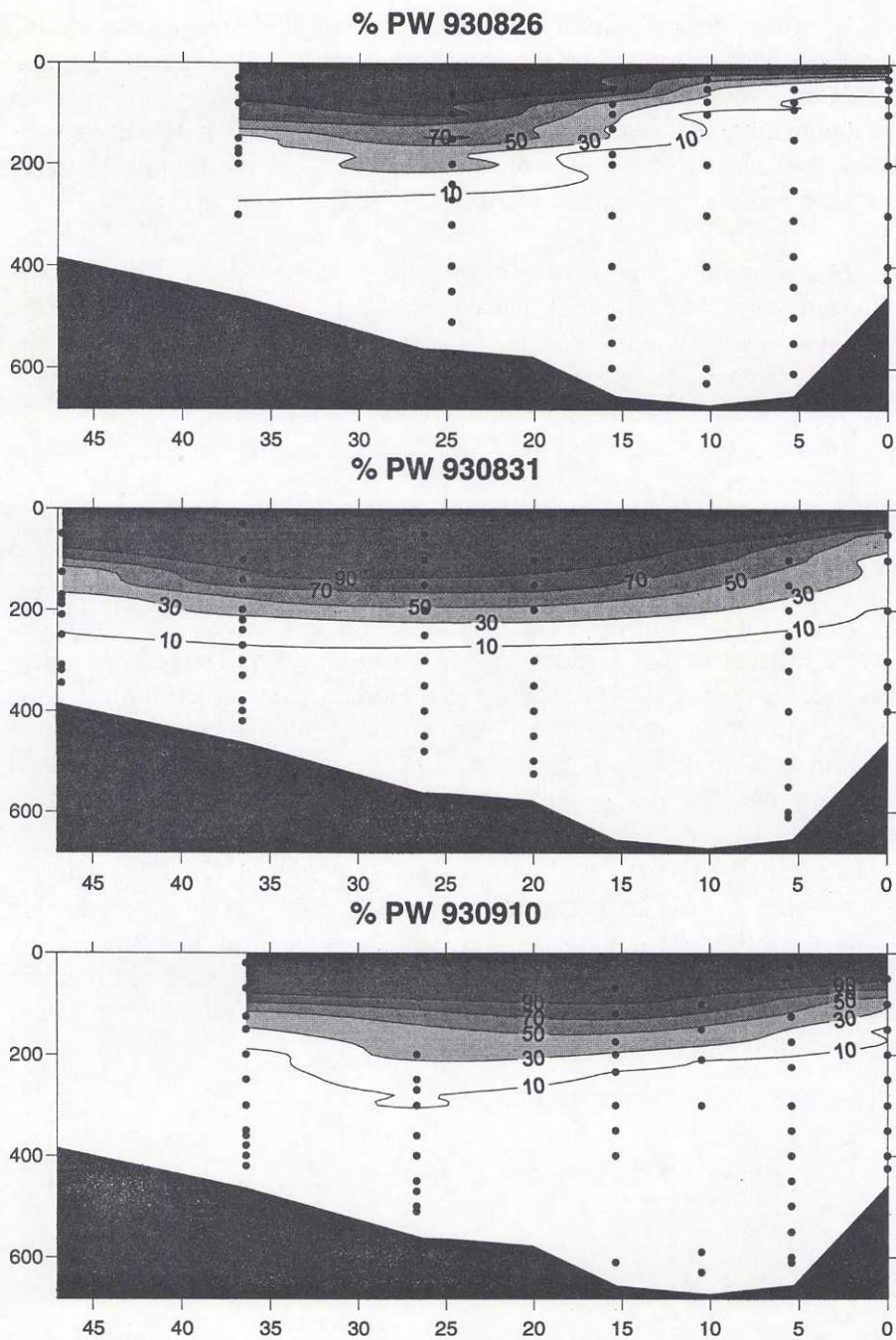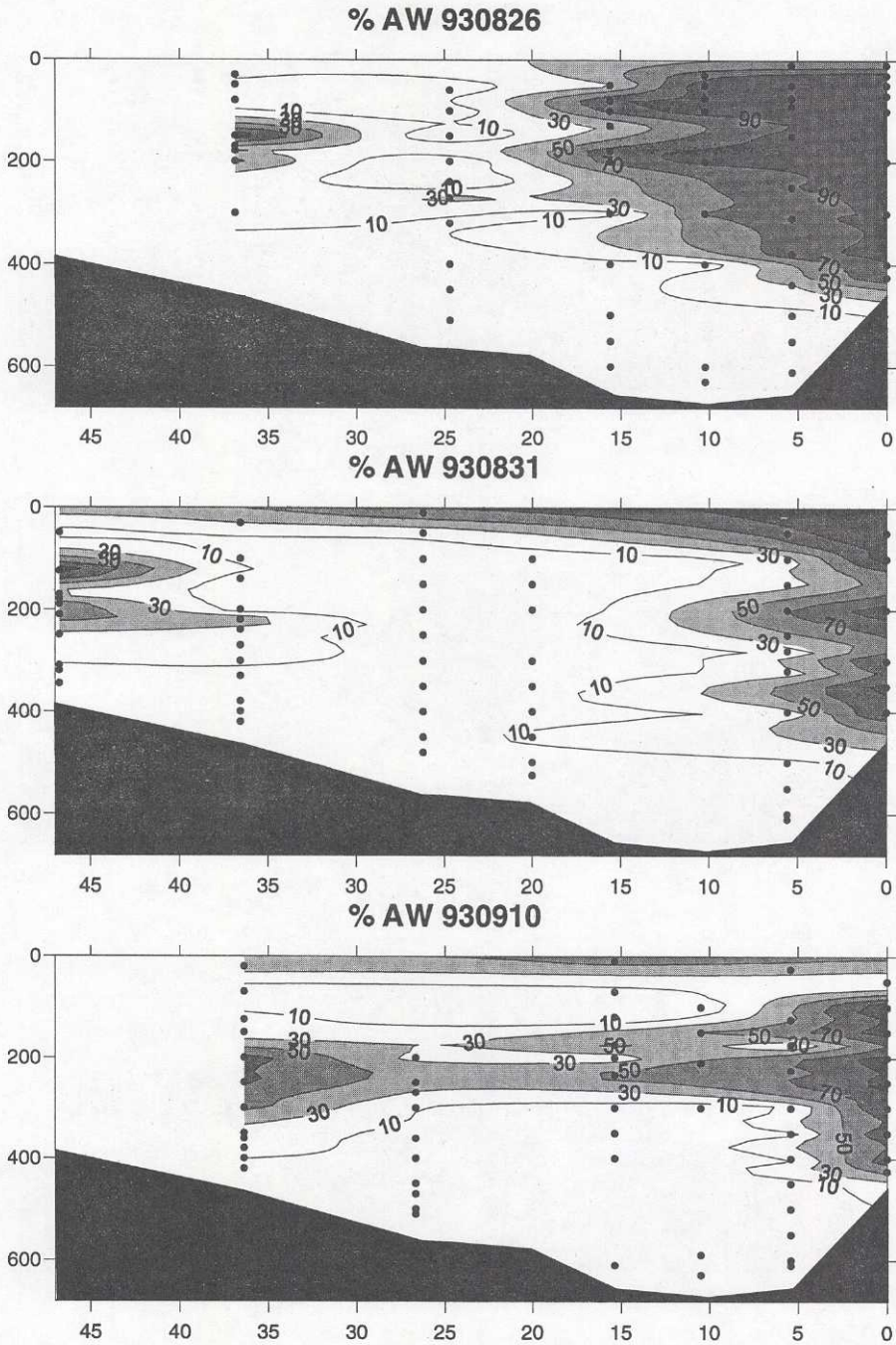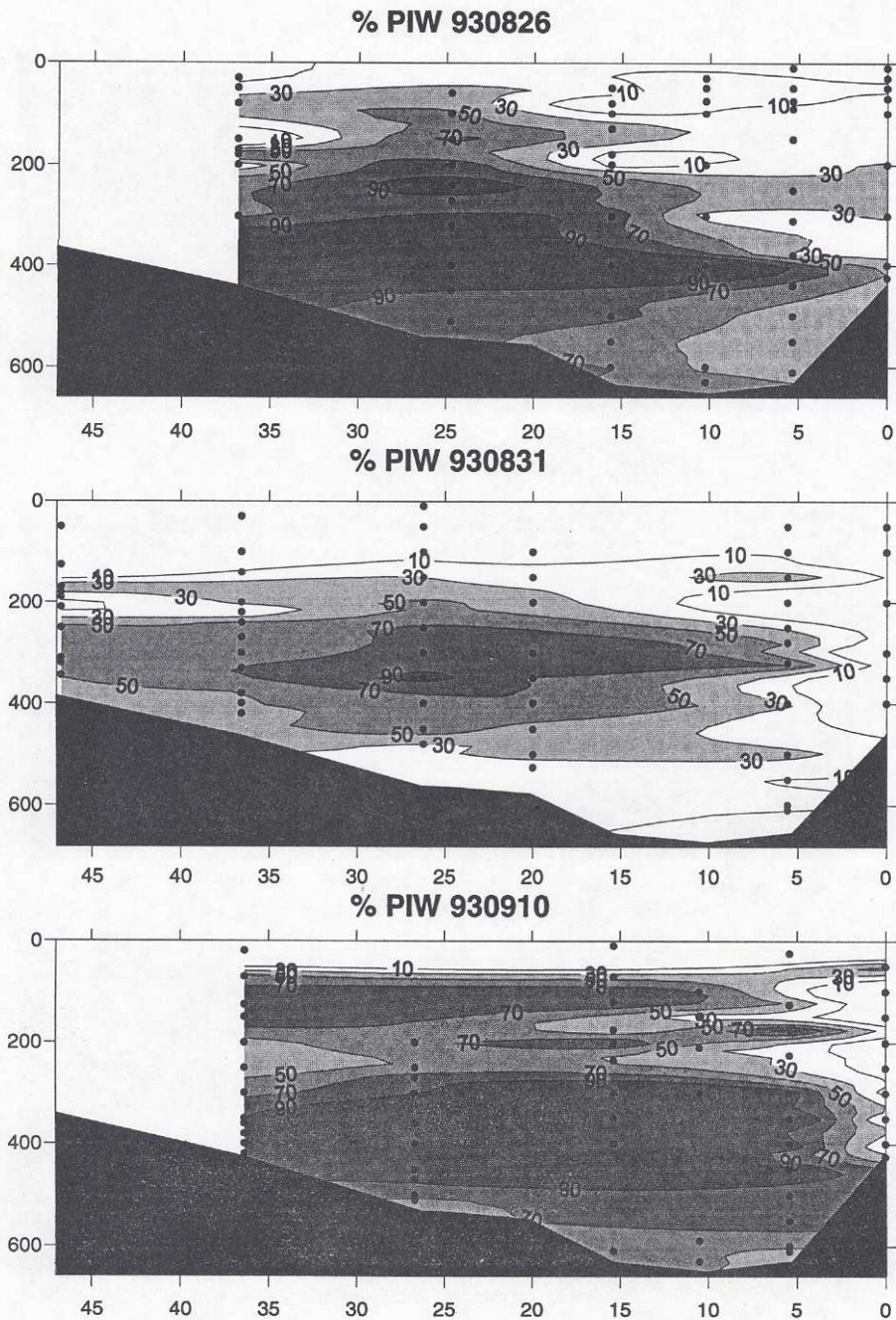
**Fig. 5.13.** *The distribution of Polar Intermediate Water (PIW) during three consecutive weeks in the Denmark Strait. Depth in metres and distance from SE in nautical miles.