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A first study of SF_6 as a transient tracer in the Southern Ocean

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Abstract

Halogenated transient tracers such as the chlorofluorocarbons CFC-11, CFC-12 and CFC-113 are commonly used in oceanographic studies. These compounds enter the ocean via the atmosphere and their transient atmospheric concentrations make them valuable as oceanic tracers. The trends of rapidly rising atmospheric concentrations of these tracers are however broken, and the oceanic signal becomes increasingly more difficult to decipher. There is a need for a new transient tracer to complement the existing suit of tracers, especially for recently ventilated water masses. One compound that looks promising in this respect is sulphur hexafluoride (SF_6), an inert gas whose atmospheric concentration is rising rapidly. In this paper, the use of SF_6 as a transient tracer in recently ventilated waters is discussed and the method for determination of SF_6 in seawater is described. Tracer data from a section in the Atlantic sector of the Southern Ocean along 6°E, from 60°S to 40°S, occupied during January 1998, are presented. The Antarctic Polar Front, found close to 50°S, was studied with a densely sampled section down to 400 m depth and SF_6/CFC-12 ratios are used to deduce ventilation ages and dilution factors. A comparison of apparent ages derived from a variety of tracers is presented together with the uncertainties in these estimates. This work demonstrates that SF_6 is a useful and valuable transient tracer for waters ventilated during the last 20 years.

1. Introduction

A variety of transient tracers together with more traditional physical parameters such as salinity and temperature provide complementary understanding of the ocean system. These transient tracers include the extensively used chlorofluorocarbons (CFCs). These are anthropogenic compounds that enter the sea surface from the atmosphere via air–sea exchange. The studies of CFCs dissolved in the ocean have helped to elucidate movement and mixing of water masses. There are only insignificant natural sources of CFCs (Jordan et al., 2000) and their atmospheric concentrations have been increasing until the early 1990s. This transient signal gives the CFCs their value as tracers in the sea. The atmospheric

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concentrations of the CFCs are well known from experimental observations for the period after the late 1970s/early 1980s (Walker et al., 2000). The atmospheric CFC concentrations for the years before that have been estimated based on industrial productions and atmospheric lifetimes (Walker et al., 2000). The solubility data for the CFCs are known as functions of salinity and temperature (Bu and Warner, 1995; Bullister and Wisegarver, 1998; Warner and Weiss, 1985). It is hence possible to estimate the time elapsed since a water parcel was in contact with the atmosphere. The first CFCs used as marine tracers and also the most widely used are CFC-11 and CFC-12 (cf. Bullister and Weiss, 1983; Warner and Weiss, 1985; Weiss et al., 1985). The use of the tracer CFC-113 was applied in the late 1970s for use in more recently ventilated water masses (cf. Bu and Warner, 1995; Wisegarver and Gammon, 1988). In a similar way, carbon tetrachloride (CCl_4) has been used for age estimates of older water masses in high latitude regions since it has been released to the atmosphere since the first decade of the 20th century (cf. Bullister and Wisegarver, 1998; Krysell, 1992; Krysell and Wallace, 1988). The use of the CFC-11, CFC-12 and CFC-113, as well as CCl_4, and any ratio between them as transient tracers in the ocean has recently been hampered by the slow rise rate, or even decline, of their atmospheric concentrations that started in the early 1990s. The ratio CFC-11/CFC-12, however, has remained virtually constant from the middle of the 1970s to the late 1980s but may again be useful for water masses ventilated from the early 1990s and onwards, since the ratio is now decreasing, as demonstrated by Min (1999). There is a need for a 'new' transient tracer, whose source function is still increasing, to add to the measurements frequently performed today.

One new transient tracer is sulphur hexafluoride (SF_6), which is a non-reactive, stable gas whose atmospheric concentration is rapidly increasing. The most important commercial use of sulphur hexafluoride is as a gaseous electrical insulator and in the processing of aluminium and magnesium, processes from which the gas is subsequently released to the atmosphere. There is only one known natural source for SF_6 and since this is a weak source, there is an extremely low natural background concentration of the compound in the environment (Harnisch and Eisenhauer, 1998). In fact, the background signal in the ocean can be regarded as nil since it is well below the analytical detection limit of the current instrumentation. The atmospheric history of SF_6 from 1978 to present is reported by Maiss and Brenninkmeijer (1998) based on measurements of archived air samples from Cape Grim, Tasmania. They also report production estimates for SF_6 back to 1953, which makes it possible to reproduce the early atmospheric history of SF_6. The atmospheric concentration of SF_6 in the Southern Hemisphere was approximately 3.99 ppt in the beginning of 1998, and is currently rising at a rate of 7% per year (Maiss and Brenninkmeijer, 1998), see Fig. 1. The yearly emission of SF_6 to the atmosphere is decreasing at present, from a peak value of 6700 tons yr^{-1} in 1995 to 4900 tons yr^{-1} in 1998 (Maiss and Brenninkmeijer, 2000). The same authors estimate that the future emission of SF_6 to the atmosphere will be reduced to about 750 tons yr^{-1}. Considering the long lifetime for SF_6 in the atmosphere (estimated to 3200 years), this future scenario means that SF_6 will continue to rise in the atmosphere by a modest 0.03 ppt yr^{-1} even after such a drastic reduction of the emission. Although such a small interannual gradient in the SF_6 concentration will make the direct use of SF_6 as a tracer difficult, the ratios of SF_6 to the CFCs

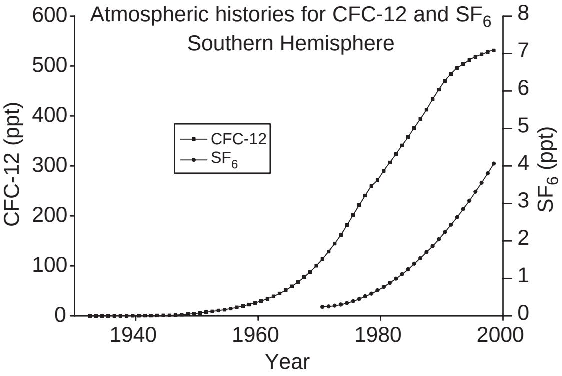


Fig. 1. Atmospheric concentrations for CFC-12 and SF_6 in the Southern Hemisphere, from Walker et al. (2000) and Maiss and Brenninkmeijer (1998), respectively.

will most likely continue to rise rapidly in the future, since the CFCs will be decreasing. Fig. 2 shows the evolution of the atmospheric ratio of SF_6/CFC-12 in the Southern Hemisphere. The solubility of SF_6 in seawater is discussed by Wanninkhof et al. (1991), and in recent work by Bullister et al. (2002), thus providing the source function for SF_6 in the ocean. Experiments further suggest that SF_6 does not adsorb onto particles and is inert in seawater (Ledwell and Watson, 1991). Sulphur hexafluoride thus fulfils many demands that are put on a transient marine tracer.

Since SF_6 has low atmospheric concentration and low solubility in seawater, its concentration in the ocean surface waters is typically less than 2 fmol kg^{-1} (2×10^{-15} mol kg^{-1}). However, due to high sensitivity for SF_6 by the electron capture detector (ECD), it is possible to measure even these minute quantities of the tracer in seawater. In spite of many favourable properties, few studies have so far been published where SF_6 is used as a transient tracer in oceanographic studies, an application suggested by Law et al. (1994). The first one is the recent work by Law and Watson (2001), where SF_6 is used in the Arabian Sea to study Persian Gulf Water inflow and associated oxygen utilisation. However, several vertical profiles of background SF_6 concentrations have been published in conjunction with different projects (cf. Law et al., 1994, 1998; Watson and Liddicoat, 1985).

