Direct observation of increasing CO₂ in the Weddell Gyre along the Prime Meridian during 1973–2008

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A R T I C L E   I N F O
Available online 1 September 2011

Keywords:
Southern Ocean
Weddell Gyre
CO₂ uptake
C₄
Weddell Sea Bottom Water (WSBW)

A B S T R A C T

The World Ocean takes up a large portion of the anthropogenic CO₂ emitted into the atmosphere. Determining the resulting increase in dissolved inorganic carbon (C₄, expressed in μmol kg⁻¹) is challenging, particularly in the sub-surface and deep Southern Ocean where the time rate of change of C₄ (in μmol kg⁻¹ decade⁻¹) is commonly expected to be low. We present a determination of this time trend of C₄ in a dataset of measurements that spans 35 years comprising 10 cruises in the 1973–2008 period along the 0°-meridian in the Weddell Gyre. The inclusion of many cruises aims to generate results that are more robust than may be obtained by taking the difference between only one pair of cruises, each of which may suffer from errors in accuracy. To further improve consistency between cruises, data were adjusted in order to obtain time-invariant values of C₄ (and other relevant parameters) over the 35 years in the least ventilated local water body, this comprising the deeper Warm Deep Water (WDW) and upper Weddell Sea Deep Water (WSDW). It is assumed that this normalization procedure will allow trends in C₄ in the more intensely ventilated water masses to be more clearly observed.

Time trends were determined directly in measurements of C₄, and alternatively in back-calculated values of preformed C₄ (C₄₀, i.e., the C₄₀ of the water at the time that it lost contact with the atmosphere). The determined time trends may be attributed to a combination of natural variability (in hydrography or biogeochemistry) and increased uptake of anthropogenic CO₂ from the atmosphere. In order to separate these natural and anthropogenic components, an analysis of the residuals of a multivariate linear regression (MLR), involving the complete time series of all 10 cruises, was additionally performed. This approach is referred to as the Time Series Residuals (TSR) approach.

Using the direct method, the time trends of C₄ in the WSDW are quite small and non-significant at +0.176 ± 0.321 μmol kg⁻¹ decade⁻¹. On the other hand, the measured concentration of C₄ in the Weddell Sea Bottom Water (WSBW) is shown to rise slowly but significantly over the period from 1973 to 2008 at a rate of +1.151 ± 0.563 μmol kg⁻¹ decade⁻¹. The spatial distribution of these determined increases of C₄ in the deep Weddell Gyre closely resembles that of the increase of the anthropogenic tracer CFC-12, this strong similarity supporting a mostly anthropogenic cause for the increasing trend of C₄. Time trends in back-calculated values of C₄₀ appear to be obscured due to uncertainties in the measurements of O₂. Finally, the shallow waters (<200 m depth) do not allow for interpretation since these are strongly affected by seasonality.

Due to the small time trend signal in the WSBW, the TSR approach does not allow for unambiguous attribution of the observed trend in C₄ in the WSBW. The residuals of the TSR method do exhibit a time trend (considered representative of the time trend of C₄₀) of +0.445 ± 0.405 μmol kg⁻¹ decade⁻¹ (i.e., only 38% of the direct observed time trend in C₄) thus only partly supporting the attribution of the measured time trend of C₄ to uptake of anthropogenic CO₂. Another TSR-derived result suggests that there is no significant time trend of biogeochemical changes. A time trend in hydrography of mixing between two deep water masses does exist, as evidenced by a slight positive time trend in the temperature of the WSBW, but is inadequate to explain the time trend of C₄.

After all, the time trend in measured C₄ is most straightforwardly ascribed entirely to uptake of C₄₀ and assuming an exponentially growing history of storage, the observed increase of C₄ in the WSBW...
suggests that a total amount of $\text{C}_{\text{ant}}$ of $6 \pm 3 \text{ mmol kg}^{-1}$ has accumulated in this water mass between the onset of the Industrial Revolution and 1995. Extrapolating the determined time trend, the rate of storage of $\text{C}_{\text{ant}}$ in the deep Weddell Gyre ($>3000 \text{ m}$, west of 20 E) is calculated to be about $12 \pm 6 \text{Tg C yr}^{-1}$ over the 1973–2008 period. This rate of storage is likely somewhat lower than the rate of export of $\text{C}_{\text{ant}}$ from the surface water into the deep Weddell Gyre, due to continuous loss of $\text{C}_{\text{ant}}$ with WSDW flowing out of the Weddell Gyre into the deep basins of the other oceans as AABW.

1. Introduction and outline

1.1. Introduction

Since the onset of the Industrial Revolution around 1780, the combustion of fossil fuels has led to increasing concentrations of $\text{CO}_2$ in the atmosphere. In 1957 the now world famous time series of atmospheric $\text{CO}_2$ measurements at Mauna Loa, Hawaii was started (Keeling, 1960). After a few years, a rise in $\text{CO}_2$ was apparent, and already in the early 1960s it was recognized that the steady increase was attributable to the burning of fossil fuels. Moreover, it was realized that a portion of the fossil fuel $\text{CO}_2$ would enter into the ocean. Postma (1964) suggested that this invasion of anthropogenic $\text{CO}_2$ into the oceans can in principle be quantified. However, at the time, the analytical precision was inadequate to distinguish within the measured dissolved inorganic carbon (DIC, hereafter $\text{C}_2$; in $\text{mmol kg}^{-1}$), the small anthropogenic (or ‘excess’) component ($\text{C}_{\text{ant}}$; in $\text{mmol kg}^{-1}$) from the large and variable natural background.

The extensive and at the time state-of-the-art dataset for $\text{C}_2$ and alkalinity collected during the GEOSecs expeditions in the 1970s (Bainbridge, 1981) led to renewed efforts to quantify $\text{C}_{\text{ant}}$ in the oceans (Brewer, 1978; Chen and Millero, 1979). Although their approach worked quite well for certain water masses, it was deemed unsuitable for worldwide application. Additionally, at the time the quality of the data was still only modest. Nevertheless, Chen (1993) did produce an estimate of the global ocean inventory (in PgC, equal to $10^{15}$ g of C) of anthropogenic $\text{CO}_2$ in the year 1980.

The next major improvement was the $\Delta^C$ approach (Gruber et al., 1996) that in combination with the higher accuracy TTO dataset (Transient Tracers in the Oceans, 1981), led to improved estimate of $\text{C}_{\text{ant}}$ and its corresponding inventory in the North Atlantic Ocean. In the early 1990s, the introduction of certified reference material for $\text{C}_1$ (CRM; Dickson, 2001) as well as detailed measurement protocols (Dickson, 1993, updated in 2007), were other major steps forward in accuracy. New high quality datasets of the world oceans, obtained by the WOCE/JGofs programs, in combination with the $\Delta^C$ approach, led to the first high accuracy estimate of the inventory of $\text{C}_{\text{ant}}$ of the world oceans (Sabine et al., 2004).

Consensus now exists concerning the inventory of $\text{C}_{\text{ant}}$ for most of the world ocean. However, the determination of the inventory of $\text{C}_{\text{ant}}$ in the Southern Ocean remains a challenge, largely because the validity for the application in the Southern Ocean of the various approaches to derive $\text{C}_{\text{ant}}$ is debatable. Vázquez-Rodríguez et al. (2009) clearly demonstrate the large range in estimates of $\text{C}_{\text{ant}}$ in the South Atlantic Ocean that are produced by the various approaches. For the deep and bottom water masses, Vázquez-Rodríguez et al. (2009), show these estimates of $\text{C}_{\text{ant}}$ to range from negligible to values as high as one-third of the concentrations in the surface water. This study aims to determine the rate of increase of actually measured $\text{C}_2$ over 35 yr (1973–2008) in the Weddell Gyre using ocean interior data from 10 successive cruises. In the little-ventilated (or ‘old’) lower Warm Deep Water (WWD) and upper WSDW, no time trend of $\text{C}_2$ is expected or observed, therefore all cruise datasets are normalized to a common level in this water body. Next, the normalized $\text{C}_2$ is gridded. From these grids, the spatial distribution along the section (55 S–70 S) of the generally increasing time trend of $\text{C}_2$ is obtained, with striking resemblance to the similar distribution of time trends in the independent anthropogenic transient tracer chlorofluorocarbon-12 (CFC-12). Moreover, for two individual key water masses (the Weddell Sea Deep Water (WSDW) and Weddell Sea Bottom Water (WSBW)) the time trend of $\text{C}_2$ (in $\text{mmol kg}^{-1} \text{decade}^{-1}$) is calculated, from which a new improved estimate of the $\text{C}_{\text{ant}}$ and its inventory in Weddell Gyre is reported. Obviously, the time trend of $\text{C}_2$ may partly be due to natural variability of water mass mixing and biogeochemistry. Any effect of water mass mixing is assessed in a simple mixing model, relying on observed temperature trends. Moreover, the novel Time Series Residuals (TSR) method is designed to extract the sought after increase of anthropogenic $\text{C}_{\text{ant}}$ and distinguish this from the natural variability. The novel TSR method relies on the measured $\text{C}_2$ and a suite of independent ancillary measured variables of all 10 cruises.