*
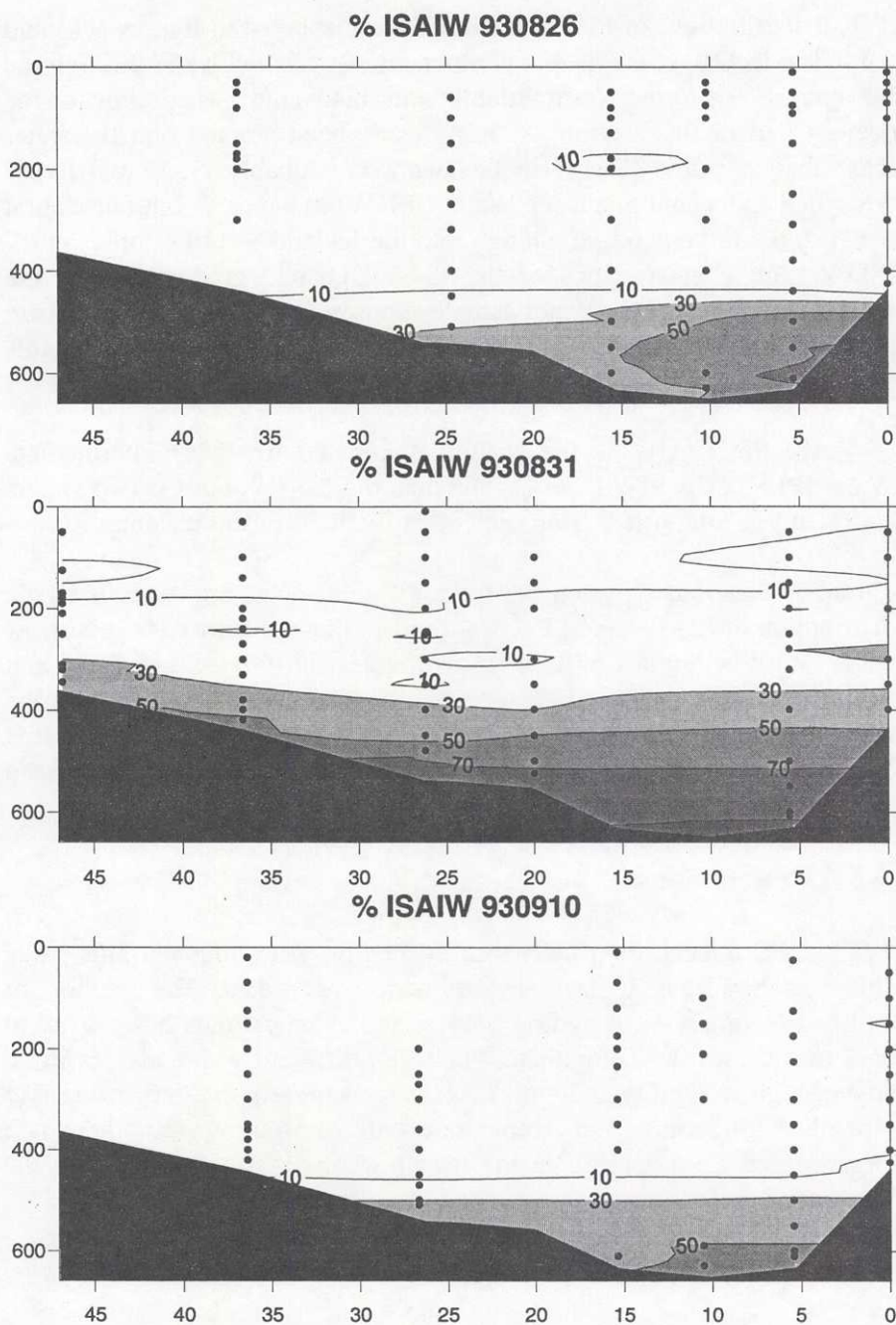
**Fig. 5.14.** *The distribution of Iceland Sea Arctic Intermediate Water (ISAIW) during three consecutive weeks in the Denmark Strait. Depth in metres and distance from SE in nautical miles.*