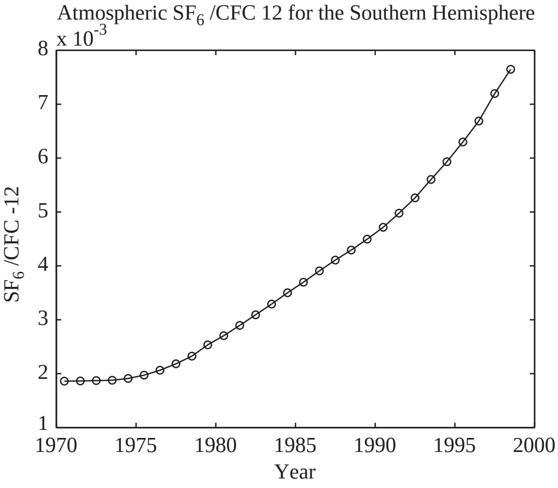


Fig. 2. Atmospheric concentration ratio between SF_6 and CFC-12 in the Southern Hemisphere.

Sulphur hexafluoride has been widely used as a deliberately released tracer in experiments such as the iron fertilisation experiment in the equatorial Pacific (Law et al., 1998) and the study of deep convection in the Greenland Sea (Watson et al., 1999). The use of SF_6 as a deliberately released tracer has somewhat hampered its use as a transient tracer in parts of the world oceans. Table 1 lists most deliberate SF_6 release experiments to date (see also Watson and Ledwell, 2000). Most of these are conducted in the surface region where the SF_6 will equilibrate with the atmosphere before being transported to the interior of the ocean and will therefore not affect the transient use of SF_6. Nevertheless, the potential of SF_6 as a transient tracer is great and its use as such will most likely increase in the future.

In this paper, we will present tracer data from a section in the Southern Ocean along 6°E from 60.5°S to 41.5°S. The SF_6 and CFC-12 data from the Antarctic Polar Front (APF) region are treated in detail.

2. Sampling and analysis

Water samples were taken at 38 stations on a section along 6°E from 60°30′S to 41°30′S in January and early February 1998 during the Swedish Antarctic Research Programme (SWEDARP) 1997/1998 expedition aboard the *S.A. Agulhas* (Turner et al., 2004). The section runs through several active frontal regions with areas of weaker stratification in between. In three areas, intense sampling down to 400 m depth was carried out: the Spring Ice Edge (SIE) the Winter Ice Edge (WIE) and the APF. See Fig. 3 for a map of the investigated area. Due to analytical difficulties the SIE section could not be completed with regard to SF_6. Water samples were collected with 8 L Niskin bottles on a rosette. The CFCs were normally the first sample to be drawn from the Niskin bottles followed by SF_6. However, no sample deeper than 3100 m could be obtained due to limitations of the ship's winch.

Table 1
Experiments where SF_6 has been used as a deliberately released tracer in the ocean

Experiment	Area	Amount released (kg)	Depth of release (m)	Reference
Mixing August/September 1985	Santa Monica Basin 34°N 119°W	0.2	790	Ledwell and Watson (1991)
Mixing May 1988	Santa Cruz Basin 34°N 119.5°W	1.45	1500	Ledwell and Bratkovich (1995)
CRP	North Sea		Surface	Watson et al. (1991)
March 1989	52.5°N 3.5°W	0.04		
October 1989		0.04		
Georges Bank Experiment	Georges Bank 41.5°N 68°W	8	20	Wanninkhof et al. (1993)
EPOCH	North Sea			Nightingale et al. (2000)
February 1992	52°N 4°E	0.045	30	
February 1993		0.034	20	
NATRE May 1992	Canary Basin 25°N 29°W	139	310	Ledwell et al. (1993)
IRONEX October 1993	Equatorial East Pacific 5°S 90°W	0.0511	Surface	Martin et al. (1994)
IRONEX II May 1995	Equatorial East Pacific 3.5°S 104°W	0.07	Surface	Cooper et al. (1996)
Mixing February 1996	Brazil Basin 22°S 18°W	110	4000	Polzin et al. (1997)
FSLE April 1996	West Florida Shelf 29°N 84°W		20	Wanninkhof et al. (1997)
PRIME June 1996	Northern North Atlantic 59°N 20°W	0.05	Surface	Law et al. (2001)
ESOP August 1996	Greenland Sea 75°N 2°W	320	300	Watson et al. (1999)
ASGAMAG October 1996	North Sea 52°N 4°E		Surface	
ACSOE/MAGE June 1998	Northern North Atlantic 59°N 21°W	0.05	Surface	
SOIREE February 1999	Southern Ocean 61°S 140°E	0.165	15	Boyd et al. (2000)
CARUSO/EISENEX 2000/2001	Southern Ocean			

The analytical system used for the analysis of SF_6 is based on vacuum sparge sample extraction followed by gas chromatographic separation and detection by ECD. The system is similar to a system described by Law et al. (1994). Water samples are introduced into the system by a vacuum created in the purge chamber. The sample inlet is placed into the water bottle, the purge chamber is isolated from the purge gas flow and a vacuum is created in the purge chamber. The low

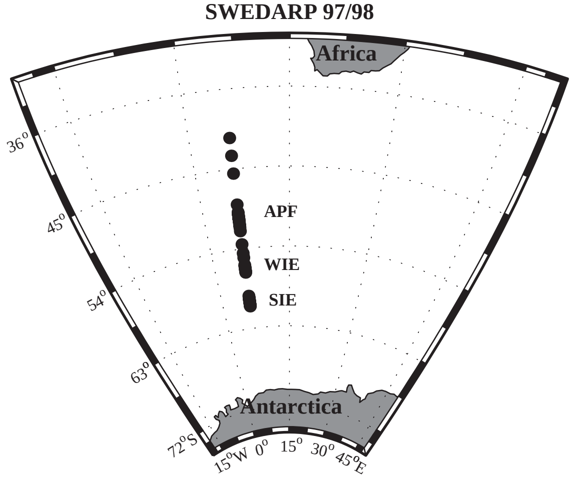


Fig. 3. A map of the station network for water samples obtained during the SWEDARP 1997/1998 campaign. The location of the SIE, the WIE and the APF is indicated in the figure. The cruise track is from south to north starting January 1 and ending February 2, 1998.

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. When the water has been introduced into the system, nitrogen purge gas enters the purge chamber through a stainless-steel frit in the lower part of the purge chamber. The water sample is purged for a total of 300 s and close to 100% of the SF_6 is transferred from the water sample onto the trap. For this study of SF_6 as a transient tracer approximately 350 ml of seawater was used for each analysis.

