Direct measurement reveal insignificant storage of anthropogenetic CO2 in the abyssal Weddell Sea

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Direct measurements reveal insignificant storage of anthropogenic CO_2 in the abyssal Weddell Sea

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Abstract. In the northern Weddell Gyre at the prime meridian, Total TCO_2 changes in the Weddell Sea Bottom Water (WSBW) have been investigated. Following a suggestion by [*Poisson and Chen, 1987*], the TCO_2 difference at potential temperatures of 0.2°C and −0.8°C was determined using data from 1996 and 1998. No significant difference was found to similar differences for the years 1973 and 1981 reported by Poisson and Chen. Thus, over a period of 25 years an at most minor amount of anthropogenic CO_2 has penetrated into the WSBW at this location. This suggests that this abyssal subpolar region is relatively unimportant for the storage of anthropogenic CO_2. The same core of WSBW exhibited a marked increase of chlorofluorocarbon (CFC). For the Southern Ocean, therefore, CFCs are apparently of limited value as analogues of anthropogenic CO_2, in contrast to some other ocean provinces.

Introduction

Since the start of their release into the atmosphere in the first part of the 20th century, anthropogenically produced chlorofluorocarbons (CFCs) have invaded the oceans. There they have been widely used for studying ocean circulation and ventilaton. Being anthropogenic and readily detectable, CFCs are also considered useful near-analogues for anthropogenic CO_2 in the oceans [*Wallace*, 1995]. This is of interest since the latter is hard to determine as it constitutes a small contribution over a huge and variable background concentration of inorganic carbon. However, as CFCs and CO_2 are species with different physico-chemical behavior in the oceans with different input functions, it is recognized that the congruency will not be perfect. For the North Atlantic and Indian Oceans a great similarity of the distributions of anthropogenic CO_2 and CFCs has been reported [*Körtzinger et al.*, 1999; *Sabine et al.*, 1997]. As usually done in such studies, anthropogenic CO_2 is estimated using indirect back-calculating techniques [*e.g. Gruber et al.*, 1996] with inevitable inherent assumptions. Here we address the case of the Southern Ocean, by presenting repeated measurements of CFCs, combined with an estimate of anthropogenic CO_2 entirely on the basis of measured data covering 25 years, thus avoiding all uncertainties of back-calculation and modeling.

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Background and results

Fig. 1 illustrates the time-dependent invasion of CFC-11 (CCl_3F) into the northern Weddell Sea along the prime meridian. In this area, the water flow is eastward within the northern limb of the Weddell Gyre, the cyclone that dominates the circulation of the subpolar region of the Atlantic sector of the Southern Ocean. All three distributions reveal a CFC-11 maximum at the bottom, hugging the base of the North Weddell Ridge. This maximum is part of the Weddell Sea Bottom Water (WSBW), which ventilates the abyssal Weddell. WSBW is formed west of the section in the Weddell Sea proper, from relatively warm Circumpolar Deep Water (locally called Warm Deep Water, WDW) and a surface water component. Due to this component, the CFC-11 increase in the abyss reflects the CFC-11 content of the surface water, passing on the increasing atmospheric CFC-11 signal. Evidently, the CFC-11 concentration in the maximum core substantially increased from 1984 [*Weiss et al.*, 1990] via 1992 to 1998. The increase is highly significant, as the measurement accuracy is between 0.004 and 0.006 pmol kg^{-1} [*Weiss et al.*, 1990; *Bulsiewicz et al.*, 1998]. Also in the rest of the water column the CFC-11 concentrations have increased. The CFC-11 minimum zone in Fig. 1 characterizes the WDW. This water mass originates from the Antarctic Circumpolar Current and the actual source waters were still free of CFC-11 in Drake Passage in 1990 [*Roether et al.*, 1993]. Apparently the WDW picks up limited amounts of CFC-11 *en route*, so that the minimum concentrations also increase in time, but the levels generated are small.

Because of the substantial and increasing CFC-11 concentrations in the WSBW core, we anticipated that this core would carry a significant amount of anthropogenic CO_2. For estimating this contribution, we apply the method of *Poisson and Chen* [1987], i.e., we employ the difference between the TCO_2 concentrations of the WDW at 0.2°C and the WSBW at −0.8°C, and compare it with the corresponding differences in data up to 25 years earlier. The idea is that WDW should carry negligible anthropogenic CO_2 because this water mass is old, i.e., it has been formed when the anthropogenic CO_2 level in the atmosphere was still very low, while WSBW is recently ventilated so that addition of anthropogenic CO_2 is definite. It follows that anthropogenic CO_2 should be reflected in a TCO_2 increase in the WSBW as compared to the WDW. The point is that this approach avoids the usual standardization problems with pre-1990 data. Such data can be subject to considerable offsets, making comparison with other data a risky business, while our data collected in the 1990s have been standardized with the widely used certified reference material which guarantees cross-data set consistency. With the present method, in fact, only the precision of the data matters, which significantly enhances the reliability of data set comparisons.

