Chlorofluorocarbon distribution in the ross sea water masses

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CHLOROFLUOROCARBON DISTRIBUTION IN THE ROSS SEA WATER MASSES

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Chlorofluorocarbon (CFC11, CFC12 and CFC113) data, collected during the 2000–2001 austral summer, within the framework of the activities of the Climatic Long-Term Interactions for the Mass-Balance in Antarctica (CLIMA) Project of the Italian National Program for Antarctic Research (PNRA) in the Ross Sea, are discussed in the context of hydrographic observations. These data provide an overview of CFC distribution in some of the characteristic water masses found in the Ross Sea. The highest values of CFCs are found in the Antarctic Surface Water (AASW), because of the exchange with the atmosphere, while the lowest concentrations and the highest temperatures define the presence of Circumpolar Deep Water (CDW) in the cast of the analyzed samples. High Salinity Shelf Water (HSSW) can be identified by the highest salinity and by the relatively high content of CFCs. Moreover, the CFCs are useful tracers to study the mixing and overflow processes near the shelf break. In particular, chlorofluorocarbons trace the intrusion onto the shelf of Modified Circumpolar Deep Water (MCDW) off Cape Adare. The relative age of this water mass derived from CFCs ratios indicates that ventilation occurred between 1973 and 1979. The thermohaline structures and CFC distribution reveal at the shelf break the presence of HSSW already mixed with MCDW. Consequently, the density value of the bottom layer is not high enough to produce a strong overflow along the shelf break, causing a less intense ventilation of the deep oceans.

Keywords: Ross Sea; CFC; Ventilation time; Water masses; Shelf–slope interactions

1   INTRODUCTION

Measurement of anthropogenic trace substances has been established as a useful tool in oceanographic studies (Mensch *et al.*, 1998; England and Maier-Reimer, 2001). Tracer data supplement information provided by standard hydrographic parameters, such as temperature and salinity. Since the 1980s, anthropogenic chlorofluorocarbons CFC11 and CFC12, and more recently CFC113, have been used as chemical tracers of ocean circulation and mixing processes (Schlosser *et al.*, 1991).

CFCs are defined as 'transient tracers' because of their time-dependent nature. Production and release of CFCs started in the 1930s, and the atmospheric concentrations showed an exponential increase up to the 1980s. During the 1980s, they increased linearly, and a further

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significant reduction in growth rate has been observed since late 1989 (Mensch et al., 1998; Walker et al., 2000).

Atmospheric chlorofluorocarbons cross the air–sea interface and dissolve in surface seawater. At the equilibrium, the concentration of a dissolved CFC is a function of its concentration in the overlying atmosphere and of the salinity and temperature of the seawater (Bullister and Weiss, 1988). The equilibrium concentration of CFC11, CFC12 and CFC113 in the near-surface waters, as a function of time, can be reconstructed from atmospheric concentrations, taking into account modelled values of sea surface temperature and salinity (Schlosser et al., 1991; Mensch et al., 1996b; 1998). This is the so-called input function.

Figure 1 shows the input functions of CFC11, CFC12 and CFC113 for near surface water in equilibrium with the atmosphere in the Ross Sea derived from model calculation ($\theta = -1.8 \,^{\circ}C$ and $S = 34.40$). CFCs are not known to be influenced by biological processes and are very stable compounds (England and Maier-Reimer, 2001).

From the surface layer, the dissolved CFCs can be mixed downward in the water column. Chlorofluorocarbons are redistributed vertically by convection and subduction and then horizontally by interior ocean currents and mixing (England and Maier-Reimer, 2001). These processes modify the original atmospheric CFC imprint. The resulting distributions can be used to trace ocean mixing and circulation pathways and to evaluate the rates of these processes (Bullister and Weiss, 1988).

It is possible to follow the tracer signal in the water transported in regions far away from the water mass source area and to derive time information by comparing it with the original signal (Schlosser et al., 1991). Oceanographers refer to the 'age' of seawater as the time elapsed since a given water parcel was last exposed to the atmosphere (England, 1995). CFC content and CFC11:CFC12 or CFC11:CFC113 ratios enable a distinction between recently ventilated waters (high concentration) and old water (low concentration).

An understanding of the age of water and ventilation timescale is important for several reasons. For instance, ventilation timescales shed new light on the role of the oceans in modulating the climate change in the world's environment (England, 1995). Several studies on CFCs have been carried out to determine the processes and rates of deep-water ventilation and bottom-water formation in the Southern Ocean (Schlosser et al., 1991; Trumbore et al., 1991; Mensch et al., 1996a; 1998).

Shelf waters around Antarctica contain relatively high concentrations of dissolved CFCs. On the Antarctic slope, while shelf water (SW)s sink and mix with ambient waters to form new bottom waters, they inject CFCs into the oceanic bottom layers (Orsi et al., 1999). The Ross Sea is one of the major sites in forming Antarctic Bottom Water (AABW), defined by a neutral density $(\gamma^{n}) \geq 28.27 \,kg\,m^{-3}$, which plays an important role in ventilating the deep ocean.