The high volatility of SF_6 makes it a difficult species to trap efficiently without applying very low temperatures to the trap. This can be overcome by the use of an efficient adsorbent. For this purpose eight different adsorbents were evaluated for their SF_6 retention at different temperatures. It was found that carboxen 1000 was the only one, of those tested by us, that could retain SF_6 at temperatures above $-30\,^{\circ}$C. Carboxen 1000 did in fact retain SF_6 at temperatures as high as $+5\,^{\circ}$C. Carboxen 1000 is a pyrolysed polymer with an active surface area of $1200\,\mathrm{m^2\,g^{-1}}$, and has been used for trapping the volatile CFC replacement compounds, hydrofluorocarbons and hydro-CFCs (O'Doherty et al., 1993a, b). For this work we used a 200 mm long 1/8″ OD (1.5 mm ID) stainless-steel tubing filled with Carboxen 1000 (45/60 mesh, Supelco). A vortex tube (ITW Vortec), (Bruno, 1993), in which compressed air is utilised for cooling, lowers the temperature of the trap to $-7\,^{\circ}$C during the purge phase. For desorption, the trap is rapidly heated to about 250 °C by dissipating a power of 300 W across the trap. During the desorption phase, carrier gas is routed through the trap and transports the contents of the trap to the separation column. This main column consists of a 3 m long 1/8″ stainless-steel tube packed with molecular sieve 5A (80/100 mesh, Supelco). A post-column with the same material as the main column but only 30 cm long is used as a pressure buffer after the main column. The main column is kept at ambient temperatures and the post-column is located in the gas chromatograph (GC) oven at 40 °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. High purity nitrogen gas is used as carrier gas at a flow of $35\,\mathrm{ml\,min^{-1}}$, and the separation takes about 2.5 min. A complete analytical cycle takes 12 min, allowing a sample throughput of 5 injections/h. Although the analysis time is twice that reported by Law et al. (1994), 6 min, no attempts were made here to reduce the analysis time since the throughput of CFC samples was the same, i.e. $5\,\mathrm{h^{-1}}$.

Standardisation is achieved by injection of various volumes of standard gas of concentration 48.8 ppt, either via the trap or directly onto the column, while the temperature and pressure of the sampling loop are logged. Two loops with nominal volumes of 250 and 1000 μl connected to a sampling valve facilitate the injection of different standard volumes. The response of the detector is linear for SF_6 in the low and relatively narrow concentration range encountered in seawater. Multiple injections of 1000 μl of standard gas were regularly performed to monitor the drift of the detector. The standard gas was produced by the dilution of pure SF_6 in N_2 and is calibrated against a standard gas prepared at Plymouth Marine Laboratory, England. This standard gas was in

Table 2
Performance of the analytical system during the expedition

Tracer	Analytical error	Limit of detection	Calibration error (%)	Saturation error (%)
CFC-12	0.7% or 0.005 pmol kg^{-1}	0.03 pmol kg^{-1}	1.5	5.5
CFC-11	1.9% or 0.006 pmol kg^{-1}	0.01 pmol kg^{-1}	0.6	4.9
CFC-113	3.6% or 0.027 pmol kg^{-1}	0.05 pmol kg^{-1}	2.0	11.3
CCl_4	2.6% or 0.006 pmol kg^{-1}	0.01 pmol kg^{-1}	0.5	5.6
SF_6	3.1% or 0.06 fmol kg^{-1}	0.05 fmol kg^{-1}	2.0	5.3

Note: The sample-to-sample precision is calculated as the standard deviation of 10 replicate measurements of the same water sample drawn from different Niskin bottles, or the system blank, whichever is the largest. The water samples were collected at 80 m depth at 60°S. The calibration error is the uncertainty in the calibration gas. The saturation error reflects the variability of surface water samples collected during the entire cruise; see text.

turn calibrated against the standards used by M. Maiss, Heidelberg, Germany. For precision of the measurements and for the limits of detection, see Table 2. The detection limit of SF_6 is slightly higher compared to some other studies (Law et al., 1994, 1998; Wanninkhof et al., 1991) that report limits of detection of 0.03 fmol kg^{-1} for similar sample volumes. It is also high compared to the present conditions of the instrument. The reason for this is a small background originating from the sampling procedure, which has been compensated for. As a result of this the precisions of the measurements were affected slightly. Measurements below 0.05 fmol kg^{-1} SF_6 were rejected and set to below detection limit. One should also observe that the instrument precision is based on samples taken from different Niskin bottles on the same depth when comparing them with values derived from samples taken from the same bottle.

The detection of SF_6 is achieved by a Varian 3400 CX GC equipped with an ECD kept at 350 °C. Varian's Personal Computer (PC) chromatographic software "Star" is used to integrate the SF_6 peak, to control chromatographic events and the temperatures in the GC oven and gas sampling loops, and to monitor the trap temperature. All timed events in the purge and trap system, such as actuating valves and solenoids, heating the trap and starting data acquisition are controlled by a PC-operated relay card. The system is thus fully automated and a single command on the PC starts the whole analytical process. For a more detailed description of the analytical system see Tanhua (1997).

In addition to SF_6, five other halogenated tracers were measured on a separate analytical system during the cruise. These tracers were CFC-11, CFC-12, CFC-113, methyl chloroform (CH_3CCl_3) and carbon tetrachloride (CCl_4). This system consists of a dual channel purge and trap unit connected to a GC (Varian 3400) equipped with two megabore columns (J&W, DB624, 75 m) and two ECDs kept at 350 °C. A volume of 30 ml of seawater is purged of its CFC content by a flow of N_2 gas (80 ml min^{-1}) for 10 min. The tracers were trapped in open capillary traps, kept near liquid nitrogen temperatures and desorbed from the trap by heating to 100 °C in boiling water. The gas chromatographic separation was performed isothermally at 70 °C with helium as carrier gas. The CFCs were standardised to the SIO93 scale by the injections of standard gas. Fogelqvist (1999) describes the analysis of CFCs in seawater in detail. For information on the analytical precisions and limits of detection obtained during the cruise, see Table 2.

3. Results and discussion

3.1. Apparent age/chlorofluorocarbon-ventilation age

The age of a water mass is considered to be the time elapsed since the water parcel was exposed to the atmosphere, where it can be modified by ocean/atmosphere transfer processes such as exchange of heat and dissolved gases and by biological processes in the surface layer. A water parcel that leaves the surface of the ocean will carry with it a signal that is dependent on the actual conditions at the time of exposure to the atmosphere. The length of time a water parcel is exposed to the atmosphere will affect the extent to which any transfer occurs, which in turn will affect to what degree the trace gases are saturated.

The process of obtaining the "true" age of a given water mass from its measured tracer concentration is not always straightforward. This is because a given parcel of water may actually be a mixture of fluids of differing origins, tracer concentrations and therefore ages. Since the relationship between tracer concentration and age is not a linear one, direct interpretation of the true water age from an average concentration will yield a biased true age estimate. For this reason the concept of "apparent age" is adopted. This is the age, which we obtain assuming that no mixing with other water masses has occurred. Mixing of two parcels of differing tracer concentrations and ages will lead to some weighted average tracer concentration that most likely will not represent the average age. In this paper, the apparent age concept is used, and any age referred to should be considered as an apparent age.

Provided that conditions such as temperature, salinity and saturation during formation of a water mass are known, certain calculations can be made. For instance, if a water mass is assumed not to have mixed with any other water mass, the concentration of a single CFC tracer can provide a good age estimate. This scenario is however seldom the case, and another commonly used approach is to use the ratio of two CFCs. This approach is not as sensitive to any unknown deviations from 100% saturation as is the single tracer approach. Provided that both CFCs are equally saturated, their ratio will be negligibly changed. If a recent water mass (and hence with high concentrations of CFCs) is mixed with a water mass with no or low CFC content, the CFC ratio will not change greatly and the age estimate will be heavily biased in favour for the younger component. The age derived from a single tracer will, in this example, not be biased in the same way. The mixing patterns in the ocean and the non-linear source function of the tracers are in most cases such that the age derived from tracer data is biased to yield younger ventilation ages than the "true" ventilation ages. Wallace et al. (1992) and Thiele and Sarmiento (1990) discuss some aspects of calculating apparent ages from tracer data in more detail.