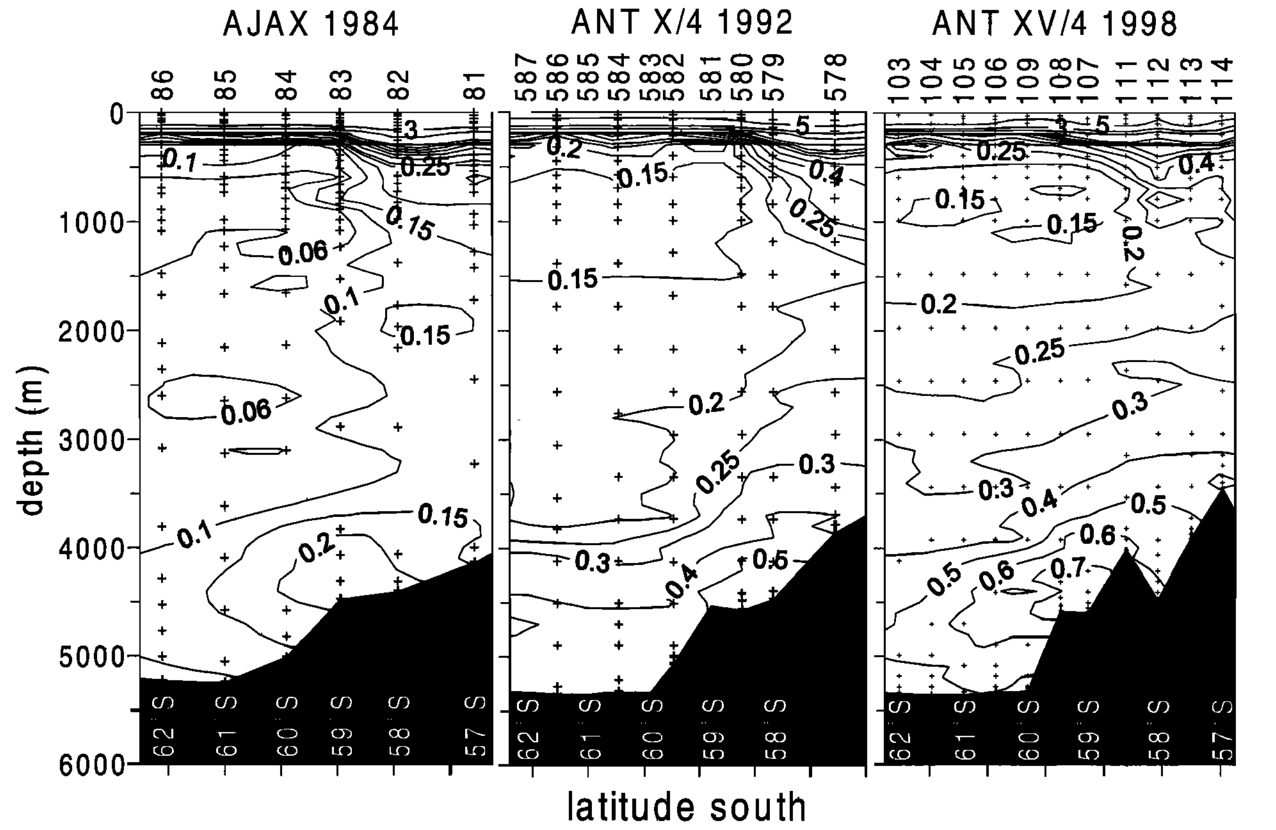

Figure 1. Three sections of CFC-11 (pmol kg^{-1}) covering a period of 14 years for the region between 57 and 62°S along the prime meridian in the northern Weddell Gyre. See also Klatt et al.

In Fig. 2 TCO_2 data from the area between 57°S and 62°S at the prime meridian is shown as a TCO_2 - potential temperature (θ) diagram for the year 1998. This area was chosen to correspond with that of the investigation by *Poisson and Chen* [1987]. Only deep water data ($\geq$ 500 m) from below the salinity maximum of the WDW are displayed; the upper boundary of the potential temperature was set at 0.4°C. Data with $\theta > 0.2$°C are part of the WDW. Water colder than −0.7°C is WSBW which is locally produced in the Weddell Sea. It has a low TCO_2 concentration because its surface water component is relatively low in TCO_2.