High Salinity Shelf Waters (HSSW) and Ice Shelf Water (ISW) are two important constituents of AABW. HSSW is formed by brine release during sea-ice formation in the polynya around Terra Nova Bay, located near the western coast of the Ross Sea and in particular along the southern part of Victoria Land (Manzella et al., 1999). HSSW is the densest and most saline water mass of the entire Pacific sector of the Southern Ocean (S ranges from 34.75 to 35.00). One branch flows southward, under the Ross Ice Shelf (RIS) taking part in the production of Deep Ice Shelf Water (DISW) underneath the RIS (Jacobs et al., 1985).

DISW is one of the most important SWs, characterized by temperatures below freezing point at atmospheric pressure. It is found primarily on the central continental shelf from where it migrates northward to the shelf break to contribute to the formation of AABW (Jacobs et al., 1985; Bergamasco et al., 2004; Budillon et al., 2002; Rivaro et al., 2003; Rubino et al., 2003).

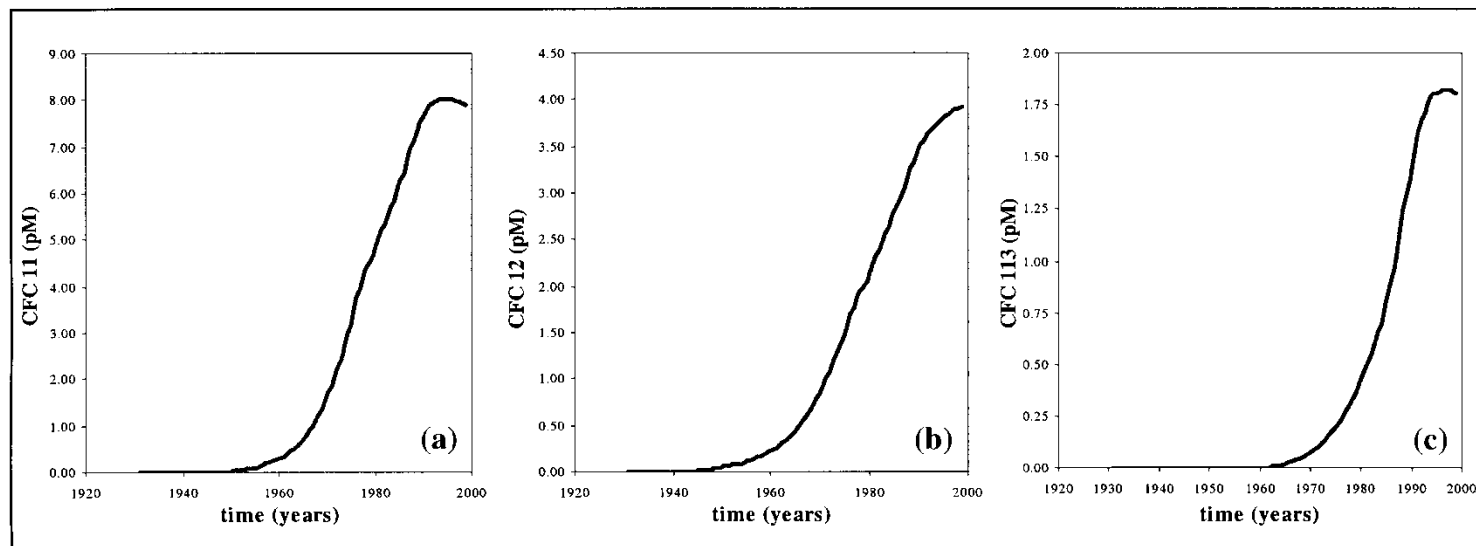FIGURE 1   Input functions of chlorofluorocarbons: (a) CFC11; (b) CFC12; (c) CFC13 for near surface waters of the Ross Sea ($\theta = -1.8\,^{\circ}$C, $S = 34.40$) in equilibrium with the atmosphere.

The other branch of the HSSW is known to move northward on the continental shelf to the shelf break (Budillon *et al.*, 1999; 2003). At the shelf slope, HSSW mixes with the entraining branches of CDW, the most voluminous water mass within the Antarctic Circumpolar Current.

A different water mass, the Modified Circumpolar Deep Water (MCDW), characterized by a subsurface maximum of potential temperature and a minimum of dissolved oxygen, originates from the mixing of the CDW with shelf and surface waters (Jacobs *et al.*, 1985; Budillon *et al.*, 1999; 2003).

The chlorofluorocarbon distribution found in some sectors of the Ross Sea is reported in this paper. The aim of measuring CFCs was to evaluate the timescales of ventilation and mixing processes involving various water masses in the shelf area and at the shelf break. The results are discussed in relation to hydrographic observations.