Several stations of the 1973 GEOSecs expedition comprised the first suitable observations along the Prime Meridian in the Weddell Gyre. Since then, this hydrographic section along the 0-meridian has been (more or less extensively) occupied by at least another 9 expeditions that performed high-quality measurements of $\text{C}_2$ and additional relevant oceanic properties, (Tables 2 and 3). To the best of our knowledge this is the longest existing ocean section time series of $\text{C}_2$ data. Therefore this is a uniquely promising section for assessing the rate of increase of $\text{C}_2$. Moreover it serves as a field test of the novel TSR approach for extracting the increasing $\text{C}_{\text{ant}}$ signal from noise due to natural variability. On the other hand the Southern Ocean south of 50 S is often considered to feature only low concentrations of anthropogenic carbon (e.g., Sabine et al., 1999; Hoppema et al., 2001; but see Lo Monaco et al., 2005a, 2005b). This conceivable constitutes a challenge for the demonstration of the direct $\text{C}_2$ time trend and the TSR approach for discerning $\text{C}_{\text{ant}}$. However in the coming decades, and already in regions with a higher rate of increase (notably the North Atlantic Ocean: Pérez et al., 2008, 2010; Olafsson et al., 2009; Peng and Wanninkhof, 2010), both the direct $\text{C}_2$ time trend approach and the Time Series Residuals method are expected to deliver a strong signal of increasing $\text{C}_2$ and increasing $\text{C}_{\text{ant}}$, respectively.

1.2. Outline

After a brief introduction of the unique hydrography of the Weddell Gyre (Section 2), we will discuss in more detail the preceding concepts and approaches for quantifying the invasion of anthropogenic $\text{CO}_2$ into the oceans (Section 3). Firstly, five different published original approaches for determining the total inventory of $\text{C}_{\text{ant}}$ in the ocean interior are recognized, and discussed with regard to assumptions and uncertainties, notably for the Southern Ocean (Section 3.1). Secondly, we mention three approaches for quantifying the change of such $\text{C}_{\text{ant}}$ (i.e., $\Delta\text{C}_{\text{ant}}$) between two successive cruises along one and the same transect (Section 3.2). Thirdly we introduce the novel Time Series Residuals (TSR) approach for extracting from a suite of several cruises along one transect the rate of increase of $\text{C}_{\text{ant}}$ (Section 3.3).
Next, in text Sections 4 through 7, both the direct $C_T$ time trend method and the TSR approach are applied to the suite of 10 cruises over 35 yr along the Prime Meridian transect in the Weddell Gyre, aiming to establish the rate of increase of $C_T$ and $C_{ant}$, respectively.

2. Hydrography

The Southern Ocean comprises all waters south of the Subtropical Front situated at about 40°S, while the Antarctic Ocean proper comprises all waters south of the Polar Front situated at about 50°S (Deacon, 1984). The hydrography of the Antarctic Ocean is dominated by the wind-driven Antarctic Circumpolar Current (ACC), which flows relatively unhindered around Antarctica at all depths (Fig. 1). The eastward flows of wind and ocean currents also drive the Weddell Gyre, which rotates cyclonically (i.e., clockwise) between the Antarctic continent to the south, the Antarctic Peninsula to the west and the ACC to the north and east. The eastern-most extension of the Weddell Gyre is located at 25–30°E.

Several water masses flow into and out of the ACC and the Weddell Gyre (Fig. 2). From the north, at depths below about 1500 m, North Atlantic Deep Water (NADW) mixes into the ACC. However, before reaching the ACC, as well as within it, the NADW is deflected upward by the denser Antarctic Bottom Water (AABW) from the south, which wedges itself underneath the NADW. In the ACC there is large-scale mixing of several water masses including the NADW, resulting in a relatively homogeneous water mass called Circumpolar Deep Water (CDW). South of the ACC, the shallowing CDW penetrates southward toward the Antarctic continent at a depth of about 250–750 m. Being distinctly warmer (potential temperature $\theta > 0.5$ °C, see Table 2 for definitions) and saltier than the overlying, frigid and fresh polar water masses, it is locally referred to as Warm Deep Water (WDW). Strong and continuous circumpolar westerly winds cause upwelling of the WDW at latitudes between 60°S and 65°S in the Weddell Gyre. The upwelled waters are subsequently redistributed. A small fraction flows southward, replenishing the downwelling waters near the continent. A larger fraction flows northward where, between 50°S and 45°S, it subducts to depths of about 1000 m, and subsequently flows toward the equator as Antarctic Intermediate Water (AAIW).
The AABW, spilling from the intermediate and deep depths of the Weddell Basin over and through the Mid-Atlantic Ridge (MAR) and the South–West Indian Ridge (SWIR), flows northward into the South Atlantic and South Indian basins (Fig. 1). In the Weddell Basin, the pool of AABW (locally referred to as Weddell Sea Deep Water, WSDW) is replenished from below, by formation of dense water at sites along the edge of the Antarctic continent and the ice shelves of the Weddell Sea. The dense water flows downslope, entraining significant amounts of WDW, and accumulates near the bottom or at depths according to the density it achieves. This continuous supply of cold \((\theta < -0.7\, ^\circ C)\) water — referred to as Weddell Sea Bottom Water (WSBW) — forces the near-bottom pool to extend upward where it is mixed into the overlying water (Foster and Carmack, 1976; Klatt et al., 2005).

Typical features of the surface water at the margin of the Weddell Basin (i.e., relatively low temperature, salinity, nutrients and \(\text{CaCO}_3\); high oxygen and CFCs) are retained during its transfer to depth. The characteristics of the WDW, the water mass that influences the Weddell Basin over and through the Mid-Atlantic Ridge on the other hand, largely takes place along the Antarctic continent, under strong influence of ice-formation in the Weddell Sea on the other hand, largely takes place along the Antarctic continent, under strong influence of ice-formation in the Weddell Sea on the other hand, largely takes place along the Antarctic continent, under strong influence of ice-formation in the Weddell Sea on the other hand, largely takes place along the Antarctic continent, under strong influence of ice-formation in the Weddell Sea. Much of the uncertainty about the inventory of \(\text{C}_{\text{ant}}\) stems from this unique local hydrography. In the North Atlantic and Arctic oceans, deep water formation is generally thought to result from deep convection of cool, dense surface waters in wintertime. These waters have been cooled during extensive contact with the overlying atmosphere, meanwhile also exchanging gases such as CFCs, \(\text{O}_2\) and \(\text{CO}_2\). Deep water formation in the Weddell Sea on the other hand, largely takes place along the Antarctic continent, under strong influence of ice-shelves (i.e., often preventing direct air/sea gas exchange). The waters contributing to the nascent deep water generally have only recently upwelled. The unknown and likely variable degree to which they equilibrate with the atmosphere before reaching the ice-shelf zones, makes their ability to sequester anthropogenic \(\text{CO}_2\) difficult to predict or quantify.

3. Concepts and approaches to derive \(\text{C}_{\text{ant}}\) and its change in the ocean interior

Firstly, five different published original approaches for determining the total inventory of \(\text{C}_{\text{ant}}\) in the ocean interior (Section 3.1) are recognized, and discussed with regards to assumptions and uncertainties, notably for the Southern Ocean. Secondly, we mention three approaches for quantifying merely the change of such \(\text{C}_{\text{ant}}\) (i.e., \(\Delta\text{C}_{\text{ant}}\)) between two successive cruises along one and the same transect (Section 3.2). Thirdly we introduce our novel approach for extracting from a suite of several cruises along one transect the rate of increase of \(\text{C}_{\text{ant}}\) (Section 3.3): the Time Series Residuals (TSR) approach. Finally, all three groups of approaches are summarized in Table 1.

3.1. Determination of the concentration of \(\text{C}_{\text{ant}}\) in the ocean interior

3.1.1. \(\text{C}_{\text{ant}}\): the \(\text{C}_T^p\) approach

The gradual uptake by the ocean of anthropogenic \(\text{CO}_2\) from the atmosphere is detectable, in principle, as the ensuing gradual rise of \(\text{C}_T\) at the surface and eventually within the ocean interior. However, the presence and variability of biogeochemical processes in the ocean interior obscure these trends, and may need to be compensated for in order to be able to observe the increasing \(\text{C}_T\). Remineralization of organic matter and the dissolution of calcium carbonate (\(\text{CaCO}_3\)) do not only influence \(\text{C}_T\) but also the concentrations of dissolved oxygen (\(\text{O}_2\)) and total alkalinity (\(\text{A}_T\)), respectively. The stoichiometric ratios of these biogeochemical reactions have been shown to be fairly uniform in the oceans (Redfield et al., 1963; Anderson and Sarmiento, 1994). Therefore, by conversely using the changes in \(\text{O}_2\) and \(\text{A}_T\) from their preformed (i.e., at the time a water mass by its subduction loses contact with the atmosphere) values in the original surface water, these biogeochemical effects on \(\text{C}_T\) can be quantified and subtracted from the measured \(\text{C}_T\) in the interior ocean. This yields the reconstructed (or ‘back-calculated’) \(\text{C}_T\) that a water parcel had at the time of formation at the surface (preformed \(\text{C}_T^p\):)

\[
\text{C}_T^p = \text{C}_T - \psi_{\text{O}_2}(\text{AOU}) - 0.5(\text{A}_T - \text{A}_T^p + \psi_{\text{O}_2,N}(\text{AOU}))
\]

Here, AOU (apparent oxygen utilization) represents the amount of oxygen consumed by remineralization of organic matter. The AOU is defined as the difference between the measured \(\text{O}_2\) of an ocean interior water sample and the preformed concentration, \(\text{O}_2^p\), which is calculated (following Weiss, 1970) as the dissolved \(\text{O}_2\) presumably in equilibrium with atmospheric \(\text{pCO}_2\), using the measured values of salinity and temperature of the sample. The term \(\psi_{\text{O}_2,N}(\text{AOU})\) yields the amount of carbon released (as \(\text{CO}_2\)) during biological respiration, calculated from the stoichiometry of consumption of \(\text{O}_2\) and production of \(\text{CO}_2\) (\(\psi_{\text{O}_2,N}\)) and AOU. The value of preformed \(\text{A}_T^p\) is estimated from conservative properties of a water mass (any one or a combination of \(\theta, S, \text{PO}\) or NO; Broecker, 1974), using relationships determined between the measured \(\text{A}_T\) and these properties in the formation region of the subducted water mass. The factor of 0.5 here reflects the fact that the dissolution of \(\text{CaCO}_3\) increases \(\text{C}_T\) at half the rate at which it increases \(\text{A}_T\). The extra term \(\psi_{\text{O}_2,N}(\text{AOU})\) corrects the estimate of dissolution of \(\text{CaCO}_3\) (derived from the change of \(\text{A}_T\)) for the slight effect on alkalinity of the release of nitrate ion during remineralization of organic matter (Brewer and Goldman, 1976).