The distributions of PIW and ISAIW are displayed in figures 5.13 and 5.14. The ISAIW is the deeper component of overflow water through the Denmark Strait to the North Atlantic and this water mass dominates the deepest part of this section. As has already been pointed out, the water mass that is called ISAIW in this work is probably close to what is described as Iceland Sea Deep Water (ISDW) in paper V, but our station network did not extend far enough into the Iceland Sea to sample "pure" ISDW. The characteristics of the ISAIW change gradually from the bottom upwards and the water samples chosen to define the ISAIW here are the deepest and most northerly of the samples collected during this cruise, and is a clear endpoint in the score plot (Fig. 5.3).

Above the ISAIW is the section dominated by Polar Intermediate Water (PIW). The PIW is less saline than the ISAIW, but the two waters are readily distinguished from each other by their tracer concentrations.

Large variations between the three different dates are obvious in the distribution of ISAIW and PIW. It is evident that the amount of overflow water and its composition is highly variable with time. Smith 1976 and Aagaard and Malmberg (1978), report that the dense outflow from the Denmark Strait is dominated by outflow pulses at 1.9-day intervals. It is of course impossible to draw any conclusions on any interval between pulses of overflow water from this data set.

## 5.4 Conclusions

The CFC tracers are usually used for dating water masses. This study aimed to highlight a new way of using tracer data. The method of multivariate analysis of hydrographical and chemical data has proved to be a useful tool in distinguishing between different water masses in an area of high variability and with water masses present that are different to separate with salinity and temperature only. It is shown that there is a large degree of variability in the overflow of dense water through the Denmark Strait.

# 6. Sources and sinks of halocarbons in seawater

The sources of halocarbons in seawater are both of in-situ and anthropogenic origin, the latter mainly via the air-sea interface, as discussed in section 4.1. There are a number of possible sinks for halocarbons in seawater. These are; 1. adsorption onto particles or bioaccumulation followed by burial in the sediment 2. evaporation to the atmosphere 3. biological degradation and 4. chemical decomposition. The importance of these sources and sinks on the halocarbon chemistry in the marine environment and its implications will be discussed below.

## 6.1 The natural source

There is a natural background of halocarbons in all natural marine waters. These halocarbons are produced naturally, either directly from algal or bacterial production, or they are products from chemical reactions in seawater with other naturally produced halocarbons as precursors. To use a certain halocarbon as a marine tracer, it is important to understand its source as accurately as possible. A high natural background will restrict its use as a tracer whereas a well defined point source will promote it. Since halocarbons are volatile compounds, a net flux of halocarbons from the water to the atmosphere is generally expected.

Production of halocarbons by marine macroalgae has been demonstrated by several workers and was first indicated by Lovelock et al. (1973) and Lovelock (1975). Dyrssen and Fogelqvist (1981) and Fogelqvist (1985) have reported on the distribution of brominated halocarbons in seawater. Gschwend et al. (1985) measured the concentrations of several halocarbon compounds in different species of macroalgae. Manley et al. (1992) showed the production of bromoform, dibromomethane and methyl iodide by 11 species of macroalgae. Nightingale et al. (1995) found elevated concentrations of several halocarbons in beds of *Laminaria digitata*, and tests of 11 species of macroalgae indicated production of some or all of these compounds. It seems clear that macroalgae do produce halocarbons, but the magnitude of formation, which species of algae that are active in formation and which halocarbons are actually being produced is still an area for further research.

From open ocean surface water, the presence of several halocarbon compounds has been reported, suggesting that at least some halocarbons are produced by planktonic organisms. Klick and Abrahamsson (1992) report findings of several iodinated compounds in the open ocean and propose microalgal production of these compounds. Production of methyl chloride was observed by Moore et al. (1995), but in this case they propose bacterial production. Apart from planktonic microalgae producing halocarbons, algae living in ice are reported to release brominated halocarbons to their surroundings (Sturges et al., 1992; Sturges et al., 1993). Elevated concentrations of four iodinated compounds are reported in ice pore water in Antarctica (Fogelqvist and Tanhua, 1995) and it is suggested that these compounds are produced by the ice algae. Besides direct production of halocarbons by algae or bacteria, certain halocarbons may have an indirect source in the seawater via chemical reactions. A natural but abiotic photochemical source for methyl iodide has been demonstrated by Moore and Zafiriou (1994). Moore et al. (1995) report that chloroiodomethane also appears to be produced under the influence of light. From laboratory experiments, it has been shown that several species of marine phytoplankton release halocarbons (e.g. Moore et al., 1995; Tokarczyk and Moore, 1994; Abrahamsson et al., 1995; Pedersén et al., 1996).

Natural sources of carbon tetrachloride have been proposed (Lovelock et al., 1973, Fenical, 1982), and algal production has been demonstrated in laboratory experiments (Abrahamsson, personal communication). Wallace et al. (1994) however rule out the possibility of a natural background of $CCl_4$, the atmospheric preindustial background being less than 0.1 ppt. Although natural sources have been proposed for most halogenated compounds, there is no evidence, to the best of my knowledge, for natural production of fluorinated compounds. This is important to keep in mind when discussing the use of halocarbons as marine tracers. Although bacterial decomposition may be an important sink for halocarbons, the net outcome of biological activity is that it acts as a source rather than a sink for most halocarbon compounds in seawater.

## 6.2 Particulate sinks

Another possible sink for halocarbons in the ocean is accumulation onto particles and downward transport. Bioaccumulation is dependent on the lipophilicity of the compound and hence the partition coefficient between water and the biota as well as the amount of particulate organic material available for bioaccumulation. This issue is discussed by Krysell and Wallace (1988). They used measured values for the partition coefficient between freshwater algae and seawater for carbon tetrachloride and estimated values, based on their octanol-water partition coefficient, for CFC-11, -12 and $CH_3CCl_3$. Their conclusion is that particle flux in the open ocean should not affect any of these compounds. This statement may not hold true for more shallow inshore waters with a much higher particle flux. By applying the formula given by Krysell and Wallace (1988) and assuming that the adsorbed compounds are redissolved to the water phase in a 100 metres thick bottom layer of a water column, using a particulate organic carbon (POC) flux of 200 g m$^{-2}$ y$^{-1}$ as reported from Departure Bay by Stephens et al. (1967) as an upper limit for near shore flux and by updating the time-averaged halocarbon tracer concentrations to 1996, it is possible to calculate a surplus concentration of the halocarbon tracers derived from the POC flux. The results of such a calculation are given in table 6.1. The calculations assume that all the POC reaches the bottom water column and is remineralised there, thus the values given in the table are to be considered as upper limits of the halocarbon tracer flux. It is clear from the table that the resulting bottom water concentrations may not be negligible. In most near shore waters this halocarbon tracer surplus would not be noticed because of rapid ventilation, but in some cases, such as fjords with limited ventilation of the bottom water, the particulate flux may have an impact on the halocarbon tracer concentrations.

| Compound | Concentration (pmol L$^{-1}$) |
|---|---|
| CFC-11 | 0.22 |
| CFC-12 | 0.06 |
| CFC-113 | 0.04 |
| $CCl_4$ | 0.77 |
| $CH_3CCl_3$ | 0.76 |

**Table 6.1**. *An upper limit of the halocarbon tracer concentrations derived from POC flux in an area with high POC flux and where the halocarbons are redissolved in a 100 m thick water layer, for further discussion see text.*

## 6.3 Evaporation to the atmosphere

The air-sea exchange is important for the distribution of halocarbons in the sea. The halocarbons are generally rather insoluble in seawater, so partition to the atmosphere is favoured. For halocarbons produced in the seawater, the atmosphere will generally act as a sink (e.g. Lovelock et al., 1973; Liss, 1986; Moore and Tokarczyk, 1992; Nightingale et al., 1995). Naturally produced halocarbons play an essential role in the global cycling of halogens (i.e. chlorine, bromine and iodine). For anthropogenic halocarbons which are released from human activity to the atmosphere, e.g. the CFCs, the atmosphere will act as a source for halocarbons to the sea. If there is a sink for the compound within the seawater (e.g. Butler et al., 1991; Butler, 1994, paper II, IV and VI), this will enhance the flux from the atmosphere to the sea. For anthropogenic halocarbons whose atmospheric concentrations are decreasing, and which are persistent in the ocean, the air-sea flux may change direction in the future.

## 6.4 Chemical decomposition

Chemical decomposition of halocarbons in cold seawater is, in most circumstances, a slow process. In general, transformation of halocarbons can be divided into two classes: those that require external electron transfers (oxidations and reductions) and those that do not (substitutions and dehydrohalogenations), see Table 6.2. Of these reactions, hydrolysis and reduction are considered the most important sinks for halocarbons in the marine environment (with the exception of evaporation to the atmosphere), and they will be discussed in more detail. For an extensive discussion on transformation of halocarbons, see Vogel et al. (1987).