2   MATERIALS AND METHODS

2.1   Study Area and Sampling

Water samples were collected in the late summer 2000–2001 aboard the RV *Italica* cruise, in the framework of the CLIMA Project as part of the PNRA activities. Sampling involved a large-scale survey to monitor the general hydrological characteristics of the Ross Sea and a mesoscale survey at the shelf break near Cape Adare, to study both the interaction and the mixing between the SWs and the CDW. Out of 129 hydrological stations investigated, 50 were sampled for CFC analyses. Figure 2 shows the map of the area with the position of the casts.

Conductivity temperature depth (CTD) casts were performed using a Sea Bird Electronics SBE 9/11 probe with double temperature and conductivity sensors flushed at a constant rate. The CTD was coupled to a Carousel water sampler SBE 32. Temperature and conductivity sensors were calibrated at the SA-CLANT Centre of La Spezia (Italy) before and after the cruise. During the cruise, the CTD temperature was controlled by means of two SIS RTM4200 digital reversing platinum thermometers. At every station, two samples of water collected near the bottom layer, were analyzed on board using an Autosal Guildline Salinometer. Hydrological data were then corrected and processed according to international procedures (UNESCO, 1988). Standard algorithms (UNESCO, 1983) were used to compute derived quantities such as potential temperature, salinity and potential density anomaly.

Water samples for tracer analyses were collected from 12 l Niskin bottles, equipped with an epoxy-coated stainless steel spring, in 60 ml glass ampoules avoiding any contact with air. All ampoules were flame-sealed in an ultra-pure N_2 atmosphere. The flame-sealed ampoules were stored in dark, cold conditions ($+4\,^{\circ}C$).

2.2   Analytical Procedures

Samples were analyzed at Lamont-Doherty Earth Observatory, Columbia University (Palisades, NY), according to the methods described by Bullister and Weiss (1988) and Smethie *et al.* (1988). The CFCs were analyzed with a specific purge and trap gas chromatographic system with a ^{63}Ni electron capture as detector. A 5090 Hewlett Packard GC was used with a precolumn of Porasil C and an analytical column packed with Carbograph 1 (60–80 mesh) phase, 183 cm in length.

Calibration was done using synthetic air, prepared from ultra-pure O_2 and N_2, containing known amounts of CFC11, CFC12 and CFC113. Hence, an accurate concentration of these compounds was obtained (Bullister and Weiss, 1988). By this standard, all reported concentrations relate to the SIO 1999 scale (Walker *et al.*, 2000).
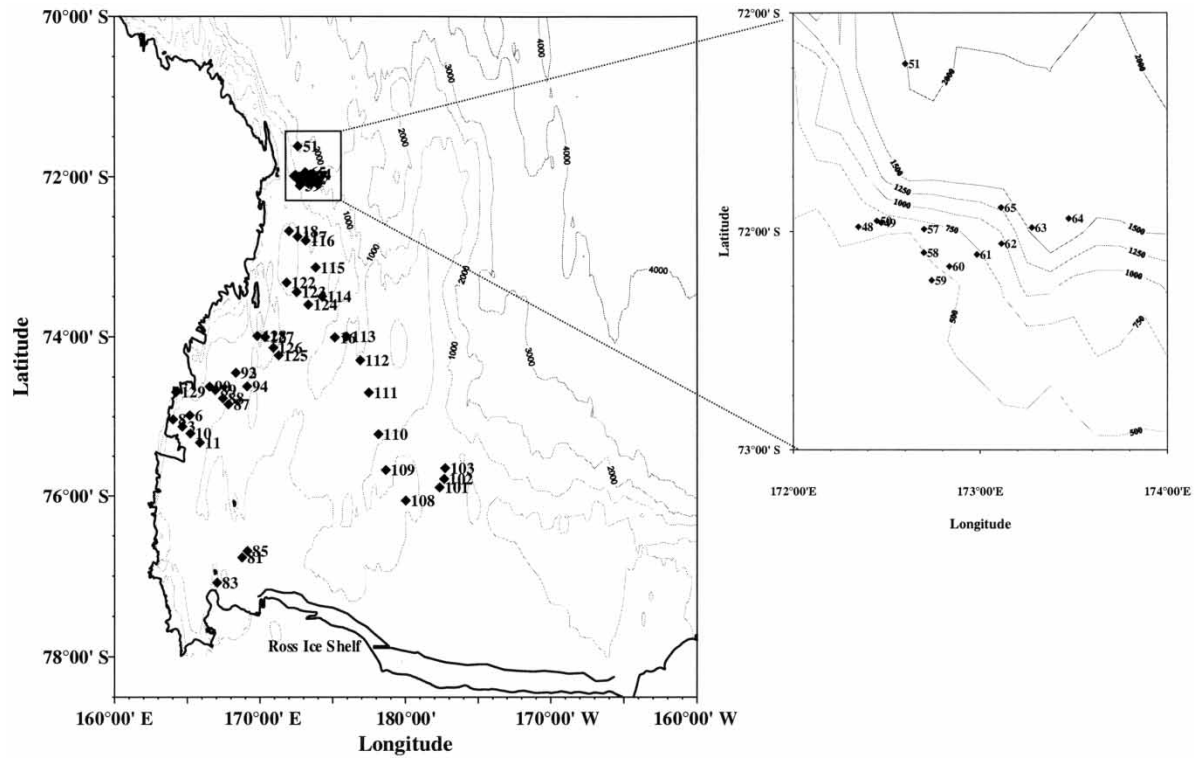
FIGURE 2   Bathymetry of the Northwestern Ross Sea with station locations from the 2000–2001 summer CLIMA cruise.