Here we use the concept of equilibrium tracer mole fraction, P, to compensate for differences in solubility arising from variations in temperature and salinity. Although this effect is small in the confined APF region, there are considerable temperature gradients throughout the complete section. The value of P is calculated as follows (Doney and Bullister, 1992):

$$P = \frac{C_{\text{seawater}}}{F(\Theta, S)},$$

where C_{seawater} is the concentrations of the tracer in the water sample and $F(\Theta, S)$ is the solubility of the tracer as a function of potential temperature and salinity. For CFC-12 we have used the solubility function provided by Warner and Weiss (1985) and for SF_6 that of Bullister et al. (2002). The obtained P values are then matched to the Southern Hemisphere atmospheric history of the compound, which was obtained from Walker et al. (2000) for CFC-12 and from Maiss and Brenninkmeijer (1998) for SF_6 by ways of interpolation. We have assumed that the atmospheric pressure is 1 atm over the surveyed area. We have opted to use dry air mole fractions of the tracers rather than partial pressures. The main benefit of doing this is that the effect of water vapour of the moist air at the water-saturated interface is taken into account in the calculation of F, the solubility function, in the relationship discussed by Weiss and Price (1980) and Warner and Weiss (1985). The dry air mole fractions are further the unit in which the atmospheric histories of the CFCs and SF_6 are presented in Walker et al. (2000) and Maiss and Brenninkmeijer (1998). Thus by knowing the dry air mole fraction of a tracer in a water sample it is straightforward to asses an apparent age to this water sample, given the limitations discussed above.

The $P_{\text{CFC-12}}$ and P_{SF6} tracer ages derived by this method are plotted vs. each other in Fig. 4A. The

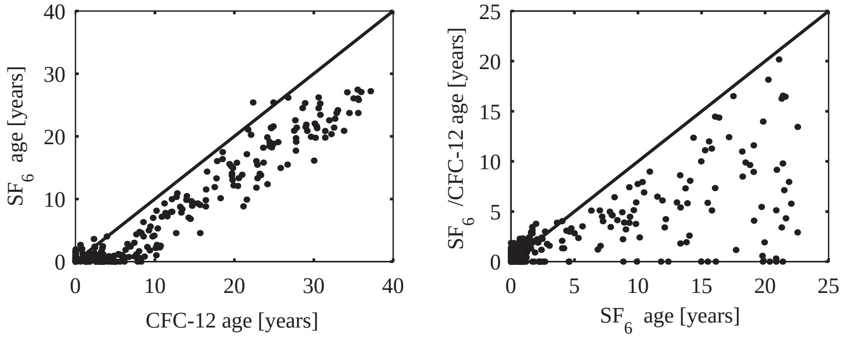


Fig. 4. Left panel shows apparent age estimates based on P_{SF6} plotted vs. estimates based on $P_{CFC\text{-}12}$. Right panel shows apparent ventilation ages derived from the ratio $P_{SF6}/P_{CFC\text{-}12}$ vs. the ages derived from P_{SF6} alone. All estimates are obtained making the assumption that no mixing has taken place. The deviation of the data points from the line of equal age indicates that in fact mixing did take place. Assuming mixing only between a water mass carrying the tracer signal and under-lying water with no tracer signal, it is possible to calculate a dilution factor for each water sample, see text. Data are corrected for the differences in saturation between the species.

solid line with slope 1 and intercept 0 is where one would expect all data points to be centred, in an ideal case where both mole fractions give the same apparent ages. It is however clear that there is a bias towards higher apparent age derived from CFC-12 compared to that derived from SF_6. Due to the different shape of the atmospheric input functions for CFC-12 and SF_6 (Fig. 1), the calculated tracer ages will differ if applied to a mixed water mass. For instance, imagine a water mass that contain equal amounts of water equilibrated at the surface each year between 1975 and 1998, i.e. 1/23 of that water mass was equilibrated in 1975 and so forth. Such a water mass would have a true mean age of 11.5 years, if sampled in 1998, and would have a $P_{CFC\text{-}12}$ age of approximately 11.9 years, whereas the P_{SF6} age would only be 10.2 years. The $P_{CFC\text{-}12}$ age is thus biased to give a higher ventilation age. This effect is due to the decline in the rate of atmospheric increase rate for CFC-12. This can partly explain the difference in apparent ages of the relatively recently ventilated water samples shown in Fig. 4A. It is also clear that since the rate of increase for CFC-12 in the atmosphere is low at present (Fig. 1), a slight deviation from equilibrium with the atmosphere results in a large difference in calculated apparent age. This is also reflected in the scatter of CFC-12 apparent ages in the surface layer. Based on the data collected during the cruise, 97% saturation for CFC-12 has been used for the apparent age calculation, whereas SF_6 was only saturated to 87%. There is a certain amount of scatter in the saturation data, which could be due to factors such as differences in ice cover and local weather. There seems to be a tendency for CFC-12 to be slightly under-saturated in the colder southern part of the section. The difference in saturation between the two species can partly be explained by the differences in the rate of increase of the atmospheric concentration for the two species and by the slightly higher piston velocity for CFC-12. Haine and Richards (1995) demonstrate that the rate of atmospheric increase as well as piston velocities influence the saturation in the mixed layer. The differences in saturation between CFC-12 and SF_6 are probably larger at present than it was prior to 1990 when the rates of increase of the atmospheric concentrations for the two species were similar. This could also explain some of the differences in the age estimates presented in Fig. 4A.

The other way to obtain apparent ventilation ages is to utilise the ratio between two tracers. We once again use $P_{CFC\text{-}12}$ and P_{SF6} since the $P_{SF6}/P_{CFC\text{-}12}$ atmospheric ratio has increased rapidly since the mid-1970s (Fig. 2). The ratio age at any date before that is uncertain due to the low concentrations of SF_6, and hence a larger uncertainty in the SF_6 analysis. The SF_6 atmospheric history as inferred from production estimates (Maiss and Brenninkmeijer, 1998) suggests that the $P_{SF6}/P_{CFC\text{-}12}$ ratio actually decreased rather than increased with time before the mid-1960s. Considering these two facts, we have opted to filter the data and to discard those ratios derived from P_{SF6} values lower than 0.40 ppt, which corresponds to the atmospheric concentration in the mid-1970s, assuming that the saturation level of SF_6 in the water is 87%.