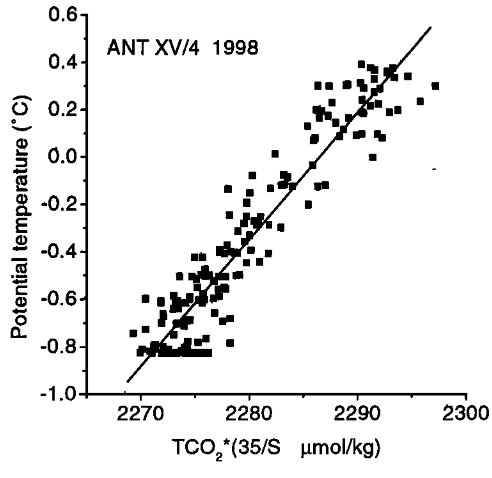

Figure 2. Relationship between potential temperature and normalized Total CO_2 for "Polarstern" cruise ANT XV/4 (1998) for the region 57-62°S on the prime meridian. Regression line is drawn through all data below the salinity maximum. Normalization to salinity 35 is done to account for TCO_2 changes due to salinity (water mass) changes. TCO_2 has been determined by the coulometry technique. Certified reference material supplied by Prof. Andrew Dickson (Scripps Institution of Oceanography) was used.

A regression line is drawn through the potential temperature - TCO_2 relationship (Fig. 2). The linear relationship is highly significant. However, a non-linear structure can be discerned in the lower temperature range (Fig. 2), which is expected [*Hoppema et al.*, 2001] and related to an additional source of ventilated deep water joining the northern limb of the Weddell Gyre from the Weddell-Scotia Confluence [*Orsi et al.*, 1999]. Accounting for this non-linearity, we calculated regression lines only for data with potential temperature higher than −0.5°C. With these regression data, the TCO_2 concentration at a potential temperature of 0.2°C was calculated (Table 1). For a potential temperature of −0.8°C we computed a mean of all data points with potential temperature between −0.83°C and −0.77°C (Table 1). For data from 1996 and 1998, the TCO_2 differences between those two temperatures are not significantly at variance (Table 1).

Discussion

Our TCO_2 differences between potential temperatures of 0.2 and −0.8°C for 1996 and 1998 are set against the older data of *Poisson and Chen* [1987] from the same region in the northern Weddell Sea (Table 1). For the 1973 GEOSECS data these authors report a TCO_2 difference between 0.2

Table 1. Normalized TCO_2 at two potential temperatures and their difference; the latter's analogue also for oxygen and CFC-11. All units in μmol kg^{-1}, except Δ CFC-11, which is in pmol kg^{-1}

cruise	$NTCO_2$ at 0.2°C	$NTCO_2$ at -0.8°C	Δ $NTCO_2$	Δ oxygen	Δ CFC-11
GEOSECS 1973	2286.0[a]	2269.6[a]	16.4 ± 15[a]	45.9 ± 2.0[b]	n.d.
WEPOLEX 1981	2281.5[a]	2267.1[a]	14.4 ± 6[a]	n.d.	n.d.
ANT XIII/4 1996	2287.9 ± 2.3	2271.4 ± 1.7	16.5 ± 2.9	46.5 ± 1.4	n.d.
ANT XV/4 1998	2289.5 ± 2.4	2273.4 ± 1.8	16.1 ± 3.0	47.1 ± 1.5	0.626 ± 0.025
ANT X/4 1992	-	-	-	-	0.436 ± 0.034
AJAX 1984	-	-	-	-	0.186 ± 0.017

n.d. not determined
[a] taken from Poisson and Chen [1987]
[b] GEOSECS stations 85, 87, 88, 89, 90 from within the Weddell regime

and −0.8°C of 16.4 μmol kg^{-1}, while for the 1981 WEPOLEX data they find 14.4 μmol kg^{-1}. These values are not significantly different from ours for the 1990s (Table 1). To make sure that this finding is not due to water mass changes, we executed the same procedure for dissolved oxygen. No significant change is found (Table 1) which means that no major water mass changes should have occurred. We may therefore conclude that over a period of as long as 25 years little anthropogenic CO_2 has penetrated into the bottom waters of the eastern Weddell Sea. Such penetration would show up as a decrease in time in the TCO_2 difference between the two water masses, while the values in Table 1 rather indicate a minor increase.