The standard deviation of the method was $\pm 0.01\,\mathrm{pmol\,kg^{-1}}$, and the detection limit was also $0.01\,\mathrm{pmol\,kg^{-1}}$ for all three CFCs. The CFC concentrations in a water sample (CFC_{seawater}) can also be expressed in terms of the solubility function, F, with the relation (Weiss and Price, 1980):

$$CFC_{\mathrm{seawater}} = P_{CFC} \times F,$$

where P_{CFC} is the equilibrium partial pressure, and F is the CFC solubility function, derived by Warner and Weiss (1985) from the following polynomial form:

$$\ln F = a_1 + a_2(100/T) + a_3 \ln(T/100) + a_4 \ln(T/100)^2$$
$$+ S[b_1 + b_2(T/100) + b_3(T/100)^2],$$

where T is the potential temperature (K), S is the salinity, and a_1, a_2, a_3, a_4, b_1, b_2 and b_3 are constants.

CFC-based age estimates of the water masses can be derived utilizing the increase with time in the atmospheric CFC partial pressures or the ratio of two CFCs (*i.e.* CFC11/CFC12, CFC113/CFC11, CFC12/CFC113). Since the rates of increase in CFCs in the atmosphere have been different, the ratio of two CFCs has changed with time, and sometimes it can be used to determine the age of a water mass (Trumbore *et al.*, 1991). In both cases, the age estimates are computed by matching seawater values with the corresponding point in the atmospheric time history, assuming solubility equilibrium in the surface waters (Doney *et al.*, 1997).

3   RESULTS AND DISCUSSION

Figure 3a and b illustrate the correlation between CFC11 and potential temperature. In particular, Figure 3a shows the distribution of all analyzed samples, while Figure 3b refers to samples collected at intermediate and bottom depths only.

The highest values of CFC11 reported in Figure 3a are related to AASW, varying between 6 and 7 $\mathrm{pmol\,kg^{-1}}$. According to Jacobs (1985), AASW corresponds to the mixed layer, characterized during summer by a high variability in terms of temperature and salinity, because of solar heating and ice-melting processes. CFC11 data fluctuations in this water mass might be caused by short-term variability of the surface layer dynamics. In fact, the adsorption of CFCs from the atmosphere can be controlled by the sea-ice cover, which has a strong impact on the ocean–atmosphere interaction (Budillon *et al.*, 2000). CFC11 saturation percentage (*i.e.* the degree of solubility with the atmosphere) of the surface samples ranges between 72 and 95% because of these physical processes, particularly the ice coverage rate.