In a case study of the AAIW, flowing from its formation region at the Antarctic Polar Front to the low latitude South Atlantic, Brewer (1978) was able to calculate \(\text{C}_T^p\) over the 45°S–4°S range, and from this derived the corresponding atmospheric \(\text{pCO}_2\) value to decrease from \(\sim 300\ \mu\text{atm}\) at 45°S to \(\sim 250\ \mu\text{atm}\) between 20°S and the Equator. Taking into account the \(\sim 30 \pm 10\ \mu\text{atm}\) range of the \(\text{pCO}_2\) disequilibrium with the atmosphere at the formation region at 50°S, a pre-industrial atmospheric \(\text{pCO}_2\) of \(\sim 280\ \mu\text{atm}\) was obtained. Similarly, Chen and Millero (1979) reported the gradual increase of oceanic \(\text{CO}_2\) for the intermediate depth salinity minimum and the deep temperature minimum along a complete Atlantic section (50°S–50°N).

The \(\text{C}_{\text{ant}}\) of a water sample can be calculated by subtracting from \(\text{C}_T^p\) the pre-industrial value of \(\text{C}_T^p\) (\(\text{C}_T^p\) preind; Poisson and Chen, 1987; Körtszinger et al., 1998):

\[
\text{C}_{\text{ant}} = \text{C}_T - \text{C}_T^p\ \text{preind}
\]

The \(\text{C}_T^p\) preind is assumed to be equal (and constant through time) for all samples within a water mass, and is generally obtained from the interior of the water mass under consideration, if that can be determined (from absence of anthropogenic tracers such as tritium or CFCs) to be still uncontaminated with \(\text{C}_{\text{ant}}\) (i.e., \(\text{C}_T^p\) preind = \(\text{C}_T^p\) interior). For more shallow water masses, however, even the inner part may have already become contaminated with \(\text{C}_{\text{ant}}\). For such cases, one needs to resort to calculate \(\text{C}_T^p\) preind using the following equation:

\[
\text{C}_T^p\ \text{preind} = f(S, T, \text{A}_T^p, \text{pCO}_2\ \text{preind})
\]

where \(\text{pCO}_2\) preind is the assumed \(\text{pCO}_2\) of the surface water in pre-industrial times. However, because subducting waters are generally not in equilibrium with the overlying atmosphere
Table 1
A selection of techniques available for the calculation of the concentration of anthropogenic CO2 ($C_{ant}$), or the increase therein ($\Delta C_{ant}$), in the ocean. Some of the major perceived strengths and drawbacks of each are given in the table. See further text Section 3.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Refs.</th>
<th>Comment</th>
<th>Required measurements</th>
<th>Strengths</th>
<th>Assumptions made</th>
<th>Drawbacks/sensitivities</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Determining $C_{ant}$</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>$C_{T}$</td>
<td>Brewer (1978) and Chen and Millero (1979)</td>
<td>Shiller (1981)</td>
<td>$O_2$, $C_T$, $A_T$</td>
<td>Conceptually simple</td>
<td>Surfaces histories of $C_{ant}$, $O_2$ and $A_T$. No diapycnal mixing</td>
<td>Requires pre-industrial reference water mass; hence difficult for worldwide application</td>
</tr>
<tr>
<td>$\Delta C^*$</td>
<td>Gruber et al. (1996)</td>
<td>Matsumoto and Gruber (2005)</td>
<td>$O_2$, $C_T$, $A_T$, transient tracer</td>
<td>Reduced sensitivity to some assumptions. No requirement of reference water mass</td>
<td>Surfaces histories of $C_{ant}$, $O_2$ and $A_T$. No diapycnal mixing</td>
<td>Must obtain ventilation age estimate of sample</td>
</tr>
<tr>
<td>TTD</td>
<td>Hall (2002)</td>
<td>–</td>
<td>Transient tracer</td>
<td>Independent of biogeochemical data. Inherently allows for mixing</td>
<td>General shape of TTD. Surface histories of CFC and $C_{ant}$</td>
<td>TTD difficult to infer for certain regions</td>
</tr>
<tr>
<td>TrOCA</td>
<td>Touratier and Goyet (2004a, 2004b)</td>
<td>Yool et al. (2010)</td>
<td>$O_2$, $C_T$, $A_T$</td>
<td>Easily implemented</td>
<td>TrOCA$^4$-parametrization may be extrapolated to higher temperatures</td>
<td>TrOCA$^4$-parameterization likely not widely valid</td>
</tr>
<tr>
<td>TSS</td>
<td>Tanhua et al. (2007)</td>
<td>–</td>
<td>$\Delta C_{ant}$ (see below)</td>
<td>Conceptually straightforward</td>
<td>TSS has been reached. Surface history of $C_{ant}$</td>
<td>Requires $\Delta C_{ant}$ of samples</td>
</tr>
<tr>
<td><strong>Determining $\Delta C_{ant}$</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Change in $C_T$</td>
<td>This study (trend)</td>
<td>–</td>
<td>$C_T$</td>
<td>Uses only high accuracy data ($\pm 0.1%$)</td>
<td>Biogeochemical noise smaller than $\Delta C_{ant}$</td>
<td>Aliases in hydrographically and biogeochemically dynamic regions</td>
</tr>
<tr>
<td>Change in $C_{T}^2$</td>
<td>Peng et al. (1998)</td>
<td>–</td>
<td>$O_2$, $C_T$, $A_T$</td>
<td>Insensitive to variable biogeochemistry</td>
<td>Uncertainty of biogeochemical corrections applied are smaller than $\Delta C_{ant}$</td>
<td>Requires use of lower accuracy ancillary data ($\pm 2%$). Aliases in hydrographically dynamic regions</td>
</tr>
<tr>
<td>MLR</td>
<td>Wallace (1995)</td>
<td>Levine et al. (2008)</td>
<td>$O_2$, $C_T$, $A_T$, nutrients</td>
<td>Insensitive to variable hydrography and biogeochemistry</td>
<td>Ancillary data are independent. $\Delta C_{ant}$ is linearly representable by ancillary data. No ‘secular’ trends</td>
<td>Requires use of lower accuracy ancillary data ($\pm 2%$). Interpretation of results is ambiguous</td>
</tr>
<tr>
<td>eMLR</td>
<td>Friis et al. (2005)</td>
<td>Levine et al. (2008)</td>
<td>$O_2$, $C_T$, $A_T$, nutrients</td>
<td>Insensitive to variable hydrography and biogeochemistry</td>
<td>Ancillary data are independent. $\Delta C_{ant}$ is linearly representable by ancillary data. No ‘secular’ trends</td>
<td>Requires use of lower accuracy ancillary data ($\pm 2%$). Interpretation of results is ambiguous</td>
</tr>
<tr>
<td>TSR</td>
<td>This study</td>
<td>–</td>
<td>$O_2$, $C_T$, $A_T$, nutrients</td>
<td>Insensitive to variable hydrography and biogeochemistry. Use of many cruises reduces sensitivity to biases</td>
<td>Ancillary data are independent. $\Delta C_{ant}$ is linearly representable by ancillary data. No ‘secular’ trends</td>
<td>Requires use of lower accuracy ancillary data ($\pm 2%$)</td>
</tr>
</tbody>
</table>
(Gruber et al., 1996; Takahashi et al., 2009), any assumed value of \( pCO_2 \)_{preind} is debatable, which jeopardizes the application of the \( C^T \) approach in shallower, more recently ventilated waters masses. Several additional problems of the \( C^T \) approach should be mentioned. The inherent assumption of \( pO_2 \) equilibrium (for calculation of AOU) with the atmosphere may be invalid, and is of strong influence on the calculated \( C_{ant} \). For example, in the Southern Ocean the air–sea gas exchange is hampered by ice cover and Lo Monaco et al. (2005a, 2005b) assume a mean vegetation area. Because \( C_{ant} \) is strongly affecting the calculated \( C_{ant} \), for which emission commenced already at \( \sim 1780 \). Finally, a constant disequilibrium value of \( pCO_2 \) between air and sea is assumed, yet in reality this value likely varies over the years (Metzl, 2009).

### 3.1.2. \( C_{ant} \): the \( \Delta C^T \) approach

The \( \Delta C^T \) technique (Gruber et al., 1996) overcomes an important shortcoming of the \( C^T \) method in that it allows the \( pCO_2 \) disequilibrium in the formation region to be quantified from measurements even for water masses that are contaminated with \( C_{ant} \), provided that the age of the water sample is known. The \( \Delta C^T \) technique defines \( C_{ant} \) as follows:

\[
C_{ant} = C^T - C_{eq280} - C_{diseq}
\]

(4)

The first two terms on the right hand side of Eq. (4) comprise ‘\( \Delta C^T \)’ such that:

\[
C_{ant} = \Delta C^T - C_{diseq}
\]

(5)

Here, \( C^T \) of the water sample is calculated according to Eq. (1), \( C_{eq280} \) is the hypothetical \( C^T \) of the water if it were in \( pCO_2 \)~equilibrium with the pre-industrial atmosphere of 280 ppm (at the \( S \), \( T \) and \( A^2 \) of the sample), and \( C_{diseq} \) represents the small difference versus \( C_{eq280} \) due to air–sea \( pCO_2 \) disequilibrium in the formation area. Because \( C_{diseq} \) is not expected to be the same for all water masses, it is generally determined for each of a number of isopycnal intervals (layers of water between distinct lines of equal density).