Hydrolysis rates of organic compounds in water are reported by Mabey and Mill (1978). Jeffers et al. (1989) measured the rate of hydrolysis for chlorinated compounds at various pH and temperature, and claim that hydrolysis is not a pH dependent, but a temperature dependent first-order reaction. Carbon tetrachloride and methyl chloroform, for example, have half-life times of 2790 and 74 years, respectively, at $0^{\circ}C$, but only 40 and 1 years, respectively, at $25^{\circ}C$ (Jeffers and Wolfe, 1989). This has important implications for the use of carbon tetrachloride and methyl chloroform as marine tracers, as discussed in section 6.5. The hydrolysis of chlorofluorocarbons is generally believed to be much slower than the hydrolysis of carbon tetrachloride.

| **I. Substitution** |
| --- |
| Hydrolysis:<br>$RX + H_2O \rightarrow ROH + HX$<br><br>Other nucleophilic substitutions:<br>$RX + Nu^- \rightarrow RNu + X^-$ |
| **II. Dehydrohalogenation**<br><br>$RXC\text{-}CRH \rightarrow RC=CR + HX$ |
| **III. Oxidation**<br><br>$\alpha$-hydroxylation:<br>$RCXH + H_2O \rightarrow RCXOH + 2H^+ + 2e^-$<br><br>Epoxidation:<br>$$RC=CRX + H_2O \rightarrow RC\overset{\overset{\textstyle O}{/\ \backslash}}{\ \ \ }CRX + 2H^+ + 2e^-$$ |
| **IV. Reduction**<br><br>Hydrogenolysis:<br>$RX + H^+ + 2e^- \rightarrow RH + X^-$<br><br>Dihalo-elimination:<br>$RXC\text{-}CRX + 2e^- \rightarrow RC=CR + 2X^-$<br><br>Coupling:<br>$2RX + 2e^- \rightarrow R\text{-}R + 2X^-$ |

**Table 6.2.** *Possible transformations of halocarbons in marine waters. Table from Vogel et al. (1987).*

The carbon-halogen bond strength is increasing in the order $I^-<Br^-<Cl^-<F^-$. This is important for the further discussion on chemical degradation. For substitution reactions, bromine is lost more readily than chlorine from a halocarbon such as $CHBr_2Cl$. Generally, increased halogenation leads to slower substitution reactions and longer half-lives. Consider, for

example, the hydrolysis half-life series of bromomethane (0.1 year), dibromomethane (183 years) and tribromomethane (686 years) at $20^{\circ}C$ (Mabey and Mill, 1978). Second-order nucleophilic substitution reactions between halocarbons and hydrogen sulphide in highly reducing conditions in groundwater have been reported by Schwarzenbach et al. (1985), yielding very persistent and hazardous volatile sulphur-containing compounds. Barbash and Reinhard (1989) examined substitution reactions of sulphur nucleophiles, such as $H_2S$, towards halogenated organic compounds in natural waters. They conclude that dehalogenation reactions including sulphur may be important for halocarbons, especially brominated compounds, in hypoxic waters.

Elimination reactions that produce alkenes may occur in water. Elimination of HX from an alkane is termed dehydrohalogenation. This reaction is strongly influenced by the number and kind of halogen substituents, monohalogenated compounds do not easily undergo dehydrohalogenation whereas more halogen substituents promote this reaction. Brominated compounds seem to undergo dehydrohalogenation reactions more readily than chlorinated ones.

The first oxidation reaction in Table 6.2 leads to an alcohol, which is further transformed to an aldehyde when a hydrogen ion (from the hydroxyl group) and the halide are split off the alcohol. The second oxidation, epoxidation, is the first step in an oxidation promoted by cytochrome P450-containing monooxygenase. The epoxide is normally short-lived, with several possible products, both reduced (alcohols) and oxidised (acids).

Due to the electronegative character of halogen substituents, halocarbons often behave as oxidants, and are reduced in the process. The more halogen substituents an aliphatic compound has, the more oxidised it is and the more susceptible it is to reduction. This is in contrast to the case of hydrolysis, where the more halogenated compound is the more stable one. Further, the carbon-halogen bond gets stronger in the following order; $I^-<Br^-<Cl^-<F^-$. Therefore brominated compounds are more susceptible to reduction than are chlorinated compounds, and the fluorinated compounds should be the most stable. Reduction of halocarbons in seawater can follow any of three possible pathways (Table 6.1). The pH of seawater is generally around 8 and thus the $H^+$ concentration around $10^{-8}$ M, whereas the concentrations of halocarbons are typically in the order of $10^{-12}$ M. This makes the reaction of hydrogenolysis far more likely to happen than that of coupling. Also the

configuration of most halocarbons of interest in this study makes the reaction of dihalo-elimination impossible. Hydrogenolysis is thus considered the most important reduction reaction for halocarbons in seawater.

A variety of electron carriers are available in living systems (e.g. cytochromes, flavoproteins, haemoproteins, chlorophylls and iron-sulphur proteins). Many of these may be capable of catalysing the reduction of halocarbons enzymatically. For instance cytochrome P450 has been reported to mediate reduction of halocarbons (Vogel et al., 1987, and references therein). Cytochrome P450 is the last component of an electron-transport chain, and is important for detoxification of foreign substances.
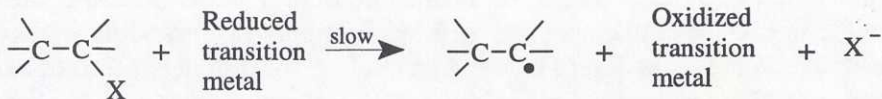
In living organisms, transition metals are often located in active sites on the macro-molecules that are used for electron transfer and these may be active in the reduction of halocarbons. It has, for instance, been shown that iron (II) porphyrins, in the presence of a reducing agent, catalyse reductive dehalogenation of chlorinated methanes and ethanes in water (Klecka and Gonsior, 1984). The iron porphyrin unit is the active site on macromolecules such as haemoglobin, cytochromes and catalases and are thus present in most living organisms. Suboxic/anoxic seawater containing decaying organic matter is also likely to contain free iron porphyrins available for the reduction of halocarbons. When halocarbons are reduced, the reducing agent is likely to be organic matter sinking through the water column. In the Black Sea, for instance, there is a substansial flux of Particulate Organic Matter (POM) from the surface layer and a remineralisation in the upper 100 metres of the water column (Karl and Knauer, 1991). A number of other transition metal complexes, including cobalt, chromium and nickel complexes, may also be involved in the reduction of halocarbons in a similar way. It must be stressed, however, that the reduction of halocarbons has little impact on the oxidation of organic matter, since the concentration of halocarbons is very low, and is only of interest for the halocarbon chemistry itself.

Not only are the transition metal complexes active in redox reactions, but also the free transition metal ions. Results reported by Klecka and Gonsoir (1984) indicate that free Fe(II) ions enhance the reductive dehalogenation of carbon tetrachloride to chloroform in aqueous solution, although at a slower rate than the transformation with iron porphyrins present. In seawater, there is usually a concentration maximum of Mn, Fe and Co at the oxic/anoxic interface (for instance in

the Black Sea and in the fjord Framvaren, Norway) where these compounds are cycled between their reduced, soluble, and oxidised, insoluble states and thus concentrated. It is therefore possible that free Mn(II), Fe(II) and Co(II) could play an important role in the reduction of halocarbons in the marine environment.

Reduction of halocarbons by hydrogenolysis is a two-step reaction which often involves the oxidation of a transition metal (Table 6.3). The first reaction step involves the formation of an alkyl radical. This step is, in most cases, the rate-limiting step. In the second step, several reactions can happen. In the case of hydrogenolysis the alkyl radical reacts with a hydrogen ion.

---

First, rate-limiting, step:

$$\overset{|}{\underset{|}{C}}-\underset{\underset{X}{|}}{\overset{|}{C}} \;+\; \begin{matrix}\text{Reduced}\\\text{transition}\\\text{metal}\end{matrix} \;\xrightarrow{\text{slow}}\; \overset{|}{\underset{|}{C}}-\underset{\bullet}{\overset{|}{C}} \;+\; \begin{matrix}\text{Oxidized}\\\text{transition}\\\text{metal}\end{matrix} \;+\; X^{-}$$

---

Second step:

$$\overset{|}{\underset{|}{C}}-\underset{\bullet}{\overset{|}{C}} \;+\; H^{+} \;+\; e^{-} \;\longrightarrow\; \overset{|}{\underset{|}{C}}-\underset{\underset{H}{|}}{\overset{|}{C}}$$
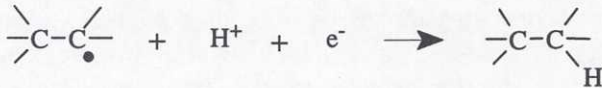
**Table 6.3.** *Reaction pathway for hydrogenolysis. The first step is, in most cases, the rate-limiting step. From Vogel et al. (1987).*

A critical factor, when considering redox-reactions, is the redox potential of a given reaction under given conditions. The redox potential is calculated according to the Nernst equation;

$$E = E^{o} - \frac{RT}{nF}\ln\left(\frac{[X^{-}][RH]}{[H^{+}][RX]}\right)$$

where $E$ is the redox potential at actual conditions, $E^{o}$ is the redox potential at the standard state, $R$ is the universal gas constant, $T$ is the absolute temperature, $n$ is electron equivalents transferred and $F$ is Faraday´s constant. $E^{o}$ can be calculated from the change in Gibbs free energy of formation ($\Delta G^{o}_{f}$) for a reduction reaction. A high redox potential means that a compound is a good electron acceptor, and thus likely to be reduced.