The linear correlation between CFC11 and temperature is very well defined ($R^2 = 0.95$) for intermediate and deep layers, as can be seen in Figure 3b. This indicates that mixing processes are fast enough to prevent CFC gradients, proving that bottom layer renewal occurs over a short timescale, otherwise the transient nature of the tracer would produce a curved correlation. This linear correlation between CFC and potential temperature has already been observed by Trumbore *et al.* (1991). In particular, SWs can be identified by the lowest temperatures (from -1.9 to $-1.8\,^{\circ}\mathrm{C}$) and by the relatively high content of CFC11, around 5 $\mathrm{pmol\,kg^{-1}}$. This highlights how recently ventilated surface waters play a significant role in the formation of deep waters.
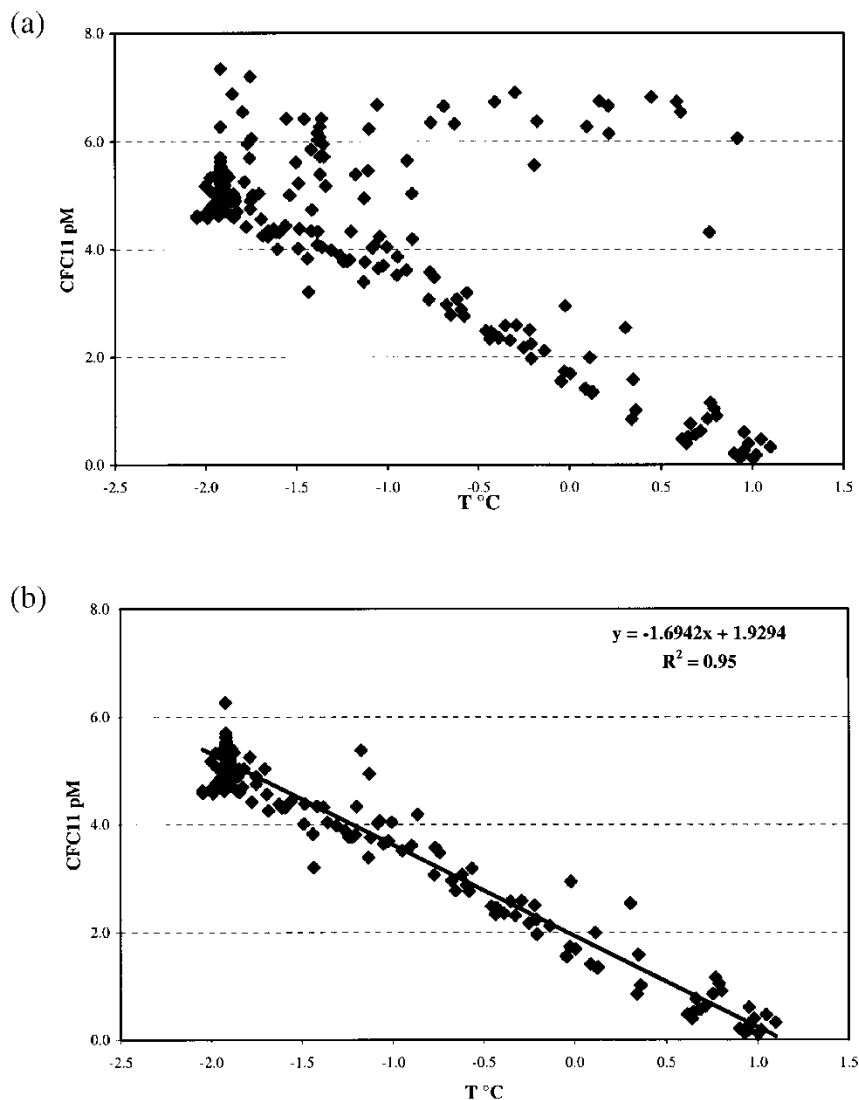
FIGURE 3   Relationship of CFC11 to potential temperature: (a) all analyzed samples; (b) intermediate- and bottom-depth samples.

The lowest CFC11 concentrations and the highest temperatures define the presence of MCDW in the cast of the analyzed samples (temperature $>0.5\,°C$ and CFC11 around $0.1\,pmol\,kg^{-1}$). These low CFC values reflect the long residence time of the MCDW.

In order to describe the vertical distribution of CFCs in relation to physical parameters, the profiles of temperature, salinity and CFC11 found in two stations are shown as an example. Table I reports hydrographic and tracer data of station 51 sampled off the shelf area, and of station 89 sampled in the Drygalski basin. Vertical profiles of temperature, salinity and CFC11 are illustrated in Figure 4a and b. Both stations report salinity increasing with depth, due to the melting processes that freshen the surface waters.

The mixed layer consists of the first 100 m in both stations. At the bottom depths in station 89, the salinity reaches the typical value of HSSW (34.84), proving that the Drygalski basin

TABLE I   Hydrographic data and CFC concentrations in stations 89 and 51.

Station	Latitude (°S)	Longitude (°E)	Depth (m)	Temperature (°C)	Salinity	CFC11 ($pM\,kg^{-1}$)	CFC12 ($pM\,kg^{-1}$)	CFC113 ($pM\,kg^{-1}$)
89	74.666	166.924	−2	−0.632	33.60	6.32	3.49	0.59
			−100	−1.884	34.71	5.07	2.65	0.44
			−200	−1.900	34.76	5.27	2.81	0.47
			−300	−1.906	34.80	5.32	2.85	0.49
			−400	−1.906	34.82	5.37	2.93	0.46
			−600	−1.916	34.83	5.29	2.90	0.47
			−800	−1.918	34.84	5.23	2.98	0.46
			−900	−1.918	34.84	5.47	3.16	0.49
			−990	−1.918	34.84	5.37	3.15	0.49
51	71.616	172.601	−2	−1.455	33.87	6.41	3.41	0.62
			−100	−1.124	34.44	3.76	2.01	0.36
			−300	0.659	34.67	0.76	0.35	0.07
			−500	1.020	34.71	0.18	0.07	0.01
			−600	1.003	34.72	0.11	0.06	0.01
			−900	0.753	34.71	0.85	0.51	0.07
			−1200	0.362	34.70	1.01	0.53	0.08
			−1500	−0.137	34.69	2.11	1.12	0.18
			−1580	−0.437	34.69	2.33	1.22	0.20
			−1644	−0.429	34.69	2.46	1.24	0.20

is one of the areas most involved in spreading this water mass. In station 51, the bottom layer's salinity value (34.69) indicates that mixing phenomena occurred between SWs and the intruding MCDW, modifying the original properties of the HSSW.

As regards temperature profiles, the water column in station 89 under the thermocline is isothermal, averaging −1.90 °C from 100 m down to the bottom. In station 51, the temperature profile shows the intrusion of MCDW, characterized by a temperature of more than 1.0 °C at about 500 m. At 1500 m, the temperature decreases below −0.4 °C, showing the presence of SWs mixed with the upper layer.