For the deepest isopycnal intervals, \( C_{diseq} \) is obtained by observing \( \Delta C^T \) versus (generally) latitude. Such a plot shows \( \Delta C^T \) decreasing from the higher latitude formation regions toward the equator (reflecting the higher \( C^T \) in recently ventilated waters) where at some latitude it reaches a baseline level (extending toward the equator) comprising all samples that have a pre-industrial ventilation history. The mean of these pre-industrial samples is taken to represent the mean \( C_{diseq} \) of the isopycnal interval. For example, Gruber et al. (1996) show that the deep (> 2000 m) water masses in the North Atlantic south of Iceland have a \( C_{diseq} \) of about \( \sim 16 \mu mol kg^{-1} \), corresponding to a \( \Delta pCO_2 \) of about \( \sim 32 \mu atm \). This suggests that these waters generally have not completed the process of taking up \( CO_2 \) from the atmosphere before they were subducted.

For shallower isopycnal intervals, no such baseline of \( \Delta C^T \) may be observed, due to the fact that the whole interval is already contaminated with \( C_{ant} \), such that \( C^T \) and thereby \( \Delta C^T \) are elevated above pre-industrial levels. However, with knowledge of the ventilation age of the samples (obtained independently from CFCs, \(^3\)H–\(^{3}\)He or other transient tracers), an alternative may be calculated for \( C_{eq280} \) that is, a \( C_{eq} \) referenced to the known atmospheric \( pCO_2 \) of the year \( t \) of formation. For instance, for a sample with ventilation age dating from the year 1990, one would calculate \( C_{eq253} \).

Subsequent assessment, over a range of latitudes (or ages), of \( \Delta C^T \) (now called \( \Delta C^T \)) once again yields a baseline that may be taken to represent \( C_{diseq} \). Gruber et al. (1996) in this manner show that relatively shallow water masses (those originally formed in the seas north of Iceland) exhibit a \( \Delta pCO_2 \) of about \( \sim 85 \mu atm \). Once \( C_{diseq} \) is determined for each isopycnal interval, the value of \( C_{ant} \) is easily calculated using Eq. (5).

Because \( C_{diseq} \) is inferred as the mean difference between \( C^T \) and \( C_{eq280} \) (or \( C_{eq} \)), its value not only represents the effects of the air–sea disequilibrium of \( pCO_2 \) at the time of subduction, but also the effects of a conceivable \( pO_2 \) disequilibrium (which affects \( C^T \)). Because \( C_{diseq} \) is subtracted from \( \Delta C^T \) to obtain \( C_{ant} \), any effect on \( C_{ant} \) is canceled out. In the same way, \( C_{diseq} \) includes the effects of any inaccuracy of the remineralization ratio values \( \psi_{O:C} \) and \( \psi_{O:N} \) of Eq. (1), which are also canceled out (again through \( C^T \)), thereby removing another source of uncertainty that is present in the \( C^T \) method.

Using the \( \Delta C^T \) method, Sabine et al. (2004) used interior ocean measurements obtained during WOCE and JGOFS studies of the 1990s to constrain the inventory of \( C_{ant} \) of the world ocean to \( \pm 19 \) Pg C in 1994.

Matsumoto and Gruber (2005) assessed the \( \Delta C^T \) method and realized that biases in its results are introduced by the assumption of constant (over time) \( C_{diseq} \) and the simplified derivation of ventilation age from transient tracers (see also Hall et al., 2004). Matsumoto and Gruber (2005) suggest that these two biases can be minimized by (i) varying \( C_{diseq} \) as a function of the uptake of \( C_{ant} \) itself, and by (ii) taking into account the age spectrum of water when determining ventilation ages, respectively. However, for the Southern Ocean the second suggestion (ii) is notably difficult, because the age spectrum of the locally formed water masses is strongly bimodal (Khatiwala et al., 2001; Hall et al., 2002; Peacock and Maltrud, 2006), and therefore difficult to establish using tracer measurements. Therefore, application to the Southern Ocean of the \( \Delta C^T \) approach remains challenging.

### 3.1.3. \( C_{ant} \): the TrOCA approach

A application of the TrOCA approach (Tracer combining Oxygen, Carbon and Alkalinity; Touratier and Coyet, 2004a, 2004b) is more straightforward. The approach requires less variables to be measured (only \( O_2 \), \( C^T \), \( A^T \) and \( \theta \)), and avoids the rather complex estimation of air–sea disequilibria for \( pCO_2 \). In the TrOCA method, first the effects of remineralization of organic matter and dissolution of calcium carbonate are compensated:

\[
TrOCA = O_2 + 1.2C^T - 0.6A^T
\]

(6)

The resulting value of TrOCA includes the \( C_{ant} \) component. Next, if the pre-industrial TrOCA (TrOCA\(^P\)) value of the water sample can be obtained, this \( C_{ant} \) component can be calculated:

\[
C_{ant} = (TrOCA - TrOCA^n)/1.2
\]

(7)

For old, deep water masses that have not been in contact with the modern atmosphere, the value of TrOCA\(^P\) is assumed to be equal to TrOCA. In order to obtain values of TrOCA\(^P\) in shallower water masses (ventilated after 1780), the observed relationship in the deep waters of TrOCA and potential temperature (and in subsequent work also \( A^T \); Touratier et al., 2007) is extrapolated to the higher \( \theta \) of the shallower, warmer, water masses. However, Yool et al. (2010) argue that the extrapolation of a single TrOCA\(^P\)-versus-\( \theta \) relationship toward shallower, warmer waters cannot represent the full range of \( pO_2 \) and \( pCO_2 \)-disequilibria encountered in the different involved formation regions and processes.
Therefore, the TrOCA approach necessarily can likely only be applied on a sub-basin scale. In the deep Southern Ocean, no required pristine water mass exists anymore, as suggested by the fact that anthropogenic CFCs are found at all depths (Klatt et al., 2002), which complicates the derivation of a locally predictive relationship for TrOCA\(^6\).

### 3.1.4. \( C_{\text{ant}} \): the Transit Time Distribution (TTD) approach

The Transit Time Distribution approach (TTD; Hall et al., 2002; McNeil et al., 2003; Waugh et al., 2006) relies on a combination of measurements of one or more oceanographic transient tracers (e.g., CFCs, SF\(_6\)), their atmospheric time histories, and hydrographic data to estimate the most likely ventilation age distribution (i.e. the TTD) of water parcels in the ocean interior. The inferred TTDs are then combined with the assumed surface water time history of \( C_{\text{ant}} \) to calculate the interior ocean concentrations of \( C_{\text{ant}} \). Waugh et al. (2006) have used the TTD method to estimate a total inventory of \( C_{\text{ant}} \) for the global ocean of 94–121 PgC for 1994.

The complete independence of the TTD method from measurements of oceanic \( C_T \) makes it a valuable complement to \( C_T \)-based approaches. However, like some of the previous approaches, the TTD approach requires assumptions of the time histories of \( C_{\text{ant}} \) and CFC in the surface ocean, which are strongly dependent on the unknown (and likely variable) time histories of equilibration with the atmosphere. Additionally, as already mentioned in text Section 3.1.2, the shape of the TTD may be difficult to quantify specifically in the Weddell Gyre, where upwelling, subduction and entrainment occur on small temporal and spatial scales. The concurrent measurements of transient tracers with strongly differing atmospheric time histories (e.g., CFC-12 and SF\(_6\); Walker et al., 2000; Tanhua et al., 2008; Fine, 2011) in principle allows for some of the uncertainty of the shape of the TTDs to be resolved. However, no datasets of SF\(_6\) in the Weddell Gyre have been described in the literature yet.

### 3.1.5. \( C_{\text{ant}} \): the Transient Steady State (TSS) approach

Given a sufficiently long time, an exponentially increasing concentration of \( C_{\text{ant}} \) at the surface of the ocean will result in a similar exponential increase of \( C_{\text{ant}} \) at depth, the so-called Transient Steady State (TSS; Tanhua et al., 2007). Therefore the rate of increase of \( C_{\text{ant}} \) at any location in the ocean interior is proportional to the concentration of \( C_{\text{ant}} \) (Gammon et al., 1982; Tanhua et al., 2007). This method thus allows the derivation of a value of \( C_{\text{ant}} \) given only the rate of change of \( C_{\text{ant}} \). However, just as for most of the above methods, the finally derived \( C_{\text{ant}} \) concentration depends strongly on the assumed time history of surface water pCO\(_2\). Nevertheless, this technique will be used in below Section 7.5 to convert the determined rate of increase of \( C_{\text{ant}} \) in the deep Weddell Sea into an estimate of the total concentration of \( C_{\text{ant}} \).

### 3.2. Determination of the increase \( \Delta C_{\text{ant}} \) between two consecutive cruises

The expected increase of \( C_T \) at the ocean surface due to the accumulation of \( C_{\text{ant}} \) is about 1 \( \mu \)mol kg\(^{-1} \) yr\(^{-1} \), against a background concentration in the order of 2000 \( \mu \)mol kg\(^{-1} \). In deeper waters, this increase will be smaller and therefore more difficult to discern against the large background value. Moreover, the signal may be obscured by variability of formation and mixing of deep water masses (Fahrbach et al., 2004) and variability of biological processes (Sabine et al., 2008). We discuss three published approaches for quantifying the increase in \( C_{\text{ant}} \) (\( \Delta C_{\text{ant}} \)) between two successive cruises along one and the same transect.

#### 3.2.1. \( \Delta C_{\text{ant}} \): determination of the change in \( C_T \) or \( C_T^0 \)

Early determinations of the increase of \( C_{\text{ant}} \) between (once) repeated ocean sections were reported by Hoppema et al. (1998) and Peng et al. (1998). The former study in the western Weddell Sea explicitly considered variable formation properties of water masses. The latter study accounted for the confounding effects of variability in such natural processes as water mass mixing and biology, evaluating the increases of \( C_T^0 \) along isopycnal surfaces.