Discussed in paper IV is the role of the reduction of halocarbons in the Black Sea, where there is a sharp gradient between the oxic surface water layer and the anoxic deep water layer, and hence also a gradient in redox potential. The results in that paper clearly demonstrate that the halocarbons are removed from the water column in the interface between oxic and anoxic waters. It is noticed that the redox potentials for reduction of halocarbons are higher than, for example, that of reduction of nitrate to nitrite. It is further concluded that reduction may be an important sink for halocarbons in seawater.

## 6.5 Persistence of the halocarbon tracers

The important question of whether or not the transient tracers CFC-11, -12, -113, $CCl_4$ and $CH_3CCl_3$ will be affected by chemical decomposition will be discussed here. The main removal mechanisms for these compounds in seawater should generally be hydrolysis, in well oxygenated waters, and reduction, in oxygen depleted waters and in addition possible biological sinks. The lifetime of CFC-11, -12 and -113 with respect to hydrolysis in seawater is considered to be so long that no breakdown will affect their use as tracers, although the hydrolysis rate constants for these compounds are lacking in the literature. The hydrolysis of carbon tetrachloride and methyl chloroform is discussed by Krysell and Wallace (1988) and in the response by Jeffers and Wolfe (1989). It is concluded that the hydrolysis rate for methyl chloroform is fast enough (half-life 74.2 year at $0^o$C) to make it unsuitable as a marine tracer. Carbon tetrachloride on the other hand seems to be stable enough for use in cold waters (half-life 2790 years at $0^o$C), but hydrolyses rapidly in warm waters (half-life 40.3 years at $25^o$C) and $CCl_4$ should therefore be used with care in warm waters. However, Meridith et al. (1996) found deficits of carbon tetrachloride in recently formed Weddell Sea Deep Water (WSDW) and Weddell Sea Bottom Water (WSBW) and at the summer temperature minimum of Antarctic Surface Water (ASF). They demonstrate that $CCl_4$ can be removed from cold and well oxygenated waters and argue that another sink other than an oxygen or temperature-dependent sink must operate. They suggest a biological sink present in Shelf Water (SW) formed in the biologically active part of the ocean, and the $CCl_4$ deficit is then transferred from the SW to WSDW and WSBW during their formation. However, they do not present any $CCl_4$ data from the SW.

Bullister and Lee (1995) found removal of CFC-11 from the anoxic and strongly reducing waters of the Black Sea and the periodically anoxic basin the Saanich Inlet, Canada, B.C. They also investigated the low oxygen, but not anoxic, mid-depth waters of the eastern tropical Pacific, and found that CFC-11 is persistent there. Lovely and Woodward (1992) found consumption of CFC-11 and -12 in anoxic sediments and soils. Wallace et al. (1994) found evidence for the removal of $CCl_4$ in the thermocline in the South Atlantic Ocean and were able to estimate the half-life to 1-5 years. They suggest three different mechanisms for the removal of $CCl_4$, a temperature dependent reaction, removal of bacterial activities in low oxygen areas or scavenging from the water by the high flux of POC. Removal of $CCl_4$ from seawater with as much as 200 µmol $L^{-1}$ are reported in paper IV, and the area with the largest deficit in $CCl_4$ found by Wallace et al. coincides with a low oxygen region. From papers II and IV it is concluded that it is not possible to use $CCl_4$ as a transient tracer in oxygen depleted waters. Indications that methyl chloroform is unstable in anoxic waters were also presented in paper IV. Measurements of the halocarbon tracers in the superanoxic fjord Framvaren are presented in paper VI. It is concluded that CFC-12 seems to be stable to reduction, whereas CFC-11, CFC-113, $CCl_4$ and $CH_3CCl_3$ are all degraded in anoxic seawater. From modelling efforts it was possible to estimate the rate of reduction of the halocarbon tracers from the top 30 metres of the anoxic layer. The estimated half-lives were; $11\pm3$, $5.0\pm0.3$, $4.8\pm0.3$ and $2.5\pm0.8$ years for CFC-113, CFC-11, $CH_3CCl_3$ and $CCl_4$, respectively. Bullister and Lee (1995) calculated half-lives for CFC-11 between 11.6 and 1.6 years for the Black Sea, with the shortest half-lives in the deeper and more anoxic layers. Our results are within this range.

The differences in persistency between the five halocarbon tracers can possibly be correlated to the number of fluorine atoms present in the compound. The carbon-fluorine bond is stronger than the carbon-chlorine bond, making reduction of a fully chlorinated compound more favourable than for a compound with fluorine atoms present. The least stable compound to reduction in our investigations, $CCl_4$, is fully chlorinated whereas the most stable CFC-12 ($CCl_2F_2$) has two fluorine atoms present. Methyl chloroform is not a fully halogenated compound and its redox potential is thus lower than that for a compound which is. The redox potential for a compound is dependent on the redox reduction taking place, for CFC-12, for instance, there are two possible redox reactions. The reaction where a fluorine is substituted with a hydrogen yields a very low redox potential whereas if a chlorine is substituted, the redox potential for CFC-12 is much higher. In table 6.4 there is a list of the

redox potentials for the most favoured redox reactions for the halocarbon tracers. The potentials are calculated for standard state ($E^o$), i.e. 25°C and are not compensated for concentration differences between reactants and products. The equations below were used for the calculation, $\Delta G^o_f$ taken from the Thermodynamics Research Center Data Project, Texas A&M University. The Gibbs free energy of formation in aqueous phase, $G^o_f(aq)$, can be calculated from the corresponding parameter in gaseous phase, $G^o_f(g)$ if the Henry´s Law constant is known. Because of the lack of reliable Henry´s Law constants for some of the products, $\Delta G^o_f(g)$ has been used instead of $\Delta G^o_f(aq)$ for the halocarbons, the error on $\Delta G^o_f(aq)$ is regarded as being relatively small.

$$RX + H^+ + 2\,e^- \leftrightarrow RH + X^-$$
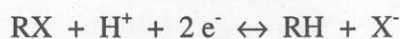
$$\Delta G^o_f = \sum G^o_f \text{ products} - \sum G^o_f \text{ reactants}$$

$$E^o = -\Delta G^o_f / nF$$

| Compound | redox-potential for the most favoured reaction (V) | Number of posible reactions |
|---|---|---|
| CFC-12 | 0.23 | 2 |
| CFC-11 | 0.30 | 2 |
| CFC-113 | 0.22 | 4 |
| $CCl_3CH_3$ | 0.21 | 1 |
| $CCl_4$ | 0.34 | 1 |

**Table 6.4.** *Redox potentials for the halocarbon tracers at standard state and the number of possible hydrogenolysis reactions.*

It can be concluded that some caution when interpreting halocarbon tracer data from oxygen depleted seawater, and for $CCl_4$ and $CH_3CCl_3$ also in warm oxygenated waters, is recommended. To what extent reduction of halocarbons in seawater is a pure chemical process or a bacterially mediated process is still an open question, as is the question of which reductants or catalysts are active in seawater.

# 7. Acknowledgements

I wish to thank all my friends and colleges at the Department of Analytical and Marine Chemistry that have made my time at the department very fun and interesting. I also wish to express my gratitude to all friends and colleges I have met during expeditions, that have made life at sea so rewarding.

Most of all I want to thank associate professor Elisabet Fogelqvist, my scientific supervisor, for always helping me on the way, for always having time for my questions and for learning me very much during these years. It has been very fun.

Special thanks are due to:

Anders and Marie, the other team members of the "halocarbon tracer-group", for always showing happy faces and being great company.

Dr. Mikael Krysell, who introduced me to the world of marine tracers and of purge and trap.

Professors David Turner, David Dyrssen and Daniel Jagner for inspiring me in the field of analytical and marine chemistry, and for many valuable discussions.

Liz and David Turner for help with the English language.

Kenneth, Leo and Berne for technical support, copying and making nice computerised drawings.

Co-authors in the papers presented in the thesis for excellent co-operation.

All my friends at Institute of Marine Sciences, Erdemli, Turkey, for the friendship and generosity.

Gustaf and Martin for countless hours of discussions on "the perfect cruising yacht", will we ever get there?

All my friends both inside and outside the department that has made life in Göteborg so good.

My family for always encouraging and supporting me in my interest for sciences, you made it all possible.