With regard to CFC distribution, the CFC11 profile is reported as an example of the common trend found for these tracers. As previously mentioned, the highest values of CFC11 are found in the surface layer (6.32 and 6.41 pmol kg^{-1}) because of the exchange with the atmosphere.

The surface water was 85 and 82% saturated for station 89 and 51, respectively, suggesting that the ice coverage, which was widespread during the austral summer of 2000–2001, limited the gas-exchange processes. As already observed by Trumbore *et al.* (1991), variations above and below the surface equilibration line are likely to be caused by local wind-induced vertical mixing, recent removal and melting of the sea ice cover and rapid surface heating.

As regards the distribution with depth, in station 89 values remain high along the entire water column, averaging around 5.30 pmol kg^{-1}. This feature proves that the intermediate and deeper layers have recently been ventilated, and it is consistent with the hypotheses that ventilation of these water masses is driven by intense ice formation, brine release and vertical convection in winter coastal polynyas, as previously observed by Jacobs (1985).

Otherwise, in station 51, the CFC11 concentration shows a higher variability; in fact, below the surface water, the CFC11 concentrations drop rapidly to values as low as 0.11–0.18 pmol kg^{-1} in the MCDW core. The presence of CFC11 at such a low in MCDW indicates that this water mass interacted with the atmosphere several decades ago, when atmospheric levels of CFC were very low. Below MCDW, the CFC11 concentration increases towards the bottom, where it reaches 2.46 pmol kg^{-1}, indicating that a high amount of recently ventilated water is present in the bottom waters.

(a)
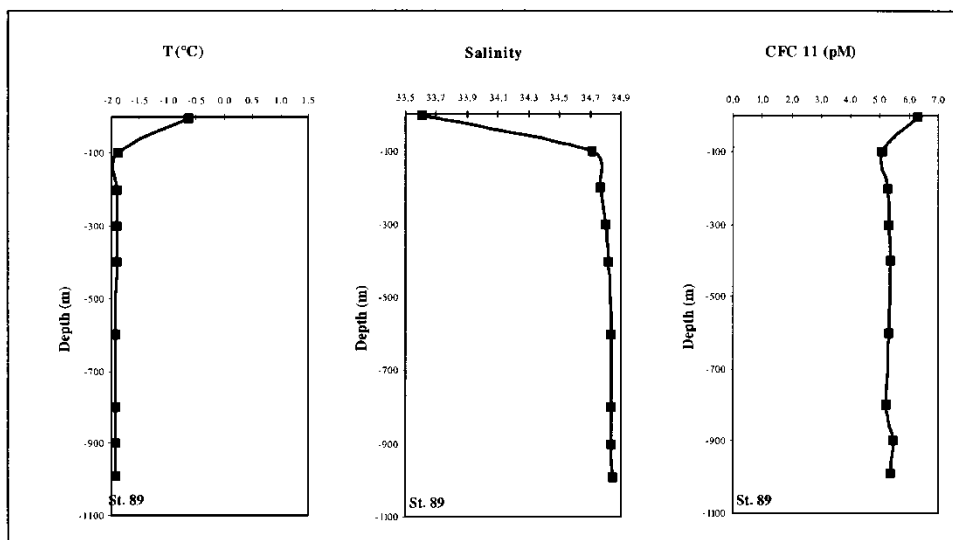
(b)

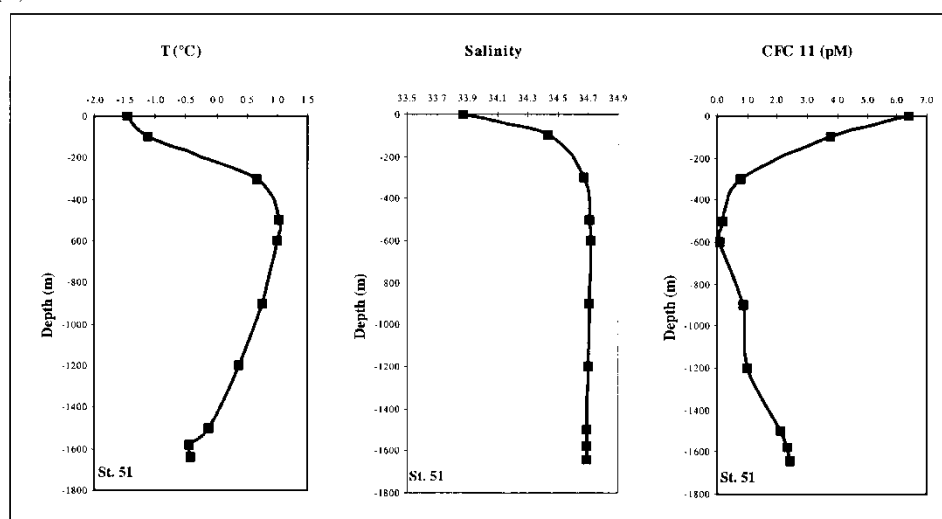FIGURE 4   Vertical distribution of temperature ($^{\circ}$C), salinity and CFC11 (pM kg^{-1}): (a) station 89; (b) station 51.