#### 3.2.2. \( \Delta C_{\text{ant}} \): the Multivariate Linear Regression (MLR) approach

Wallace (1995) proposed the use of a Multivariate Linear Regression (MLR) technique to assess the changes in \( C_{\text{ant}} \) between two subsequent occupations of the same ocean station or section. The technique correlates measured values of \( C_T \) with a suite of ancillary tracers in order to determine these changes, while accounting for some of the variability in hydrographic conditions and biological activity.

Firstly, for one single cruise, a mathematical relationship is derived between the measured \( C_T \) and the values of ancillary physical and biogeochemical properties that are known to be related to the natural sub-surface variability of \( C_T \). These properties (generally \( \theta, S, \) one or more nutrients, \( O_2 \) or AOU and \( A_{\text{R}} \)) are independent of increasing \( C_{\text{ant}} \), but represent the natural processes affecting \( C_T \): the mixing of water masses, remineralization of organic matter and dissolution of CaCO\(_3\). The approach does not require knowledge about remineralization ratios or mixing processes. The derived MLR is used to predict the values \( C_T^{\text{MLR}} \) and by comparison with the actually measured \( C_T \) values, the residuals \( (C_{\text{MLR}} - C_T) \) are obtained. In practice, these residuals are normally distributed around zero, with a typical standard deviation in the order of 4 \( \mu \)mol kg\(^{-1} \). Subsequently, for a second cruise some years later, the MLR relationship of the first cruise is combined with the ancillary values of the second cruise, to derive \( C_{\text{MLR}} \). Finally, by comparison of the depth profiles of \( C_{\text{MLR}} \) and \( C_T \), the apparent increase \( \Delta C_{\text{ant}} \) is derived.

Application in the Indian Ocean by Sabine et al. (1999) resulted in an estimate of the increase of \( C_{\text{ant}} \) in the Indian Ocean north of 35\(^\circ\)S. McNeil and coworkers used this technique to demonstrate the invasion of both \( C_{\text{ant}} \) and the \( \Delta^{13}C_T \)-signal into the Southern Ocean south of Australia (McNeil et al., 2001). Peng et al. (2003) reported an increase of anthropogenic CO\(_2\) in the Pacific Ocean over two decades. Matear and McNeil (2003) found reasonable agreement between the MLR-method and the TTD technique (Section 3.1.4) in the Southern Ocean.

#### 3.2.3. \( \Delta C_{\text{ant}} \): the Extended Multivariate Linear Regression (eMLR) approach

In the original MLR approach (Section 3.2.2), the derived \( \Delta C_{\text{ant}} \) is affected by errors of both the suite of ancillary measurements and the measured \( C_T \) values. The extended MLR (eMLR; Friis et al., 2005) aims to minimize the effect of the errors of the ancillary measurement. Here one derives, again using MLR, a unique relationship for each of two cruises and uses the difference between the coefficients of the two relationships as a predictor of \( \Delta C_{\text{ant}} \) between the cruises. The eMLR approach has been applied by several investigators (e.g., Olsen et al., 2006; Tanhua et al., 2007; Sabine et al., 2008; Hauck et al., 2010). The approach is deemed less sensitive than the original MLR-method to systematic errors (biases) in the ancillary data of each cruise. Nevertheless, the sensitivity of the results to biases in the measurements of \( C_T \) of either involved cruise remains. This jeopardizes the application of this method, notably in the Weddell Gyre where time trends in \( C_{\text{ant}} \) are deemed to be small.

Every technique used to determine anthropogenic changes in \( C_T \) between two cruises is sensitive to biases in the data of either
et al. (2008) argue and illustrate that the (e)MLR approaches do not necessarily yield accurate results in the presence of trends in the ancillary data that persist over the period of interest (so-called secular trends). The warming of shallow water masses due to global warming is a case in point.

3.3. The Time Series Residuals (TSR) approach for multiple repeat cruises along one transect

Here we introduce an approach for extracting from a suite of multiple cruises along one transect the rate of increase of $C_{\text{ant}}$ during the time interval spanning these cruises. This TSR approach is applied to a suite of 10 cruises along the Prime Meridian transect in the Southern Ocean during the 1973–2008 time interval. The inclusion of 10 cruises aims to minimize the effects of systematic errors in both the suite of ancillary measurements and in the measured $C_T$ values. For 10 cruises, one overall MLR relationship is determined. Next, this overall relationship is used to calculate $C_{T\text{residual}}$, and by comparison with actually measured $C_T$, the $C_{T\text{residual}}$ is regressed against sampling date (1973–2008). Following the same premises as the MLR and eMLR approaches, it is expected that increasing (over time) values of $C_{T\text{residual}}$ reflect the increase in the concentration of $C_{\text{ant}}$ in a water mass. As with the MLR-method, the application of the TSR approach does not require knowledge of the surface water gas disequilibria or remineralization ratios.

Seasonal variability in $C_T$ in shallow waters is to a large extent represented by the MLR (Friis et al., 2005). Therefore, the TSR method allows the determination of time trends in $C_{\text{ant}}$ (i.e., $C_{T\text{residual}}$) in shallow waters. This in contrast with $C_T^0$ and $C_T$, which both are expected to show strong variations in shallow waters between the different seasons in which the data were collected.

4. Data collection

The shipboard methods of the most recent cruise are described (Section 4.1), followed by the chosen database of the preceding nine cruises (Section 4.2). Of all ten cruises, stations south of ~55°S and (generally) within 5° of longitude from the Prime Meridian were selected, representative for the Weddell Gyre. The locations of all stations are shown in Fig. 3. The cruises span the period from 1973 to 2008.

4.1. Shipboard analyses

The most recent data used in this paper, from PFS Polarstern cruise ANT–XXIV/3 (Cape Town—Punta Arenas, 10 February–16 April 2008; Fahrbach and de Baar, 2010) have not been published before. During this cruise, about 2800 samples were analyzed on two identical instruments (VINDTA 3C, MARIANDA, Kiel, Germany), with each instrument measuring both $C_T$ and $A_T$. Collection and analysis was in accordance with the standard operating procedures outlined by Dickson et al. (2007). Samples were analyzed immediately after sampling, hence were not poisoned. Occasionally, samples were analyzed on both instruments concurrently, thereby allowing for instrument-to-instrument comparison.

Measurements of $C_T$ were performed using the coulometric method (Johnson et al., 1993). Determinations of $A_T$ were performed by an acid titration following the standard settings of the VINDTA (Mintrop et al., 2000). In order to set the measurement accuracy, certified reference material (CRM, Dickson, 2001) was analyzed at least three times per day. On both instruments, measurements of CRM deviated from the certified values less than 0.5% for both $C_T$ and $A_T$ (i.e., less than circa 12 µmol kg$^{-1}$). Post-cruise processing and correction of the data resulted in a dataset that is deemed to be of excellent quality for $C_T$, with typical short-term reproducibility of around 1.4 µmol kg$^{-1}$ for both instruments.
Intercomparability of the instruments is considered to be excellent, with the difference in final $C_T$ values between them (as inferred from about 400 samples that were run on both instruments) being $0.1 \pm 1.9 \text{ mol kg}^{-1}$. Results of $C_T$ of the two instruments were merged into one dataset, of which the overall accuracy is estimated to be better than $\pm 2 \text{ mol kg}^{-1}$. Results for $A_T$ of one of the two instruments were discarded due to excessive drift. The estimated accuracy of the retained $A_T$ dataset of the other instrument is $\pm 4.0 \text{ mol kg}^{-1}$.

Data for dissolved oxygen was obtained from in situ sensors that were regularly calibrated against Winkler titrations, with a reported final accuracy of $\pm 4.5 \text{ mol kg}^{-1}$. Measurements of dissolved nutrients (silicate, phosphate and nitrate) were performed colorimetrically and on board with an auto-analyzer. The combined accuracy and precision of these three measurements is considered to be better than $\pm 0.5\%$, $\pm 0.5\%$ and $\pm 1.0\%$, respectively. Measurements that were concurrently made on a preliminary batch of the novel reference material for nutrients in seawater (RMNS, distributed by KANSO co. www.kanso.co.jp; Aoyama et al., 2008) confirm this accuracy.

A more detailed account of these shipboard methods is provided in electronic Supplement S1.

4.2. Additional data

From the GLODAP 1.1 database (Key et al., 2004) and the CARINA database (Key et al., 2010) the data of six cruises in the vicinity of the 0°-meridian were extracted (Table 3). For each cruise, we used the data that had received primary quality control (outliers removed, conversion to common units), but were not yet adjusted for internal consistency, because for our application the desired internal consistency will be tailored to the local region. (Please notice that the final product of GLODAP and CARINA has been adjusted for global internal consistency). Data of $C_T$ of cruises ANT-XV/4, ANT-XXII/3 and ANT-XXIV/2, which are not available in GLODAP or CARINA, have been described before and were obtained from the respective investigators (see references in Table 3).