# 8. References

Aagard, K, and Malmberg, S.-A., 1978. Low-Frequency Characteristics of Denmark Strait Overflow. **ICES**, CM 1978/C:47.

Abrahamson, K., Ekdahl, A., Colén, J. and Pedersén, M., 1995. Marine algae - a source of trichlooethylene and perchloroethylene. *Limnology and Oceanography,* **40(7),** 1321-1326.

Barbash, J.E. and Reinhard, M., 1989. Reactivity of Sulfur Nucleophiles Toward Halogenated Organic Compounds in Natural Waters. In: *Biogenic Sulfur in the Environment*. Eds, E.S. Saltzman and W.K. Cooper. ACS Symposium Series 393, American Chemical Society, Washington, USA.

Bu, X. and Warner, M.J., 1995. Solubility of Chlorofluorocarbon 113 in Water and Seawater. *Deep-Sea Research,* **42**, 1151-1161.

Bullister, J.L. and Weiss, R.F., 1983. Anthropogenic chlorofluoro-methanes in the Greenland and Norwegian Seas. *Science.* **221**, 265-268.

Bullister, J.L., 1984. Atmospheric chlorofluoromethanes as tracers of ocean circulation and mixing: measurements and calibration techniques and studies in the Greenland and Norwegian Seas. PhD. Thesis, University of California, San Diego.

Bullister, J.L. and Weiss, R.F., 1988. Determination of $CCl_3F$ and $CCl_2F_2$ in seawater and air. *Deep-Sea Research*. **35(5),** 839-853.

Bullister J.L. and Lee, B.S., 1995. Chlorofluorocarbon-11 removal in Anoxic Marine Waters. *Geophysical Research Letters*, **22(14),** 1893-1896.

Butler, J.H., Elkins, J.W., Thayne, M., Hall, B.D., Swanson, T.H. and Koropalov, V., 1991. Oceanic Consumption of CH3CCl3: Implications for Tropospheric OH. *Journal of Geophysical Research*. **96(D12),** 22347-22355.

Butler, J.H., 1994. The potential role of the ocean in regulating atmospheric $CH_3Br$. *Geophysical Research Letters*. **21(3),** 185-188.

Bönisch, G. and Schlosser, P., 1995. Deep water formation and exchange rates in the Greenland/Norwegian Seas and the Eurasian basin of the Arctic Ocean derived from tracer balances. *Prog. Oceanog.*, **35**, 29-52.

Cai, H., Wentworth, W.E. and Stearns, S.D., 1996. Characterization of the Pulsed Discharge Electron Capture Detector. *Analytical Chemistry*, **68**, 1233-1244.

Clark, J.F., Schlosser, P., Stute, M. and Simpson, H.M., 1996. $SF_6$-$^3$He Tracer Release Experiment: A New Method of determining Longitudinal Dispersion Coefficients in Large Rivers. *Environmental Science Technology*, **30**, 1527-1532.

Cunnold, D.M., Prinn, R.G., Rasmussen, R.A., Simmonds, P.G., Alyea, F.N., Cardelino, C.A., Crawford, A.J., Fraser, P.J. and Rosen, R.D., 1986. Atmospheric Lifetime and Annual Release Estimates for $CFCl_3$ and $CF_2Cl_2$ From 5 Years of ALE Data. *Journal of Geophysical Research*. **91(D10)**, 10,797-10,817.

Dickson, R.R., Gmitrowicz, E.M. and Watson, A.J., 1990. Deep-water renewal in the northerns North Atlantic. *Nature*, **344**, 848-850.

Dyrssen, D. and Fogelqvist, E., 1981. Bromoform concentrations of the Arctic Ocean in the Svalbard area. *Oceanologica Acta*. **4**, 313.

Dyrssen, D.W., Hall, P.O.J., Haraldsson, C., Chierici, M., Skei, J. and Östlund, H.G., 1997. Time Dependence of Organic Matter Decay and Mixing Processes in Framvaren, a Permanantly Anoxic Fjord in South Norway. Accepted for publication in *Aquatic Geochemistry*.

Esbensen, K., Schönkopf, S. and Midtgaard, T., 1994. Multivariate Analysis in Practice. Computer-Aided Modelling A/S, Trondheim, Norway.

Eklund, G., Josefsson, B. and Roos, C., 1978. Determination of Volatile Halogenated Hydrocarbons in Tap Water, Seawater and Industrial Effluents by Glass Capillary Gas Chromatography and Electron Capture Detection. *Journal of High Resolution Chromatography and Chromatographic Communication*. **1**, 34-40.

Fenical, W., 1982. Natural products chemistry in the marine environment. *Science*. **215**, 923.

Fisher, D.A. and Midgley, P.M., 1993. The production and release to the atmosphere of CFCs 113,114 and 115. *Atmospheric Environment*. **27A**, 271-276.

Fogelqvist, E., 1985. Carbon tetrachloride, tetrachlorethylene, 1.1.1.-trichloroethane and bromoform in Arctic Seawater. *Journal of Geophysical Research*. **90(C5)**, 9181.

Fogelqvist, E., Krysell, M. and Danielsson, L.-G., 1986. On-line liquid-liquid exctraction in a segmented flow directly coupled to on-column injection into a gas chromatograph. *Analytical chemistry*, **58**, 1516-1520.

Fogelqvist, E. and Tanhua, T., 1995. Iodinated C1-C4 hydrocarbons released from ice algae in Antarctica. In: *Naturally Produced Organohalogens* (Eds. A. Grimvall and E.W.B. de Leer) Kluwer Academic Publishers, Dordrecht, The Nederlands, 295-305.

Fogelqvist, E. and Johansson, O., 1997. Solubility of carbon tetrachloride in natural waters. Submitted to Marine Chemistry.

Golombek, A. and Prinn R.G., 1989. Global three-dimensional model calculations of the budgets and present-day atmospheric lifetimes of $CF_2ClCFCl_2$ (CFC-113) and $CHCl_2F$ (CFC-22). *Geophysical Research Letters,* **16**, 1153-1156.

Grob, K., Artho, A., Fraeunfelder, C. and Roth, I., 1990. Charcoal Open Tubular Traps for the Analysis of Air and Headspace Samples. *Journal of High Resolution Chromatography.* **13**, 257-260.

Graydon, J.W. and Grob, K., 1983. How efficient are cold traps*? Journal of Chromatography.* **254**, 265-269.

Gschwend, P.M., MacFarlane, J.K. and Newman, K.A., 1985. Volatile halogenated organic compounds released to seawater from temperate marine macroalgae. *Science.* **277**, 1033-1035.

Haine, T.W.N. and Richards, K.J., 1995. The influence of the seasonal mixed layer on oceanic uptake of CFCs. *Journal of Geophysical Research*, **100(C6),** 10727-10744.

Haine, T.W.N., Watson, A.J. and Liddicoat, M.I., 1995. Chlorofluorocarbon-113 in the northeast Atlantic. *Journal of Geophysical Research*, **100 (C6),** 10745-10753.

Happell, J.D., Wallace, D.W.R., Wills, K.D., Wilke, R.J. and Neill, C.C., 1996. A purge-and-trap capillary column gas chromatographic method for the measurement of halocarbons in water and air. Report BNL-63227, Department of Applied Science, Brookhaven National Laboratory, USA.

Hunter-Smith, R.J., Balls, P.W. and Lisss, P.S., 1983. Henry´s Law constants and the air-sea exchange of various low molecular weight halocarbon gases. *Tellus*, **35B,** 170-176.

Jeffers, P.M., Ward, L.M., Woytowitch, L.M. and Wolfe, N.L., 1989. Homogeneous Hydrolysis Rate Constants for Selected Chlorinated Methanes, Ethanes, and Propanes. *Environmental Science and Technology.* **23**, 965-969.

Jeffers, P.M. and Wolfe, N.L. with response by Wallace, D.W.R and Krysell, M., 1989. Hydrolysis of Carbon Tetrachloride. *Science.* **246**, 1638-1639.

Jenkins, W.J., 1980. Tritium and $^3$He in the Saragasso Sea. *Journal of Marine Research.* **38**, 533.

Johanssen, O.M., Sandven, S. and Johannessen, J.A., 1991. Eddy-related winter convection in the Boreas Basin. In. *Deep Convection and Deep Water Formation in the Oceans*, Eds. Chu, P.C. and Gascard, J.C.

Karl, D.M. and Knauer, G.A., 1991. Microbial production and particle flux in the upper 350 m of the Black Sea. *Deep-Sea Research.* **38(2),** S921-S942.