The $P_{SF6}/P_{CFC\text{-}12}$ ratio for the water samples is calculated and fitted to the atmospheric SF_6/CFC-12 ratio to yield a ventilation age. The ventilation age obtained in this way is plotted vs. P_{SF6} age in Fig. 4B. It is obvious that the $P_{SF6}/P_{CFC\text{-}12}$ ratio age is biased to yield younger ages compared to the age obtained from P_{SF6}. This discrepancy can be attributed to the fact that, when a water mass with a certain tracer signature mixes with a water mass that is CFC-12 and SF_6 free, the $P_{SF6}/P_{CFC\text{-}12}$ ratio will remain constant, and so will the ratio age. The P_{SF6} age will however indicate a relatively older water mass, since the SF_6 concentration now is lower due to mixing with SF_6 free water. This difference in age estimates can be used to calculate a dilution factor as described by Weiss et al. (1985). Each water sample is assigned a ventilation age as calculated from the $P_{SF6}/P_{CFC\text{-}12}$ ratio age. The corresponding atmospheric SF_6 concentration for that time is determined from the known atmospheric history, which yields the expected seawater SF_6 concentration (P_{calc}), which is to be compared with the observed SF_6 concentration (P_{seawater}). Both factors are expressed as equilibrium tracer mole fraction, P. The dilution factor (ξ) is then calculated as follows:

$$\xi = \frac{P_{\text{seawater}}}{P_{\text{calc}}}.$$

In a case where the entrained water mass is free of CFC-12 and SF_6, the dilution factor will give us the fraction of water that originates from the upper well-ventilated mixed layer, and hence the fraction of deeper, older, water. The conditions for these assumptions to be valid are almost true in this section of the Southern Ocean, where the waters under the pycnocline are free of SF_6 and have only low concentrations of CFC-12. The dilution factor should at least give a rough estimate of mixing across the pycnocline.

3.2. *Estimates of uncertainties*

Uncertainties in apparent age (δT_v) estimates are due to a number of factors. Age estimates are determined from the equilibrium tracer mole fraction (P), and uncertainties in this value will propagate into the apparent age calculation. Uncertainties in the observed equilibrium mole fraction (δP_{obs}) come from analytical errors ($\delta P_{\text{analytical}}$) and calibration errors ($\delta P_{\text{calibration}}$). In addition to that one must account for uncertainties in assessing the correct degree of saturation of the tracer in the water mass at the time of formation ($\delta P_{\text{saturation}}$). The uncertainties in the analytical procedure were determined from 10 replicate measurements of water samples from the same depth drawn from different Niskin bottles, and are determined as one standard deviation or the system blank value, whichever is the greater. The analytical errors of SF_6 and CFC-12 are regarded as independent, since these measurements were performed on two different instruments and from two different water samples. The combined analytical error to be used for the ratio SF_6/CFC-12 is then the squared sum of the fractional errors for the two measurements. In the case when the ratio age between two of the CFC species is used, e.g. CFC-12/CFC-11 or CFC-113/CFC-12, the measurements cannot be regarded as independent of each other, since the measurements are conducted on the same water sample and on the same instrument. The analytical error for those ratios is then determined as the sum of the two individual analytical fractional errors. The uncertainty in the calibration standard is derived from the calibration of the standard gases.

Possibly the largest source of error that will affect the mole fraction calculation is uncertainties in the saturation of the tracers in the surface layer. The saturation might vary on yearly and seasonal basis, mainly dependent on the depth of the seasonal mixed layer (Haine and Richards, 1995). The uncertainty in the saturation ($\delta P_{\text{saturation}}$) of this data set is estimated as one standard deviation of the measured saturation in the top 20 m of the water column, compensated for the analytical error.

The uncertainty in assessing the observed equilibrium tracer mole fraction (δP_{obs}) is then calculated as the squared sum of the errors:

$$\delta P^2_{\text{obs}} = \delta P^2_{\text{analytical}} + \delta P^2_{\text{calibration}} + \delta P^2_{\text{saturation}}.$$

The values of the uncertainties are listed in Table 2. It is clear that uncertainty in the saturation is the dominating factor determining the total uncertainty (δP_{obs}). However, in the case when a ratio between two tracers is used to determine an age, the last term in the above equation will disappear, assuming that the saturation of the tracers are dependent and cancel each other. That is, a surface water with high saturation of CFC-11 will have a equally high saturation of CFC-12. This seems to be a valid assumption for the CFCs, based on this rather limited data set. It does not seem to be entirely justified for the SF_6 vs. the CFCs, see discussion above. The saturation uncertainties have been included in the calculation of the total uncertainty for the case of SF_6/CFC-12, but not for the case of CFC-113/CFC-12 or CFC-11/CFC-12.

How well a derived mole fraction value or ratio between two can be represented as an age is further dependent on uncertainty in the atmospheric mixing ratio over time ($\delta P_{\text{atmhist}}$). Walker et al. (2000) give the errors in the atmospheric history for the CFCs and Maiss and Brenninkmeijer (1998) for SF_6. The total uncertainty of the mole fraction calculation (δP) including comparison with historic data is then

$$\delta P^2 = \delta P^2_{\text{obs}} + \delta P^2_{\text{atmoshist}}.$$

These errors (δP) propagate into our calculation of the age by way of the time varying atmospheric source functions. The source function is usually used to express the saturation mole fraction (P) in terms of time of ventilation (T_{v}), $P = P(T_{\text{v}})$. However, we invert this relationship to calculate ventilation time from a saturation mole fraction, $T_{\text{v}} = T_{\text{v}}(P)$. Thus our uncertainty in calculated ventilation time (δT_{v}) may be expressed in terms of (δP) as follows:

$$\delta T_{\text{v}} = \frac{\mathrm{d}T_v}{\mathrm{d}P}\,\delta P.$$

We therefore see that even at times when our uncertainty in the equilibrium tracer mole fraction (δP) is small, we may have relatively large uncertainties in the age when the slope of the atmospheric source function ($\mathrm{d}P/\mathrm{d}T_{\text{v}}$) becomes small (or rather when $\mathrm{d}T_{\text{v}}/\mathrm{d}P$ becomes large).

The uncertainties in apparent age calculations for some commonly used tracers and ratios between tracers are demonstrated in Fig. 5. It is evident from the figure that each tracer or ratio has a time interval where they are useful, i.e. where $\mathrm{d}T_{\text{v}}/\mathrm{d}P$ is small and δP is small, and sometimes when they are less useful, i.e. either $\mathrm{d}T_{\text{v}}/\mathrm{d}P$ is large and/or δP is large. For instance, the CFC-11 is not a useful transient tracer for water equilibrated after 1990 due to ambiguity in the atmospheric source function, but is useful for about 40 years before that. Sulphur hexafluoride, on the other hand, is useful in recently ventilated waters, but does not have a very long atmospheric history and the analytical uncertainties become significant before 1980.

It is important to remember that the effect of mixing between water masses is not addressed in these estimates of apparent age uncertainties. It is clear that mixing will affect the age estimates, see discussion above, and also that different mixing

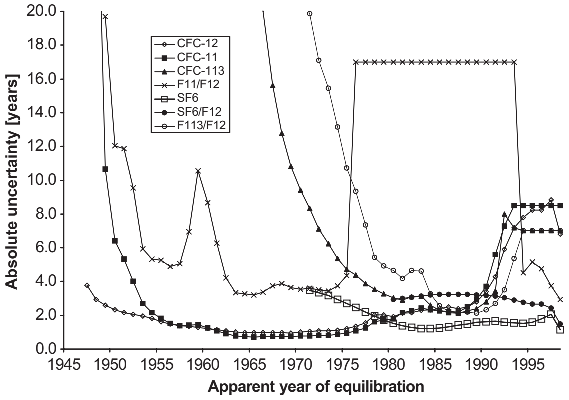


Fig. 5. Estimates of the uncertainty in age estimates using various tracers and ratios between them.

scenarios will have different impact on the age calculation depending on which tracer or ratio is used. In fact, it would be possible to find plausible mixing scenarios with the help of a suite of carefully measured tracers.