5. Data processing

This study aims to quantify the rates of storage of $C_{ant}$ in the Weddell Gyre, using data from 10 cruises conducted between 1973 and 2008. The use of multiple cruises is expected to reduce the susceptibility of the results to biases in individual cruises. Firstly, we will determine time trends directly in the actual measured data of $C_T$ that have been collected during multiple cruises along the same ocean section. Secondly, we perform a similar time trend assessment but now using calculated $C_T$ (Section 3.1.1), relying on additional measured variables ($\theta$, $S$, $O_2$ and $A_T$). Lastly, the determined time trends of $C_T$ will be separated into their natural components and anthropogenic (i.e. $C_{ant}$) components using the TSR method outlined in Section 3.3. Moreover, for the sake of comparison with previous studies in

### Table 2

<table>
<thead>
<tr>
<th>Water mass/layer</th>
<th>Abbreviation</th>
<th>Latitude (°S)</th>
<th>Depth (m)</th>
<th>Salinity</th>
<th>$\theta$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Upper 200 m)</td>
<td>SHALLOW</td>
<td>58–63</td>
<td>&lt;200</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Warm Deep Water</td>
<td>WDW</td>
<td>–</td>
<td>&gt;34.6</td>
<td>&gt;0</td>
<td></td>
</tr>
<tr>
<td>Weddell Sea Deep Water</td>
<td>WSDW</td>
<td>–</td>
<td>&gt;34.64</td>
<td>0.5 to 0.2</td>
<td></td>
</tr>
<tr>
<td>Weddell Sea Bottom Water</td>
<td>WSBW</td>
<td>–</td>
<td>&gt;34.68</td>
<td>&lt;0.7</td>
<td></td>
</tr>
</tbody>
</table>

### Table 3

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Date</th>
<th>Ship</th>
<th>Adjustments performed to the data</th>
<th>$C_T$-relevant reference</th>
<th>CRM</th>
</tr>
</thead>
<tbody>
<tr>
<td>GEOSECS</td>
<td>Jan 1973</td>
<td>Knorr</td>
<td>$-0.6$ (0) $-5$ ($-10$)</td>
<td>$0$ ($-1$)</td>
<td>No</td>
</tr>
<tr>
<td>AJAX</td>
<td>Jan–Feb 1984</td>
<td>Knorr</td>
<td>$+10.9$ (+8) $+8$ (0)</td>
<td>$-2$ ($-1$)</td>
<td>No</td>
</tr>
<tr>
<td>ANT-V/2–3</td>
<td>Jul–Dec 1986</td>
<td>Polarstern</td>
<td>$+12.8$ (+12) $+7$ (0)</td>
<td>$0$ (0)</td>
<td>No</td>
</tr>
<tr>
<td>ANT-X/4</td>
<td>Jun–Jul 1992</td>
<td>Polarstern</td>
<td>$+2.1$ (0) $-0.6$ (0)</td>
<td>$-2$ ($-1$)</td>
<td>No</td>
</tr>
<tr>
<td>ANT-X/4</td>
<td>Apr 1996</td>
<td>Polarstern</td>
<td>$-0.6$ (0) $-0.6$ (0)</td>
<td>$0$ (0)</td>
<td>No</td>
</tr>
<tr>
<td>ANT-X/4</td>
<td>May 1998</td>
<td>Polarstern</td>
<td>$-1.8$ (NA) No data</td>
<td>$0.5$ (NA)</td>
<td>No</td>
</tr>
<tr>
<td>ANT-X/2</td>
<td>Dec 2002</td>
<td>Polarstern</td>
<td>$+2.0$ (NA) No data</td>
<td>$0.5$ (NA)</td>
<td>No</td>
</tr>
<tr>
<td>ANT-XXIV/3</td>
<td>Feb 2005</td>
<td>Polarstern</td>
<td>$-0.6$ (NA) No data</td>
<td>$2.5$ (NA)</td>
<td>No</td>
</tr>
<tr>
<td>ANT-XXIV/3</td>
<td>Jan 2008</td>
<td>Polarstern</td>
<td>$+0.6$ (0) $0$ (0)</td>
<td>$0$ (0)</td>
<td>No</td>
</tr>
<tr>
<td>ANT-XXIV/3</td>
<td>Feb 2008</td>
<td>Polarstern</td>
<td>$+0.3$ (NA) $-1$ (NA)</td>
<td>$1.5$ (NA)</td>
<td>No</td>
</tr>
</tbody>
</table>

4. $C_T$ of GEOSECS was measured potentiometrically, for all other cruises $C_T$ was measured coulometrically.
5. $A_T$ of ANT-V/2&3 was calculated by GLODAP from $C_T$ and $pCO_2$. 
the region, the concentration of $C_{\text{tot}}$ will be determined with another approach, the TrOCA method.

### 5.1. Normalization in lower Warm Deep Water (WDW) and upper Weddell Sea Deep Water (WSDW)

In the Weddell Gyre, the southernmost part of the 0°-meridian section, the lower extent of the WDW together with the upper part of the WSDW, is considered the least ventilated water body (Fahrbach et al., 2011; Behrendt et al., 2011; to be concise, this part of the WSDW, is considered the least ventilated water body Weddell Sea Deep Water (WSDW).

Over the 1973–2008 period of observations, the procedure be referred to as lWDW/uWSDW. Indeed, over the period, the combined water body will in the context of the normalization processes (data not shown). Nevertheless, for each cruise there may exist a systematic offset due to calibration uncertainties. In order to remove these offsets (that in turn might give rise to erratic time trends), a normalization is applied to bring the values in the WDW of each cruise to the mean of all 10 cruises. Following the method of the normalization procedure followed to normalize cruise data in the lower WDW and upper WSDW (lWDW/uWSDW). See Section 5.1 for details.

Adjustments determined in this manner for all relevant parameters of all cruises are listed in Table 3 (i.e., $C_{\text{t}}$, $A_{\text{t}}$, $O_{\text{2}}$, $N_{\text{2}}$, $P_{\text{O}_{4}}$, $S_{\text{i}}$. Data of CFCs were not adjusted). At the latitudinal range considered, the used temperature range coincides with a depth range of about 800–2200 m, i.e., the IWDW/uWSDW. The NADW in the South Atlantic Ocean is much larger and even less ventilated than the IWDW/uWSDW and is deemed an even more suitable reference water mass, but cannot serve that purpose because five of the ten cruises in this study did not sample the NADW.

The spread of measurements around the regression line (Table 4, column ‘rmse’) is illustrative of the precision of the data of each cruise. Clearly, the precision of the analysis of $C_{\text{t}}$ has generally improved over time, from 4.0 μmol kg$^{-1}$ during GEOSECS in 1973 to 1.3 μmol kg$^{-1}$ or 2.2 μmol kg$^{-1}$ for ANT-XXIV/2 and ANT-XXIV/3, respectively. The thus adjusted datasets for $C_{\text{t}}$

![Fig. 4.](image-url) Example for $C_{\text{t}}$ of the procedure followed to normalize cruise data in the lower WDW and upper WSDW (IWDW/uWSDW). See Section 5.1 for details. (A) Regressions of measured $C_{\text{t}}$(μmol kg$^{-1}$) versus potential temperature ($\theta$)(°C) of all 10 cruises. The strongly outlying regression lines represent the data of cruises AJAX (1984) and ANT-V/2&3 (1987). (B) The determined intercepts at $\theta$=0°C of the regressions in panel (A). The black horizontal line indicates the mean intercept (2262.7 μmol kg$^{-1}$) of all cruise data (ANT-V/2&3 excepted). The black vertical lines represent the 95% confidence interval of each intercept. Data of each cruise were adjusted to make the cruise-specific intercept coincide with the mean intercept of all (non-outlying) cruises.

### Table 4
Details of the regression of $C_{\text{t}}$ versus potential temperature of cruise data from the deeper part of the WDW and the upper part of the WSDW (IWDW/uWSDW): rmse: root mean square error (i.e., measure of spread of data around the regression line). Data were adjusted to yield an intercept of 2262.7 μmol kg$^{-1}$.

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Intercept ($\mu$mol kg$^{-1}$)</th>
<th>Slope (°C$^{-1}$)</th>
<th>rmse ($\mu$mol kg$^{-1}$)</th>
<th>$n$</th>
<th>Adjustment ($\mu$mol kg$^{-1}$)</th>
<th>Discarded data</th>
</tr>
</thead>
<tbody>
<tr>
<td>GEOSECS</td>
<td>2263.3 ± 3.2</td>
<td>22.4 ± 13.5</td>
<td>4.0</td>
<td>15</td>
<td>−0.6</td>
<td>None</td>
</tr>
<tr>
<td>AJAX</td>
<td>2250.8 ± 2.1</td>
<td>21.2 ± 9.9</td>
<td>3.9</td>
<td>23</td>
<td>+10.9</td>
<td>All data</td>
</tr>
<tr>
<td>ANT-V/2&amp;3</td>
<td>2249.2 ± 0.9</td>
<td>18.7 ± 4.4</td>
<td>2.7</td>
<td>48</td>
<td>+12.8</td>
<td>None</td>
</tr>
<tr>
<td>ANT-X/4</td>
<td>2260.5 ± 1.0</td>
<td>21.0 ± 5.1</td>
<td>2.1</td>
<td>22</td>
<td>+2.1</td>
<td>≤ 635 m and 1500 m</td>
</tr>
<tr>
<td>ANT-XIII/4</td>
<td>2263.3 ± 0.6</td>
<td>20.9 ± 2.9</td>
<td>2.4</td>
<td>91</td>
<td>−0.6</td>
<td>None</td>
</tr>
<tr>
<td>ANT-XV/4</td>
<td>2264.5 ± 0.5</td>
<td>20.7 ± 2.6</td>
<td>2.4</td>
<td>105</td>
<td>−1.8</td>
<td>None</td>
</tr>
<tr>
<td>ANT-XX/2</td>
<td>2260.8 ± 0.7</td>
<td>18.7 ± 3.3</td>
<td>3.3</td>
<td>116</td>
<td>+2.0</td>
<td>None</td>
</tr>
<tr>
<td>ANT-XXI/3</td>
<td>2264.3 ± 0.4</td>
<td>20.2 ± 2.1</td>
<td>1.7</td>
<td>79</td>
<td>−0.6</td>
<td>None</td>
</tr>
<tr>
<td>ANT-XXIV/2</td>
<td>2262.0 ± 0.4</td>
<td>20.9 ± 2.0</td>
<td>1.3</td>
<td>54</td>
<td>+0.6</td>
<td>None</td>
</tr>
<tr>
<td>ANT-XXIV/3</td>
<td>2262.4 ± 0.7</td>
<td>18.9 ± 3.1</td>
<td>2.2</td>
<td>64</td>
<td>+0.3</td>
<td>None</td>
</tr>
</tbody>
</table>
and other parameters are highly internally consistent within the IWDW/uWSDW. However, the C\textsubscript{T} data of AJAX (1984) are deemed to be of insufficient quality for this study due to low spatial sampling resolution and significant station-to-station biases that cannot be objectively resolved. Therefore, the C\textsubscript{T} data of AJAX are excluded from further analysis (the remaining data of CFCs and T were used). Similarly, the southerly deep data (south of 63°S and deeper than 1500 m) of cruise ANT-X/4 are considered erroneously high by up to 7 μmol kg\textsuperscript{-1} and are also excluded from analysis. Fig. 5 shows sections of the IWDW/uWSDW-normalized C\textsubscript{T} data. Although they are not (all) used in further analyses, the data of AJAX and ANT-X/4 are shown in Fig. 5 for completeness. The adjusted analyses are of similar magnitude as those applied in CARINA and GLODAP (Table 3).