As previously mentioned, the relative age of the water mass can be derived from the CFC11:CFC12, CFC113:CFC11 or CFC113:CFC12 ratios. Values obtained for intermediate waters in station 51 indicate that this water was ventilated between 1973 and 1979. This confirms the observations already carried out on CDW by traditional chemical parameters such as dissolved oxygen, suggesting that this water mass has been segregated at mid-depths for a long time. CFC measurements provide further information regarding its age, *i.e.* the last contact that it had with the atmosphere. On the contrary, the bottom water's ratios indicate that their origin was more recent and that mixing processes occurred over short timescales.
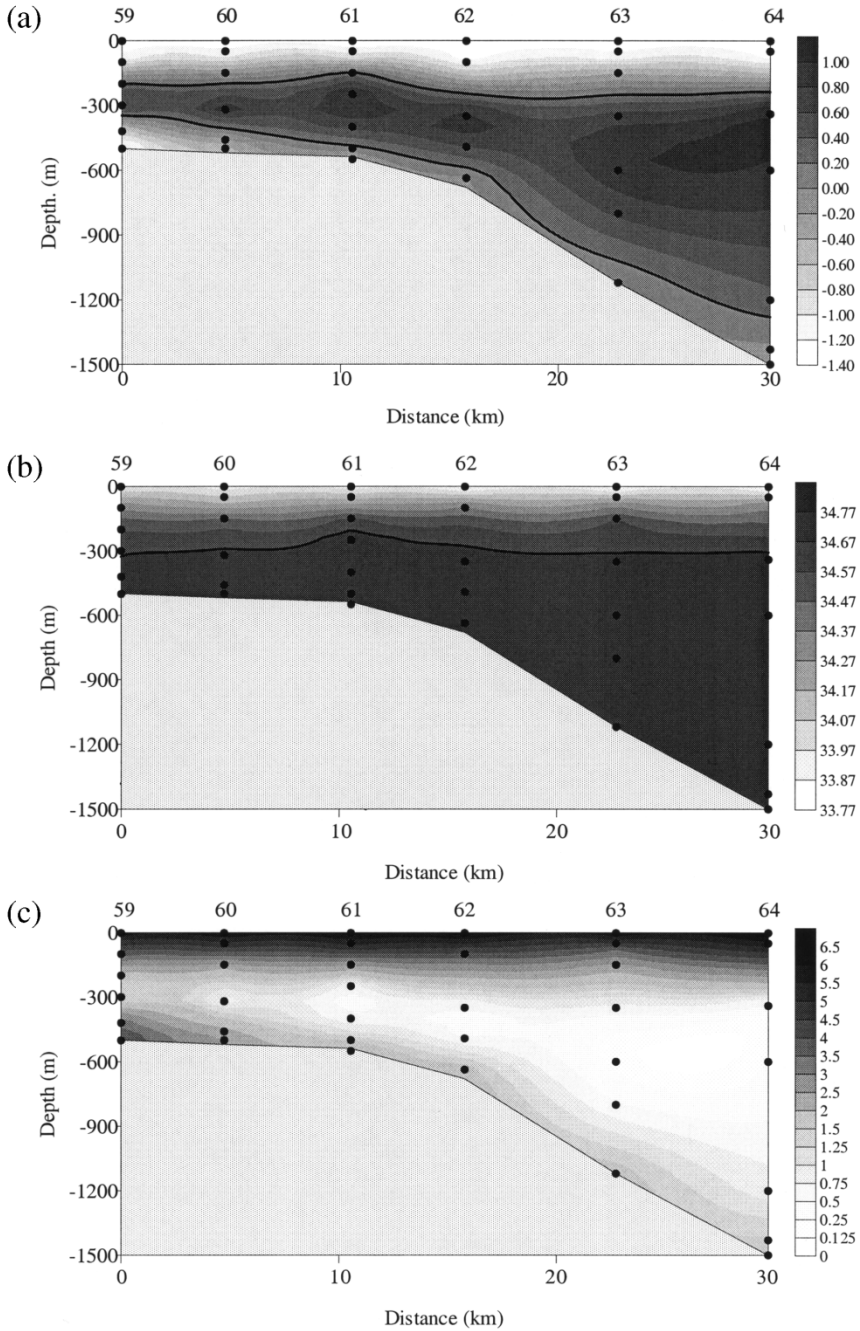
FIGURE 5   Vertical distribution in stations 59–64 of (a) temperature (°C), (b) salinity and (c) CFC11 (pM kg^{-1}).

The distribution of potential temperature, salinity and CFC11 along a section across the shelf break (stations 59–64) sampled during the Cape Adare mesoscale experiment is shown in Figure 5. Along the section in Figure 5, the warm core of CDW ($T > 1.0\,°C$) is well established off the continental slope between stations 63 and 64 (Fig. 5a). From this

core, a layer of relatively warm MCDW, outlined by the 0.2 °C isotherm, intrudes onto the shelf. A thin layer with SW of temperatures around −1.40 °C is present at stations 59–60 at about 500 m depth.