Klecka, G.M. and Gonsoir, S.J., 1984. Reductive dechlorination of chlorinated methanes and ethanes by reduced iron (II) porphyrins. *Chemosphere.* **13(3),** 391-402.

Klick, S. and Abrahamsson, K., 1992. Biogenic Volatile Iodated Hydrocarbons in the Ocean. *Journal of Geophysical Research.* **97(C8),** 12,683-12,687.

Kolb, B., Zwick, G. and Auer, M., 1996. A water Trap for Static Cryo-Headspace Gas Chromatography. *High Resolution Chromatography,* **19,** 37-42.

Krysell, M. and Wallace, D.W.R., 1988. Arctic Ocean ventilation studied with a suite of anthropogenic halocarbon tracers. *Science,* **242,** 746-749.

Krysell, M., 1992. Carbon tetrachloride and methyl chloroform as tracers of deep water formation in the Weddell Sea, Antarctica. *Marine Chemistry.* **39,** 297-310.

Krysell, M. and Nightingale, P.D., 1994. Low moecular weight halocarbons in the Humber and Rhine estuaries determined using a new purge-and-trap gas chromatographic method. *Continental Shelf Research.* **14(12),** 1311-1329.

Law, C.S., Watson, A.J. and Liddicoat, M.I., 1994. Automated vacuum analysis of sulphur hexafluoride in seawater: derivation of the atmospheric trend (1970-1993) and potential as a transient tracer. *Marine Chemistry,* **48,** 57-69.

Law, C.S. and Watson, A.J., 1997. Slower flushing of the Arabian Sea revealed by a novel transient tracer. Submitted to Nature.

Ledwell, J.R. and Watson, A.J., 1991. The Santa Monica Basin Tracer Experiment: a study of diapycnal and isopycnal mixing. *Journal of Geophysical Research,* **96(C5),** 8695-8718.

Ledwell, J.R., Watson, A.J. and Law, C.S., 1993. Evidence for slow mixing across the pycnocline from an open-ocean tracer-relase experiment. *Nature,* **364,** 701-703.

Liss, P.S., 1986. The air-sea exchange of low molecular weight halocarbon gases. In: *The role of air-sea exchange in geochemical cycling,* Eds. P. Buat-Menard, D. Riedel, Publishing Company.

Lobert, J.M. and Baring, T.J., 1993. Ocean/Atmosphere Exchange of Trace Compounds 1992, Final Report to AFEAS on Ocean Measurements of HCFC-22, Methyl Chloroform, and other Selected Halocarbons to Address the Magnitude of the Hydrolysis Sink. Boulder, Colorado, USA.

Lovely, D.R. and Woodward, 1992. Consumption of Freons CFC-11 and CFC-12 by Anaerobic sediments and Soils. *Environmental Science and Technology.* **26(5),** 925-929.

Lovelock, J. E., Maggs. R. J. and Wade, R. J., 1973. Halogenated hydrocarbons in and over the Atlantic. *Nature.* **241**, 194-196.

Lovelock, J.E., 1975. Natural halocarbons in the air and in the sea. *Nature.* **256**, 193-194.

Lovelock, J.E. and Watson, A.J., 1978. Electron capture detector. Theory and practice II. *Journal of Chromatography.* **158**, 123.

Mabey, W and Mill, T., 1978. Critical review of Hydrolysis of Organic Compounds in Water Under Environmental Conditions. *Journal of Physical and Chemical Reference Data.* **7(2),** 383-415.

Mackas, D.L., Denmen, L.K. and Bennett, A.F., 1987. Least Squares Multiple Tracer Analysis of Water Mass Composition. *Journal of Geophysical Research*, **92, C3**, pp 2907-2918.

Malmberg, S.-A., 1972. Intermadiate Polar Water in Denmark Strait-Overflow August 1971. **ICES**, CM 1972/C:6.

Manley, S.L., Goodwin, K. and North, W.J., 1992. Laboratory production of bromoform, methylene bromide, and methyl iodide by macroalgae and distribution in nearshore southern California waters. *Limnology and Oceanography.* **37(8),** 1652-1659.

Martens, H. and Naes, T., 1989. Multivariate Calibration. John Wiley & sons.

Martin, J.H., Coale, K.H., Johnson, K.S., Fitzwater, S.E., Gordon, R.M., Tanner, S.J., Hunter, C.N., Elrod, V.A., Nowicki, J.L., Coley, T.L., Barber, R.T., Lindley, S., Watson, A.J., Van Scoy, K., Lae, C.S., Liddicoat, M.I., Ling, R., Stanton, T., Stockel, J., Collins, C., Anderson, A., Bidigare, R., Ondrusek, M., Latase, M., Millero, F.J., Lee, K., Yao, W., Zhang, Z., Friedrich, G., Sakamoto, C., Chavez, F., Buck, K., kolber, Z., Greene, R., Falkowski, P., Chisholm, S.W., Hoge, F., Swift, R., Yungel, J., Turner, S., Nightingale, P., Hatton, A., Liss, P. and Tindale, N.W., 1994. Testing the iron hypothesis in ecosystems of the equatorial Pacific Ocean. *Nature*, **371**, 123-129.

Meridith, M.P., Van Scoy, K.A., Watson, A.J. and Locarnini, R.A., 1996. On the use of carbon tetrachloride as a transient tracer of Weddell Sea deep and bottom waters. *Geophysical Research Letters*, **23;21**, 2943-2946.

Moore, R.M. and Tokarczyk, R., 1992. Chloro-iodomethane in N. Atlantic Waters: A Potentially Significant Source of Atmospheric Iodine. *Geophysical research letters*, **19(17),** 1779-1782.

Moore, R.M. and Zafiriou, O.C., 1994. Photochemical production of methyl iodide in seawater. *Journal of Geophysical Research*. **99(D8)**, 16,415-16,420.

Moore, R.M., Tokarczyk, R., Tait, V.K., Poulin, M. and Geen, C., 1995. Marine phytoplankton as a natural source of volatile organohalogens. In*: Naturally Produced Organohalogens* (Eds. A. Grimvall and E.W.B. de Leer) Kluwer Academic Publishers, Dordrecht, The Nederlands, 283-295.

Nightingale, P.D., Malin, G. and Liss, P.S., 1995. Production of chloroform and other low molecular weight halocarbons by some species of macroalgae. *Limnology and Oceanography*, 40(4), 680-689.

O´Doherty, S.J., Simmonds, P.G., Nickless, G. and Betz, W.R., 1993 a. Evaluation of Carboxen carbon molecular sieves for trapping replacement chlorofluorocarbons. *Journal of Chromatography*. **360**, 265-274.

O´Doherty, S.J., Simmonds, P.G. and Nickless, G., 1993 b. Analysis of replacement chlorofluorocarbons using carboxen microtraps for isolation and preconcentration in gas chromatography-mass spectrometry. *Journal of Chromatography*, **A657**, 123-129.

Özsoy, E., Latif, M.A., Besiktepe. S. and Gains, A., 1995. Fluorescent dye measurements of the mixing and transport of wastewater discharge in the Bosphorus. *Water Science Technology*, **32**, 61-68.

Pankow, J.F., 1991. Technique for removing Water from Moist Headspace and Purge Gases Containing Volatile Organic Compounds. Applications in Purge and Trap with Whole-Column Cryotrapping. *Environmental Sciences Technology*, **25**, 123-126.

Pedersén, M., Collén, J., Abrahamsson, K. and Ekdahl, A., 1996. Production of halocarbons from seaweeds: an oxidative stress reaction? *Scientia Marina*, **60(supl. 1)**, 255-261.

Poole, C.F. and Scheutte, S.A., 1983. Isolation and Concentration Techniques for Capillary Column Gas Chromatographic Analysis. *Journal of High Resolution Chromatography*, **6**, 526-549.

Preisendorfer, R.W., 1988. Principal Component Analysis in Meteorology and Oceanography. In*: Developments in Atmospheric Sciences No. 17*,Ed.: C.D. Mobley, Elsevier.

Prather, M. and Spivaskovsky, C.M., 1990. Tropospheric OH and the lifetimes of hydrofluorocarbons. *Journal of Geophysical Research*, **95**, 18723-18729.

Prinn, R., Cunnold, D., Rasmussen, R., Simmonds, P., Alyea, F., Crawford, A., Fraser, P. and Rosen, R., 1987. Atmospheric trends in methylchloroform and the global average for the hydroxyl radical. *Science*. **238**, 945-950.