5.2. Data gridding

Toward discerning a time trend over 35 yr, all cruises are assigned equal weight. If this is not done, then a straightforward regression would cause overrepresentation of those cruises that have most measurements. Equal weighting of the data of each cruise is accomplished by resampling all data of interest (S, T, CFC-12, C\textsubscript{F}, A\textsubscript{T}, O\textsubscript{2} nutrients) onto a common grid (spacing: 100 m depth and 0.5° latitude). The longitude of all data is set to 0 E. Care was taken not to allow the gridding routine to extrapolate data too far into depths or latitudes where infact no samples were collected.

5.3. Consideration of oxygen

Some cruises retain significant localized bias for O\textsubscript{2} even after the IWDW/uWSDW-normalization procedure outlined above. In order to illustrate this, we obtain a ‘best’ or ‘mean’ section of O\textsubscript{2} by averaging the very consistent O\textsubscript{2} sections of recent cruises ANT-XIII/4, ANT-XV/4, ANT-XX/2 and ANT-XXIV/2, and make section plots of the difference of this O\textsubscript{2}\textsuperscript{mean} and each of the O\textsubscript{2} datasets of all ten cruises used in this study (Fig. 6). It may be observed that the applied single-adjustment approach is not sufficient for eliminating all biases in the O\textsubscript{2} datasets of all cruises. For example, an offset may be seen for ANT-XXIV/3 in the deep water between 60°S and 65°S. This anomaly is not observed for ANT-XXIV/2 only 2 months earlier. Similarly, cruises GEOSECS, ANT-V/2&3 and ANT-XXII/3 also appear to have calibration problems, although for GEOSECS, which is far in the past from the subsequent cruises, deviations in the deep water arguably might be reflective of genuine changes in the deep Weddell Sea. Based on these observations, this study ignored the O\textsubscript{2} data of ANT-XXII/3 and ANT-XXIV/3, and of selected stations of ANT-V/2&3 (north of 63°S) and GEOSECS (north of 57°S). The magnitude of these (local) offsets (about 2–5 μmol kg\textsuperscript{-1}) is about as large as the stated overall accuracy of O\textsubscript{2} of cruise ANT-XXIV/3 (± 4.5 μmol kg\textsuperscript{-1}, see Supplementary material), and much larger than the ± 1% (locally about ± 2–3 μmol kg\textsuperscript{-1}) that is often stated for the accuracy of oxygen measurements in general. The uncertainty about the accuracy of O\textsubscript{2} measurements (in this study and in general) may jeopardize the application and interpretation of the back-calculation techniques that require O\textsubscript{2} (C\textsubscript{F}, TrOCA). In the back-calculation concept, an erroneously low O\textsubscript{2} yields a C\textsubscript{F} that is also too low, because a too large fraction of the measured C\textsubscript{T} is considered to result from remineralization of organic matter (see Eq. (1)).

5.4. Derivation of necessary variables

The following variables were derived from the gridded original data.

\(\text{C}_\text{F}^\text{a} \): Values of preformed C\textsubscript{F} (i.e., C\textsubscript{F}\textsuperscript{a}) were calculated for each grid point of each cruise using Eq. (1) (Section 3.1.1). The required values of A\textsubscript{MLR} and O\textsubscript{2}\textsuperscript{at} were obtained using the parameterizations of Sabine et al. (1999) and of Weiss (1970), respectively. Because the present study concerns the increase in C\textsubscript{F} over a certain period rather than its exact value, the determination of the pO\textsubscript{2} disequilibrium is not required, and we assume ΔpO\textsubscript{2} = 0%. The values of the ratios \(\psi_{OC}\) and \(\psi_{ON}\) are taken from Anderson and Sarmiento (1994) as 117/170 and 16/170, respectively.

\(A_{\text{MLR}}\): Measurements of A\textsubscript{T} are available from 4 of the 10 cruises. To improve the availability of A\textsubscript{T} (a requirement for the application of the C\textsubscript{F} and TrOCA methods), an MLR was performed of the available (WDW-adjusted) data of A\textsubscript{T} versus [salinity, T, silicate, depth, latitude]. With the derived coefficients, an artificial
Fig. 6. Section plots for the 10 cruises used in this study of the difference between (IWDW/uWSDW-normalized) O$_2$ and O$_2^{\text{norm}}$. The latter is defined as the mean IWDW/uWSDW-normalized O$_2$ of four selected, mutually consistent cruises: ANT-XIII/4, ANT-XV/4, ANT-XX/2 and ANT-XXIV/2. These section plots are deemed to be indicative of station-to-station bias in the reported data of O$_2$. These biases are not accounted for by the single normalization performed in this study. Because the data of O$_2$ of ANT-XXIV/3, ANT-XXII/3 and of selected stations of ANT-V/2&3 (north of 63°S) and GEOSECS (north of 57°S) exhibit such bias they are excluded from this study, but are retained in this figure.

Fig. 7. Depth profiles of the residuals of multivariate linear regressions (see Section 5.4) of data of (left column) A$_{\text{C}}$ versus [salinity, $\theta$, silicate, depth, latitude] and (right column) C$_{\text{C}}$ versus [salinity, $\theta$, silicate, phosphate, depth]. The top row comprises non-gridded data, bottom row comprises gridded data. Thick lines indicate the mean and standard deviation of the residuals over a moving 500 m interval. The overall standard deviation of each profile is provided as text in each panel.
variable $A_{T}^{\text{MLR}}$ was generated. In order to optimally represent the measured values of $A_{T}$ over the entire section, separate MLRs were performed for each of four intervals of potential density. The procedure was performed both for non-gridded and gridded data, in order to verify the robustness of the gridding routine. The resulting residuals of the regressions are presented in Fig. 7 (panels A, C). It can be observed that the residuals are small and neutrally distributed around zero ($0.1 \pm 2.3$ and $0.0 \pm 1.5 \text{ mol kg}^{-1}$ for non-gridded and gridded data, respectively). The shapes of the profiles are highly comparable, confirming the suitability of the employed gridding method. Since the predictive parameters were measured more often than $A_{T}$ itself, values of $A_{T}^{\text{MLR}}$ could be obtained for 9 of the 10 cruises (no silicate data of cruise ANT-XXIV/2 are available). At any location, the values of derived variable $A_{T}^{\text{MLR}}$ are much more homogenous between the cruises than the original $A_{T}$ values, which are not further used in this study. It must be noted that this application of an MLR removes any conceivable time trend from the $A_{T}$ data if this trend is not reflected in any of the constituent parameters of $A_{T}^{\text{MLR}}$. This is in accordance with the common assumption that, as yet, there has been no anthropogenic influence on $A_{T}$ distributions since the onset of the industrial revolution.

$C_{TSR}$ and $C_{\text{residual}}$. As part of the TSR approach (Section 3.3), we performed an MLR between the measurements of $C_{T}$ and ancillary variables (salinity, $\theta$, depth, $A_{T}^{\text{MLR}}$, phosphate, silicate), both for the gridded dataset and for the non-gridded dataset. All relevant data from all cruises in this study (i.e., the full 1973–2008 era) were used in a single MLR. As outlined in Section 5.3, we suspect the presence of significant inaccuracies in some of the measurements of $O_{2}$.

To avoid complicating the attribution of resulting time trends in $C_{\text{residual}}$, we employed the MLR did not use $O_{2}$ as an estimate of remineralization but relied solely on phosphate and silicate for this purpose. This is akin to the approach of Friis et al. (2005), who opted for the use of a nutrient (phosphate) instead of $O_{2}$-based AOU, because use of the latter resulted in a non-normal and depth-varying distribution of residuals. The residuals of the regression (Fig. 7, panels B, D) are reasonably small ($-0.1 \pm 2.9$ and $-0.1 \pm 1.9 \text{ mol kg}^{-1}$ for non-gridded and gridded data respectively) and provide confidence that a suitable selection of independent parameters was chosen. The slanted shape of the residuals profile does not jeopardize our application, since we are solely interested in the time trends of the residuals, rather than their actual values.