Age profiles, with error bars, for one deep station are illustrated in Fig. 6. The apparent ages are calculated using the tracers CFC-12, CFC-11, CFC-113 and SF_6, and also the ratios SF_6/CFC-12 and CFC-11/CFC-12, which are all commonly used except for the ones involving SF_6. The error bars are calculated as described above. Note that the error bars are not always symmetrical around the value. This is due to the non-linearity in the transient atmospheric signal of the tracers. The offset of the ages calculated from different tracers/ratios does primarily reflect the effect of mixing with surrounding water masses. It is evident from Figs. 5 and 6 that SF_6 and the ratio SF_6/CFC-12 are useful for recently ventilated waters when other tracer combinations fail to be very informative.

3.3. Tracer characteristics along 6°E

Along this section there is a sharp gradient in tracer concentration associated with the pycnocline (Fig. 7C). The depth of the mixed layer shoals to the south as the pycnocline becomes more pronounced. In the shallow mixed layer above the pycnocline, the tracers are more or less in equilibrium with the atmosphere. The tracer concentrations decrease rapidly with depth below the pycnocline. In the southern parts of the section, the ventilation age of the water column goes from essentially a few years old to about 40 years old within a 20–50 m depth interval. Further north, the gradient becomes less steep and some fine structure in the tracer concentration is visible within and above the pycnocline. A layer of Winter Water (WW) centred at about 100 m depth in the southern part of the section is recognised by a temperature minimum under the surface water (Fig. 7B). A salinity minimum is visible in the northern part of the section at about 500 m depth and deepens

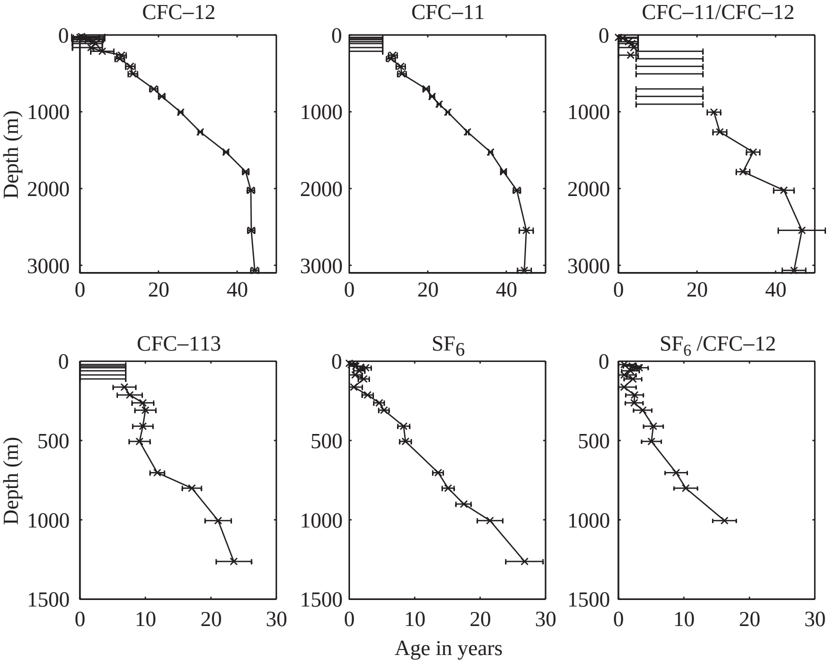


Fig. 6. Depth profiles of station 385 at 41.5°S, in where the apparent ages have been calculated using a variety of tracers/ratios of tracers. The differences in ages between the panels reflect the different responses to mixing for various tracers. Error bars are also given; see main text for details.

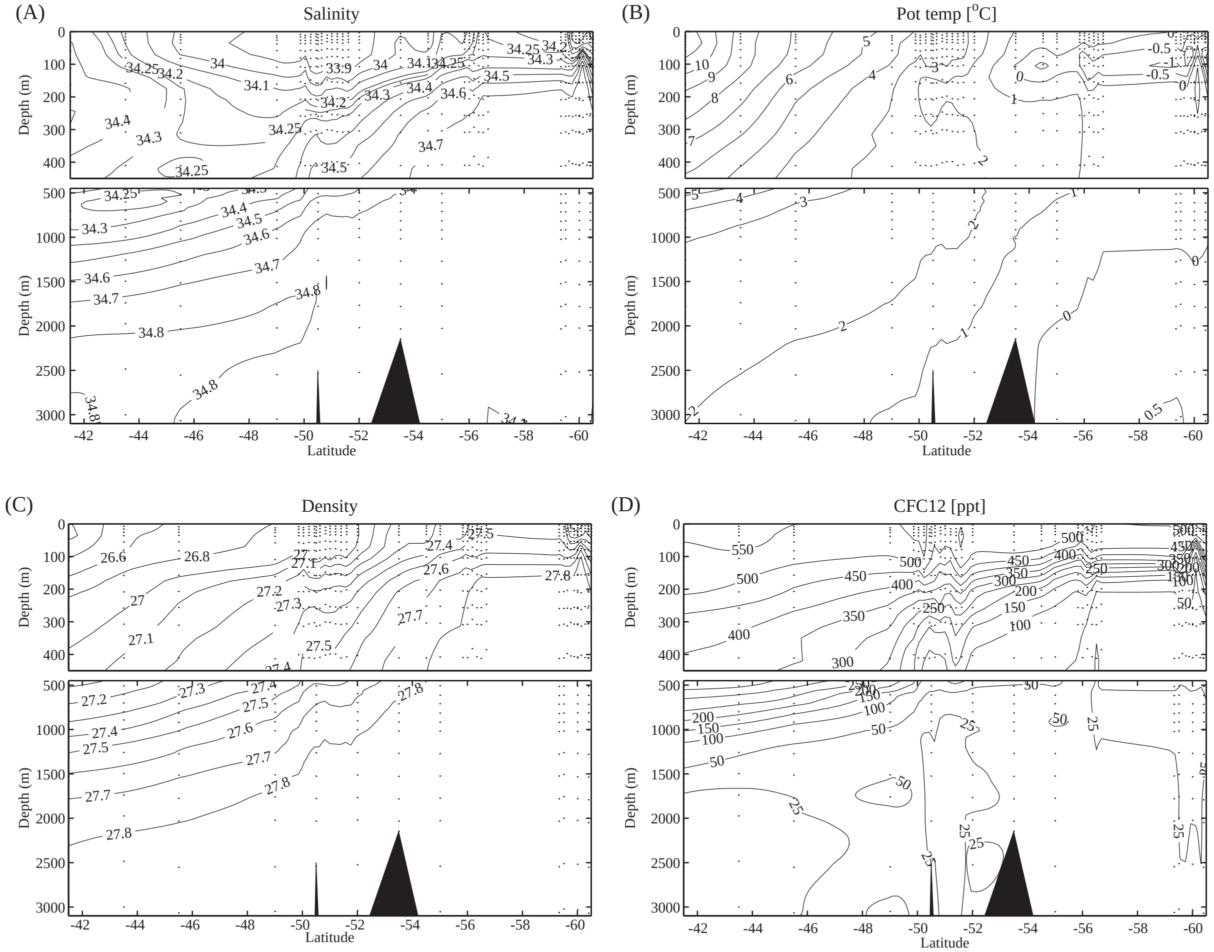


Fig. 7. (A) Salinity section along 6°E. The positions for the samples are indicated by dots and the isolines are obtained by objective interpolation with variable correlation length to account for the variable distance between stations. Note the salinity minimum in the surface region across the APF region (~50°N). Another salinity minimum at around 400 m depth north of the APF region indicates AAIW that descends to the north. (B) Temperature section, as Fig. 7a. Note the layer of cold WW at about 150 m depth in the southern part of the section. (C) Density section, as Fig. 7a. (D) CFC-12 section, as Fig. 7a. The concentration is given as equilibrium mole fraction. (E) SF_6 section, as Fig. 7a. The concentration is given as equilibrium mole fraction. (F) CFC-11 section, as Fig. 7a. The concentration is given as equilibrium mole fraction. (G) CFC-113 section, as Fig. 7a. The concentration is given as equilibrium mole fraction. (H) CCl_4 section, as Fig. 7a. The concentration is given as equilibrium mole fraction.

towards the north (Fig. 7A). This is the core of the Antarctic Intermediate Water (AAIW).