Prinn, R., Weiss, B.R., Miller, B.R., Huang, J., Alyea, F.N., Cunnold, D.M., Fraser, P.J., Hartley, D.E. and Simmonds, P.G., 1995. Atmospheric Trends and Lifetimes of $CH_3CCl_3$ and global OH Concentrations. *Sience*, **269**, 187-192.

Rhein, M., 1991. Ventilation rates of the Greenland and Norwegian Seas derived from distributions of the chlorofluoromethanes F11 and F12. *Deep-Sea Research*, **38(4),** 485-503.

Rhein, M., 1996. Convection in the Greenland sea, 1982-1993. *Journal of Geophysical Research,* **101, C8**, 18183-18192.

Schlosser, P., Bönisch, G., Rhein, M. and Bayer, R., 1991. Reduction of Deepwater Formation in the Greenland Sea During the 1980s: Evidence from Tracer Data. *Science*, **251**, 1054-1056.

Schlosser, P., Bönisch, G., Kromer, B., Loosli, H.H., Buhler, R., Bayer, R., Bonani, and Koltermann, K.P., 1995. Mid-1980s distributions of tritium, $^3$He, $^{14}$C, and $^{39}$Ar in the Greenland/Norwegian Seas and the Nansen Basin of the Arctic Ocean. *Prog. Oceanog.* **35**, 01-28.

Schwarzenbach, R.P., Giger, W., Schaffner, C. and Wanner, O., 1985. Groudwater Contamination by Volatile Halogenated Alkanes: Abiotic Formation of Volatile Sulfur Compounds under Anaerobic Conditions. *Environmental Science and Technology.* **19(4),** 322-327.

Scott, A. M., Vickers, A. K. and Decker, D., 1994. Trends in Purge and Trap. *Journal of Chromatographic science.* **32**, 328-338.

Simmonds, P.G., Cunnold, D.M., Alyea, F.N., Cardelino, C.A., Crawford, A.J., Prinn, R.G., Fraser, P.J., Rasmussen, R.A. and Rosen, R., 1988. Carbon tetrachloride lifetimes and emissions determined from daily global measurements during 1978-1985. *Journal of Atmospheric Chemistry*, **7**, 35-58.

Simmonds, P.G., O´Doherty, S., Nickless, G., Sturrock, G.A., Swaby, R., Knight, P., Ricketts, J., Woffedin, G. and Smith, R., 1995. Automated Gas Chromatograp/Mass Spectrometer for Routine Atmospheric Field Measurements of the CFC Replacement Compounds, the Hydrofluorocarbons and Hydrochlorfluorocarbons. *Analytical Chemistry*, **67**, 717-723.

Smethie, W.M., Östlund, H.G. and Loosli, H.H., 1986. Ventilation of deep Greenland and Norwegian Seas: evidence from krypton-85, tritium, carbon-14 argon-39. *Deep-Sea Research*, **33**, 675-703.

Smith, P.C., 1976. Baroclinic Instability in the Denmark strait Overflow. *Journal of Geophysical Research,* **O6**, 355-371.

Stephens, K., Sheldon, R.W. and Parsons, T.R., 1967. Seasonal variations in the aviability of food for the benthos in a coastal environment. *Ecology*, **48**, 852-855.

Sturges, W.T., Cota, G.F. and Buckley, P.T., 1992. Bromoform emission from Arctic ice algae. *Nature*. **358**, 660-662.

Sturges, W.T., Sullivan, C.W., Schnell, R.C., Heidt, L.E. and Pollock, W.H., 1993. Bromoalkane production by Antarctic ice algae. *Tellus*. **45B**, 120-126.

Sturrock, G.A., Simmonds, P.G. and Nickless, G., 1993. Analysis of chlorofluorocarbon replacement compounds by capillary gas chromatography. *Journal of chromatography*, **648,** 423-431.

Swift, J.H., AAgard, K. and Malmberg, S.V., 1980. The contribution of the Denmark Strait Overflow to the deep North Atlantic. *Deep-Sea Research*, **27A**, 29-42.

Swift, J.H., 1986. The Arctic waters. In *The Nordic Seas*, edited by B.G. Hurdle, 129-153, Springer-Verlag, New York.

Thermodynamic Research Center, Thermodynamics Tables, Non-hydrocarbons, Texas A&M University, College Station, Texas, USA.

Tokarczyk, R. and Moore, R.M., 1994. Production of volatile organohalogens by phytoplankton cultures. *Geophysical Research Letters*. **21(4),** 285-288.

Upstill-Goddard, R.C., Watson, A.J., Wood, J. and Liddicoat, M.I., 1991. Sulphur hexafluoride and helium-3 as sea-water tracers: deployment techniques and continuous underway analysis for sulphur hexafluoride. *Analytica Chemica Acta*, **249**, 555-562.

Vanema, A., 1990. The usefulness of the Headspace Analysis-Gas Chromatography Technique for the Investigation of Solid Samples. *Journal of High Resolution Chromatography*. **13**, 537-539.

Vogel, T.M., Criddle, C.S. and McCarty, P.L., 1987. Transformations of halogenated aliphatic compounds. *Environmental Science and Technology*. **21(8),** 722-736.

Voice, T.C. and Kolb, B., 1994. Comparison of European and American Techniques for the Analysis of Volatile Organic Compounds in Environmental Matrices. *Journal of Chromatographic Science*. **32**, 306-311.

WMO (World Meteorological Organization), 1989. Scientific assessment of stratospheric ozone: 1989, global ozone research and monitoring project. Report no. 20, WMO, Geneva.

Wallace, D.W.R. and Moore, R.M., 1985. Vertical profiles of CCl3F (F-11) and CCl2F2 (F-12) in the central arctic ocean basin. *Journal of Geophysical Research*. **90(C1),** 1155-1166.

Wallace, D.W.R and Lazier, J.R.N., 1988. Anthropogenic chlorofluoromethanes in newly formed Labrador Sea Water. *Nature*, **332**, 61-63.

Wallace, D.W.R., Beining, P and Putzka, A., 1994. Carbon tetrachloride and chlorofluorocarbons in the South Atlantic Ocean, 19°S. *Journal of Geophysical Research*, **99(C4),** 7803-7819.

Wanninkhof. R., Ledwell, J.R. and Broecker, W.S., 1985. Gas-exchange-wind relationship with sulphur hexafluoride on a lake. *Science*, **227**, 1224-1226.

Wanninkhof, R., Ledwell, J.R. and Watson, A.J., 1991. Analysis of Sulphur Hexafluoride in Seawater. *Journal of Geophysical Research*, **96 C5**, 8733-8470.

Wanninkhof, R., 1992. Relationship Between Wind Speed and Gas Exchange Over the Ocean. *Journal of Geophysical Research*, **97(C5),** 7373-7382.

Watson, A.J. and Liddicoat, M.I., 1985. Recent history of atmospheric trace gas concentrations deduced from measurements in the deep sea: application to sulphur hexafluoride and carbon tetrachloride. *Atmospheric Environment*, **19(9),** 1477-1484.

Watson, A.J. and Ledwell, J.R., 1988. Purposefully released tracers. *Phil. Trans. R. Soc. Lond.*, **A 325**, 189-200.

Watson, A.J., Uppstill-Goddard, R.C. and Liss, P.S., 1991. Air-Sea gas exchange in rough and stormy seas measured by a dual-tracer technique. *Nature*, **349**, 145-147.

Warner, M.J. and Weiss, R.F., 1985. Solubilities of chlorofluorocarbons 11 and 12 in water and seawater. *Deep-Sea Research*. **32(12),** 1485-1497.

Weiss, R.F., Bullister, J.L., Gammon, R.H. and Warner, M.J., 1985. Atmospheric chlorofluoromethanes in the deep equatorial Atlantic. *Nature*. **314,** 608-610.

Wine, P.H. and Chameides, W.L., 1989. Possible atmospheric lifetimes and chemical reaction mechanisms for selected HCFCs, HFCs, CH3CCl3, and their degradation products against dissolution and/or degradation in seawater and cloudwater. In*: Scientific Assessment of Stratosheric Ozone:* **2**, Word Meteorological Organization, 272-295.

Yao, W. and Millero, F., 1995. The Chemistry of the Anoxic Waters in the Framvaren Fjord, Norway. *Aquatic Geochemistry*, **1**: 53-88.

## Erratum.

CFC distributions shown in figures 3 and 4 in the paper Distribution of Water Masses on the Continental Shelf in the Southern Weddell Sea by Gammelsrød et al. are given in $\mu$mol.kg$^{-1}$. This is a missprint and should read pmol.kg$^{-1}$.

GÖTEBORGS UNIVERSITET