The salinity profile indicates a stratified water column with the highest values ($S > 34.70$) on the shelf at stations 59–61 (Fig. 5b). The thermohaline structures in this region reveal the presence of SWs already mixed with the ambient water (MCDW) making it difficult to identify the presence of a 'real' HSSW close to the bottom. Actually, in this region, a strong mixing between the CDW and SW occurred, considerably modifying the temperature/salinity characteristics of the latter; consequently, the density value of the bottom layer is not high enough to produce an overflow along the shelf break (Bergamasco et al., 2003).

The Antarctic Slope Front (ASF) is a common feature above the upper continental slope which separates the warm CDW from the cold SWs, and thus it is typically characterized by a sharp temperature increase. The ASF is also reflected by a well-known v-shape established in the salinity/density distribution near the shelf break (Jacobs, 1991).

Our results show the absence of the ASF in the investigated section, due to the weak difference between SW and CDW salinities. This is confirmed by the θ/S diagram in Figure 6, showing the presence of relatively fresher surface water from the ice melting, MCDW, and slightly saltier SW, but with salinity values comparable with those of the CDW.

Figure 5c shows the CFC11 distribution in the section. The minimum values from the continental slope at about 500 m depth are in good agreement with those reported for CDW. The CFC11 concentrations of CDW are as low as 0.3 pmol kg^{-1}.

The bottom layer on the continental shelf at stations 59–61 is enriched in CFC11 (range: 2.49–2.17 pmol kg^{-1}), reflecting the fact that it contains recently ventilated HSSW. The tracer signature of HSSW results in high CFC11 values, which were the highest found below the surface layer. This suggests recent deep vertical convection near the shelf break.

Within a few kilometers along the slope, the tracer signal decreases to 1.55 pmol kg^{-1} (station 64), confirming that the overflow of the SWs occurs on narrow scales. The plume of this water is strongly modified during its flow along the slope by the entrainment of MCDW. Depending on the volume of the HSSW, this layer may be completely eroded before
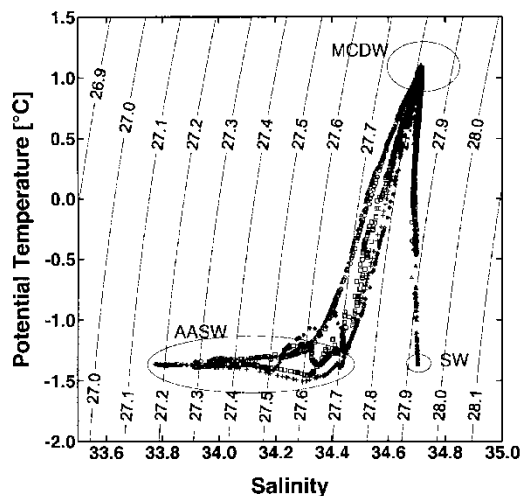

FIGURE 6 Potential temperature (°C) vs. salinity diagram for stations 59–64; AASW: Antarctic surface water; MCDW: modified circumpolar deep water; SW: shelf water.

it reaches the abyss, thereby having some influence on the production and ventilation of deep and bottom waters.

4   CONCLUSION

In this study, we analyzed chlorofluorocarbons and hydrographic data obtained in the Ross Sea, particularly in the region off Cape Adare. The results provided an overview of these tracer distributions in some of the characteristic water masses found during the 2000–2001 survey.

CFC was useful in studying the mixing processes and bottom water production near the shelf break off Cape Adare. This area is considered to be one of the sources of the Antarctic Bottom Water and is characterized by the presence of down slope phenomena of dense water originated by the mixing between HSSW and CDW. CFC as well as hydrographic parameters showed the intrusion of CDW onto the shelf and its mixing with shelf waters: this process modifies chemical and physical properties of the intruding water mass.

As regards the tracer signal, CFC concentrations measured in the CDW were the lowest ones. The relative age of this water mass derived from CFC ratios indicated that ventilation occurred between 1973 and 1979.

Concentrations of CFCs are higher near the bottom along the continental slope than in the water above. These tracer distribution patterns confirm that the bottom water originated near the surface. Nevertheless, the thermohaline structures found during the 2000–2001 meso-scale experiment in this region reveal the presence of shelf waters already mixed with MCDW, making it difficult to identify the presence of a 'real' HSSW close to the bottom near the shelf break. In fact, the typical HSSW salinity was found only in those stations sampled in the Drygalski basin near the Terra Nova Bay polynya area, where HSSW production occurs.

Chlorofluorocarbon measurements confirmed the small timescales in which HSSW was formed. Our evidence demonstrated that the signature of this water mass is weakened before it reaches the shelf break. Consequently, the density value of the bottom layer is not high enough to produce a strong overflow along the shelf break, causing a less intense ventilation of the deep oceans.

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