The deeper part of the section is dominated by Circumpolar Deep Water (CDW) and the tracer concentrations are more uniform within this water mass. Any penetration of SF_6 and CFC-113 through the pycnocline is prevented since the ventilation time of this deep water is longer than the atmospheric histories of the two compounds (Figs. 7E and G). CFC-11 and CFC-12, on the other hand, are present at all sampled depths (Figs. 7D and F). The apparent ventilation age of the CDW is roughly 40 years, based on average concentrations of CFC-12 and CFC-11 of 0.15 and 0.25 pmol kg^{-1}, respectively. There is a marked increase in tracer concentrations in the deepest parts of the southern portion of the section. This is probably due to mixing with newly formed

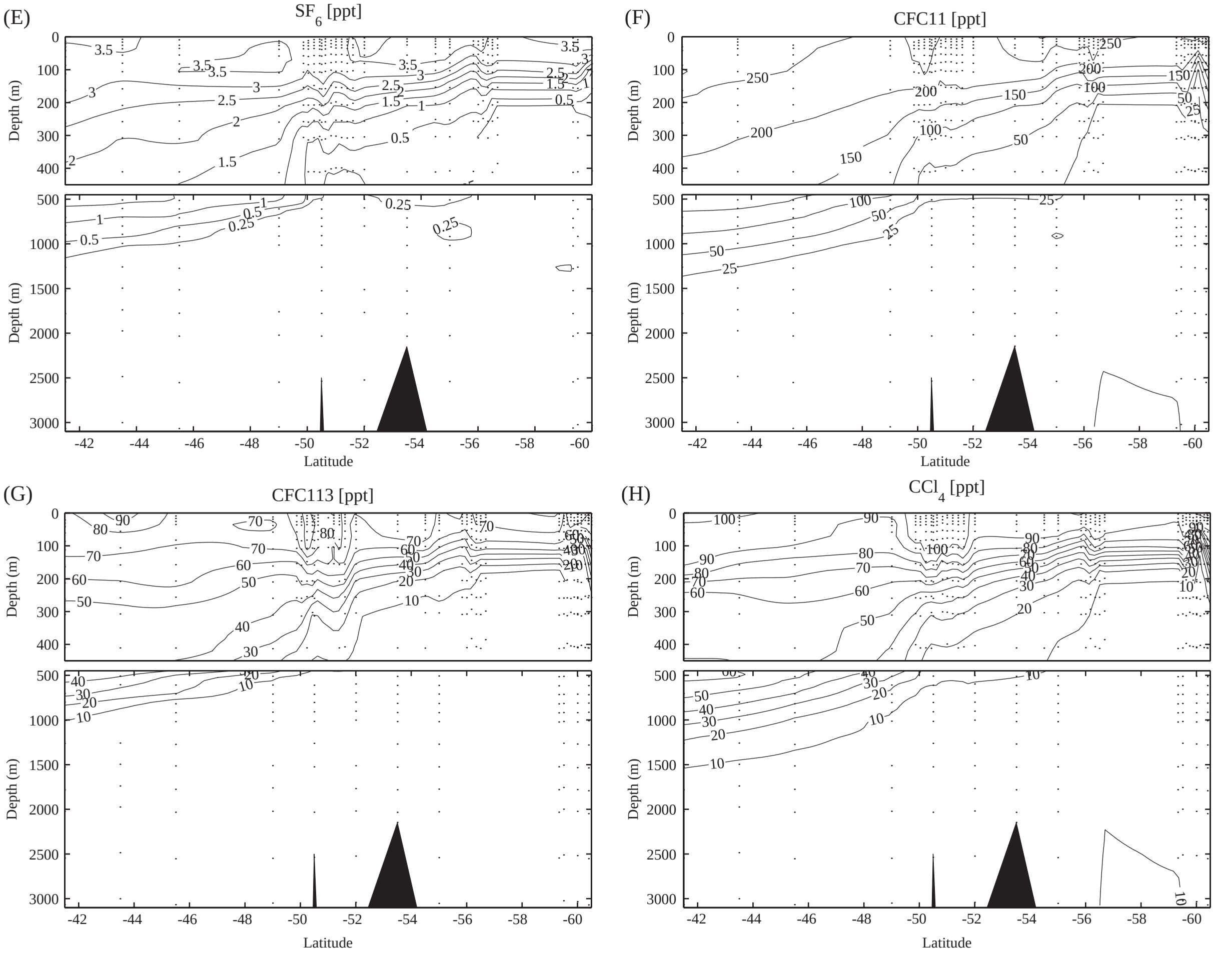


Fig. 7. (*Continued*)

Antarctic Bottom Water (AABW), but since no samples were obtained below 3000 m depth we were not able to capture the bulk of the AABW.

The CCl_4 concentrations (Fig. 7H) in the deep water (0.03–0.75 pmol kg^{-1}) do suggest a much higher apparent age than suggested by $P_{\text{CFC-12}}$ and $P_{\text{CFC-11}}$, and the ratio between them. This could be due to a non-conservative behaviour of CCl_4 or uncertainty in the source function for CCl_4. For instance, Tanhua et al. (1996) reported that CCl_4 seems to be removed in waters with oxygen concentrations of 200 µM or less, and proposed chemical reduction as a removal mechanism. Similarly, CCl_4 deficiencies were reported in the South Atlantic by Wallace et al. (1994), in the Baltic Sea by Krysell et al. (1994) and in the Weddell Sea by Meredith et al. (1996). The oxygen concentration in the deep water in this section is approximately 200 µM, suggesting a possible removal of CCl_4 in deep Antarctic Waters.