This result is in apparent contradiction to the observed, three-fold CFC-11 increase over 16 years (Fig. 1). To be more quantitative, we considered the TCO_2 difference to be a linear function of time, which, including weighing for the errors, resulted in a slight, significant increase. Moreover, we determined the maximum decrease that is statistically compatible with the data (Table 1). The result corresponds to an absolute upper limit of the TCO_2 increase in WSBW of 4.4 μmol kg^{-1} over 25 years (worst case within the 95% confidence intervals). The value may be a slight underestimate inasmuch as we have assumed the WDW to be free of anthropogenic CO_2. We therefore tentatively increase the value by 20%, which corresponds to anthropogenic TCO_2 in the two water masses being present proportionally to the CFC-11 concentrations observed in 1998 (Fig. 1). Such a minor amount of anthropogenic CO_2 at the prime meridian is in seeming contrast with a TCO_2 increase in newly formed bottom water in the western Weddell Sea within a period of only three years, which was at least partly attributable to anthropogenic input [*Hoppema et al.*, 1998]. But these waters are rather close to the formation region, and the increase was pertinent to potential temperatures near −1.2°C, i.e., much colder than at the prime meridian, so that the anthropogenic CO_2 signal should be distinctly less diluted than at the prime meridian. As for compatibility with the well-defined CFC-11 increase at the prime meridian, a partial explanation is that CFC-11 can be detected at permille levels of the ocean surface concentrations, i.e., with far greater sensitivity than anthropogenic TCO_2 in the presence of its large background of natural TCO_2.

The primary reason for the uncoupling between the uptake of anthropogenic CO_2 and CFCs is the different equilibration times in the surface water that constitutes a fraction of the newly formed WSBW. Surface water is ice covered during a (large) part of the year, which allows uptake of CFC-11 to a larger extent than uptake of anthropogenic CO_2. For CFC-11, a saturation of only about 60% in winter surface water was found in Antarctic waters [*Mensch et al.*, 1998]. For anthropogenic CO_2, the equilibration time is up to 10 times longer, so that a plausible surface saturation should be in the range of only 10-20%. Note that this refers specifically to the anthropogenic fraction of the TCO_2, while the apparent saturation of TCO_2 including the natural background may be much different. The anthropogenic surface water TCO_2 increase in equilibrium with the atmospheric increase should be approximately 1 μmol kg^{-1} yr^{-1}, which converts to 0.1 to 0.2 μmol kg^{-1} yr^{-1} applying the assumed saturation. According to *Klatt et al.* [2001], the waters in the core in question at the prime meridian are composed of about 80% of old deep water that should carry rather negligible anthropogenic CO_2, and only 20% of surface water. We thus end up with an expected increase in the order of 0.02 - 0.04 μmol kg^{-1} yr^{-1}, which is quite compatible with our result based on the observed temporal TCO_2 changes. A minor storage of anthropogenic CO_2 in the Weddell Sea deep and bottom waters is in keeping with the fact that bottom water production may be as low as 2 Sv [*Haine et al.*, 1998], a sizable fraction of which moreover escapes directly to the north [*Fahrbach et al.*, 1995]. It thus appears that the abyssal Weddell Sea is irrelevant for the storage of anthropogenic CO_2 on a global scale. Rather, the subpolar region preconditions the water masses, but the regions north of it (e.g., the Antarctic Circumpolar Current) are more effective in drawing down CO_2 [*Sabine et al.*, 1997]. Our results also confirm a recent modeling investigation [*Caldeira and Duffy*, 2000]. This confirmation is not at all trivial because modeling the Southern Ocean convective circulation is liable to artefacts.

In conclusion, CFC distributions in the ocean cannot generally be used as analogues for the invasion of anthropogenic CO_2, the subpolar Weddell Gyre being a counterexample. Thus, other methods have to be called in to estimate anthropogenic CO_2. Our data show that, in the long run, purely measurement-based estimates of anthropogenic CO_2 are a realistic option. Our data may also serve as a validation for other methods of determining anthropogenic CO_2. In particular, they indicate that estimations using the data-based back-calculation technique [*Gruber et al.*, 1996] show the correct trends in the Southern Ocean [*Sabine et al.*, 1997], even though this method has known deficiencies for this region. Results obtained using back-calculation techniques in turn exert a strong influence on other methods, such as modeling [*Caldeira and Duffy*, 2000]. Clearly, the initial validation that is presented here is vital for extrapolating to basin-wide and global scales.

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