3.4. *Ventilation age at the Antarctic Polar Front*

The densely sampled section across the APF consists of 10 stations between 52°S and 50°S along 6°E and down to 400 m depth. The area is characterised by a salinity minimum in the surface and the temperature minimum of WW at about 200 m depth (Figs. 8C and D). This section further reveals an almost linear gradient in tracer

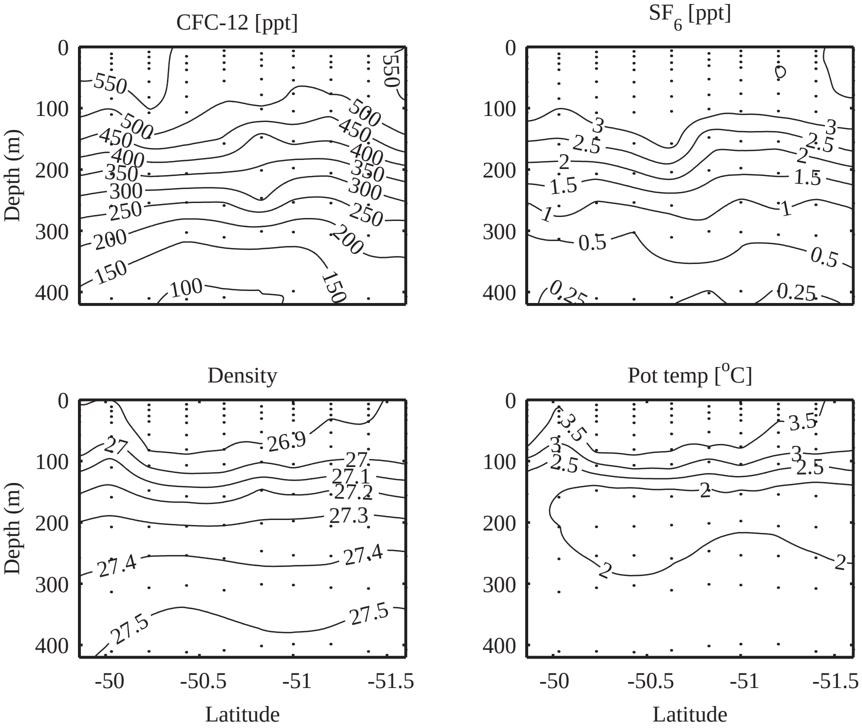
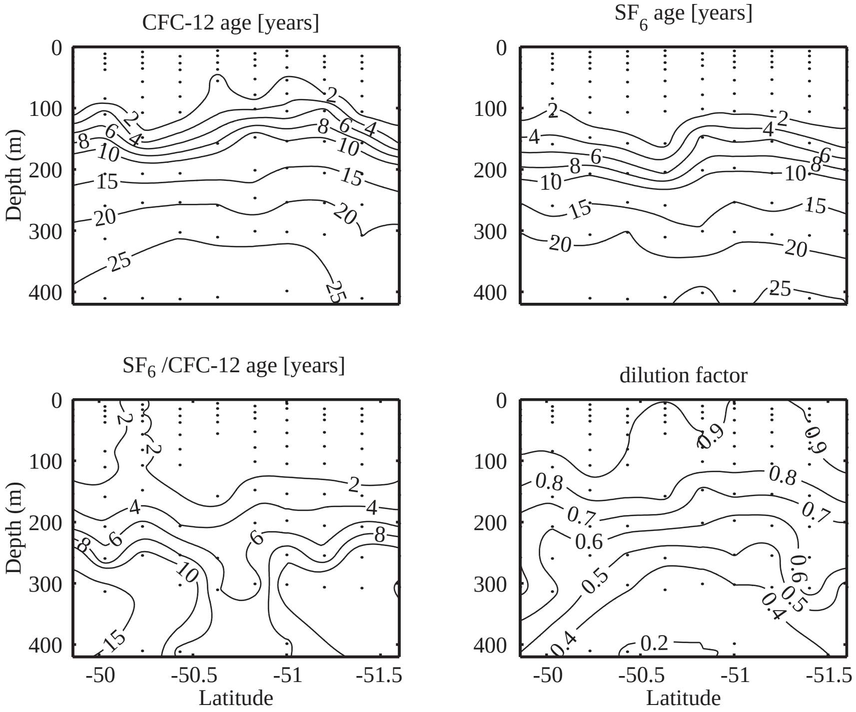


Fig. 8. Figure showing the intensely sampled APF region. The stations were occupied between January 24 and 27, 1998. The sampling points are indicated by dots. Panel a shows the CFC-12 concentration and panel b the SF_6 concentration. Note the difference in concentration range between the two species. Panels c and d display the density and temperature sections. Note the temperature minimum of WW that stretches into the section from the south at about 200 m depth.

concentrations with depth, except for the top 100 m of the water column. The CFC-12 equilibrium mole fraction ranges from saturated surface conditions to 80 ppt in the deep part of the section (Fig. 8A). The concentration of SF_6, on the other hand, ranges from under-saturated surface conditions, down to 0.16 ppt in the deep part of the section, which is at our limit of detection for SF_6 (Fig. 8B).

Apparent ventilation ages have been calculated based on the SF_6 and CFC-12 concentrations assuming no mixing with surrounding water masses (Figs. 9A and B). These calculations for CFC-12 indicate a ventilation age of the deep part of the section close to 30 years, assuming 97% saturation. The ventilation age derived from SF_6 for the same water points at slightly lower ages, about 25 years, assuming 87% saturation. The older range of this age estimate has a degree of uncertainty in it since the concentration is close to our detection limit for SF_6, and analytical errors may be of significant importance, see Fig. 5. The tendency for the $P_{SF6}/P_{CFC\text{-}12}$ ratio to yield younger ventilation ages as compared to the ages derived from P_{SF6} and $P_{CFC\text{-}12}$ is clearly shown in Fig. 9C. The ratio age for the deep water in the section barely reaches 15 years, as compared to 25 years based solely on P_{SF6} data. Based on the differences in ventilation ages between the ratio age and the P_{SF6} age we have calculated dilution factors as described above (Fig. 9D). It is interesting to note some features that are not so obvious in any of the other panels. Note especially the doming feature in the middle of the section where deep water wells up towards the surface.

It would be possible to calculate the dilution factor on this section using another tracer combination such as CFC-113 and CFC-12 in a similar manner as to the one described above. It is


CFC-12 age [years]

SF_6 age [years]

SF_6 /CFC-12 age [years]

dilution factor

Fig. 9. Section across the APF region, panels showing the apparent ages derived from P_{SF6}, $P_{CFC\text{-}12}$ and the ratio $P_{SF6}/P_{CFC\text{-}12}$. The age scale is in years and age 0 is set to January 1998. The dilution factor is the fraction of water from the surface mixed layer, assuming mixing solely between the surface mixed layer and water with low tracer content from below the pycnocline. Age estimates are corrected for the differences in saturation between the species.

however clear from the uncertainties presented in Fig. 5 that both CFC-113 and the ratio CFC-113/CFC-12 have a rather limited time period when their uncertainties are small. The use of the combination of SF_6 and CFC-12 is currently, and in the near future, the most viable tracer combination for waters with a short apparent age.

4. Summary

Sulphur hexafluoride is a promising new transient tracer for oceanographic studies to complement the established CFC tracers. Its inert properties in seawater and its rapidly growing atmospheric concentration make it a valuable tracer. One drawback of SF_6 is its low atmospheric concentration, which together with its low solubility in water makes the concentration in surface seawater about 3 orders of magnitude lower than that of CFC-11 and CFC-12. ECDs are however very sensitive to sulphur hexafluoride, which makes the analysis of "background" levels of SF_6 in seawater possible. The precision of this analysis is comparable to the analysis of the CFC tracers. The future use of SF_6 as a transient tracer is however hampered by its use as a purposefully released tracer.

It is demonstrated that while the traditional CFC tracers are ambiguous for any water mass ventilated during the last decade, SF_6 provides valuable information as a tracer. The combination of CFC-12 and SF_6 data yields information about mixing of surface water and deep water across the pycnocline in the APF region.

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