5.5. Determination of time trends along the section

For each of the measurements (and derived variables) of interest, time trends were determined at each of the grid points as follows: of each of the cruises, the value of the grid point of interest and those of the grid points immediately surrounding it, were extracted. These values (up to 90 for each grid point: there are up to 10 cruises present at each grid point, and each grid point is surrounded by up to 8 other grid points) were regressed against their time of sampling, using an ordinary least squares linear fitting routine. All grid points weighted equally in the regression. This procedure makes the results slightly less sensitive to an occasional outlying value in the grids. Since no resolvable gradients are expected on the short spatial scale from one grid point to another, this step does not sacrifice spatial resolution. The results of the regression at each grid point allow for
the derivation of parameter values for those years where data is not available. In general, trends derived in this way in the upper ∼400 m of the Weddell Gyre should not be taken to be representative of the underlying data, due to seasonality in the upper shallow waters and the limited resolution of used grid relative to the vertical variability of the water column at these depths. However, trends in $C_{\text{residual}}^{\text{CSR}}$ do allow for interpretation in the shallow water column (Section 3.3).

To illustrate this approach of linear fitting through gridded data, we process data of CFC-12. Fig. 8 shows the concentrations of CFC-12 in 1992 as inferred from the time trends through the measurements obtained on the 7 coverings of the section (AJAX, 1984 to ANT-XXII/3, 2005). Also shown are actual measurements in 1992 (ANT-X/4), as well as the inferred time trends and the uncertainty associated with these time trends. The inferred concentrations in 1992 compare very well with the gridded data of ANT-X/4 (slope of regression of data below 1000 m depth: $0.98 \pm 0.02$, $r^2=0.87$, $p < 0.001$).

Even though the results obtained from CFC-12 serve an illustrative purpose only, we note that the use of linear regressions for CFC-12 does not do justice to the well known, distinctly non-linear concentration history of this compound in the atmosphere and the surface ocean. However, the stabilization and decrease of the atmospheric concentration of CFC-12 since approximately 2003 has not likely penetrated into the deep Weddell Sea yet (Klatt et al., 2002; Huhn et al., 2008). Therefore, an approximately linear rise in interior ocean concentrations may still be expected, and is indeed observed (Fig. 9, see text Section 5.6 for details).

5.6. Determination of time trends in water mass cores

The determination of time trends at fixed locations (latitude, depth) as outlined in Section 5.5, yields results that may be plotted to reveal the spatial pattern of such trends (for example, Fig. 8C). However, the results of that procedure may occasionally be ambiguous not only because of the sometimes small amount of samples represented by each grid point, but also because of hydrographical variability at each grid point. For example, the location of a particular water mass may vary somewhat through time and is thus not always present at the same location on the grid. Detection and quantification of time trends at such a location may therefore be jeopardized. To ensure that time trends within the proper cores of water masses are nonetheless optimally quantified, an additional analysis of the data was performed in which all grid points that belonged to the core of a particular water mass (as determined by their $S$ and $\theta$ properties, see Table 2) were pooled, and time trends were determined for the data in each of these data pools. This procedure was performed for both the gridded and the non-gridded data, again in order to be able to verify that no inaccuracies result from the gridding routine. The time trends were determined by calculating for each cruise the mean values of the data in the water mass cores. Subsequently, an ordinary least squares linear fit against time was determined through these averages. A sensitivity analysis was performed using a simple statistical model. We assume that the remaining inaccuracy (after the IWDW/uWSDW-adjustment) of the measurements of $C_T$ performed before the introduction of CRM (i.e., the cruises in the period 1973–1992) is smaller than 4 µmol kg$^{-1}$. The subsequent 6 cruises did use CRM and are assumed to be accurate to within 2 µmol kg$^{-1}$. Under those assumptions, and taking into account the analytical noise in the measured $C_T$ data (Section 5.1), trends smaller than circa 1 µmol kg$^{-1}$ decade$^{-1}$ fall within the statistical uncertainty of the method (at the $p < 0.05$ level).

![Fig. 9. Time trends in the gridded data of CFC-12 (pmol kg$^{-1}$ decade$^{-1}$) in the upper shallow waters and in the cores of three water masses (WDW, WSDW, WSBW; see Table 2), determined using ordinary least squares regression. See text Section 5.6 for details.](image-url)

5.7. Determination of $C_{\text{ant}}^{\text{TrOCA}}$ for 2005

For the sake of comparison with the findings of previous studies, the concentration of $C_{\text{ant}}$ along the section is determined for the nominal year 2005 using the TrOCA method (Section 3.1.3). The required values of $O_2$, $C_T$ and $A_T$ (or rather $A_T^{\text{MLR}}$, Section 5.4) are obtained by taking the mean values of all cruises in the time interval from 2002 to 2008. We use the same $\theta$-based TrOCA$^{\text{MLR}}$-parameterization as used by Lo Monaco et al. (2005b), which is only a slight adaptation of the parameterization originally provided by Touratier and Goyet (2004b).

5.8. The carbonate system of the Weddell Gyre in a high-CO$_2$ world

The continued uptake by the oceans of anthropogenic CO$_2$ from the atmosphere will cause shifts in the oceanic carbonate system. Most notably, a strong reduction is predicted of the concentrations of carbonate ion [CO$_3^{2-}$] and hydroxide ion [OH$^-$]. These changes are of major importance for the solubility of (biogenic) CaCO$_3$ (Feely et al,
2004; Orr et al., 2005) and for the speciation of trace metals (Millero et al., 2009). In order to briefly investigate the presence of these effects in the Weddell Gyre, values were calculated of $[\text{CO}_3^{2-}]$, $[\text{pH}]$ (representing the decreasing [OH⁻]⁻), and of the saturation states of the CaCO₃-structures aragonite and calcite ($\Omega_{\text{AR}}$ and $\Omega_{\text{CA}}$) from the gridded data of [S, T, $\text{C}_T$, $\text{AM}_{\text{MAR}}$, phosphate and silicate] using CO2SYS for MATLAB (van Heuven et al., 2009). Trends were determined in these data as in Section 5.6.

6. Results

6.1. Spatial distribution of time trends along the section

CFC-12: The pattern of trends found in CFC-12 (Fig. 8C) in the deep waters reflects current knowledge about the ventilation processes of the Southern Ocean (e.g., Klatt et al., 2002). The strongest sub-surface increases are visible in the WSBW, flowing eastward along the southern side of the Mid-Atlantic Ridge (MAR), and along the Antarctic continental slope in the westward flowing water that makes up the southern limb of the Weddell Gyre. The core of the WDW (at 500–1500 m, 57–63°S) shows a very low rate of increase in CFC-12. Because the CFC-12 concentrations at the surface of the water column tightly track the (distinctly non-linear) atmospheric CFC-12 concentration history, the method of linear fitting is not applicable at these shallower depths, as is also evidenced by the high uncertainties associated with the trends (Fig. 8D). Therefore, results obtained in the upper 400 m will not be discussed and should not be taken to accurately reflect the rates of accumulation of CFC-12. In deeper waters, this problem is likely not yet as prominent (see Section 5.1). A detailed look at the trends in the cores of the water masses (Fig. 9, Table 5) shows the CFC-12 to still increase approximately linearly.

C₇: The spatial distribution of determined time trends in C₇ (Fig. 10A) qualitatively resembles that of CFC-12 in the deep region of the Weddell Gyre (Fig. 8C). Notably in the WSBW and the deeper ranges of the WSDW, rates of increase of C₇ are between 0.5 and 1.75 $\mu$mol kg⁻¹ decade⁻¹. A spatial distinction is observed between the cores of the increases in the southern and northern limb of the Weddell Gyre, in agreement with the pattern of trends in CFC-12. Again, we consider trends in C₇ that were determined in the upper 400 m of the water column not to accurately reflect real trends. It is interesting to note, though, that a near-zero (or even negative) rate of increase, associated with the upwelling region south of ~60°S, prominently appears, as does an area of strong uptake (rates over 5 $\mu$mol kg⁻¹ decade⁻¹) to the north of this divergence zone.

The near-zero rate of increase of C₇ within the WDW has been dictated by the method. The inherent assumption of a constant C₇ in the WDW is largely corroborated by the time trends in CFC-12, which are very small there (only about 30% of the bottom water trends). Additionally, we note again that pre-correction values of C₇ in the WDW did not exhibit a trend, and that the applied corrections are small. The positive trend in C₇ is also visible along the Antarctic continental slope from circa 1000 m downward, and tentatively also around 57°S, as a protrusion from the surface downward to circa 2000 m depth. These columnar features at the southern and northern limits of the Weddell Gyre resemble the observed spatial distribution of CFC-12 and the trends therein (Fig. 8A, B and C). Discussing data of CFC-11, the northern structure is interpreted by Klatt et al. (2002) as resulting from vertical mixing at the interface between the ACC and the Weddell Gyre, while the southern feature reflects the inflow from east of the Weddell Gyre of recently ventilated water.

By simple linear regression of the time trends in C₇ versus those in CFC-12 for all grid points below 750 m and between 57°S and 68°S we find a significant correlation (Fig. 11):

$$dc_7/dt = 8.4 \pm 0.4 \times d\text{CFC}12/dt - 0.23 \pm 0.04$$

(n = 1875, $R^2 = 0.48$, $p < 0.001$)  
(8)

The above relationship between the increases of CFC-12 and C₇ is not highly significant. A better correlation than this is not likely to be expected, in part due to different equilibration times of the gases in the region of water mass formation, measurement inaccuracies and the distinctly different atmospheric histories of these gases (for a detailed treatment of the latter factor, see Tanhua et al., 2006). However, the relationship provides evidence that the observed distribution of time trends in C₇ is consistent with the much more clearly resolved accumulation of CFC-12 in the deep Weddell Sea.

TSR: The spatial distribution of time trends in the derived concentrations of TSR along our section (see Fig. 10B) is not at all in agreement with the time trends found directly in the originally measured C₇ (Fig. 10A). Strongly positive trends in TSR can be seen from the Antarctic continental slope northward to 62°S, whereas the WSBW shows near-zero or negative trends. The observed pattern of time trends in TSR does not conform to known hydrographical pathways as exemplified by CFC-12 (Fig. 8C), suggesting that the observed time trends in TSR are likely spurious. The erratic pattern of trends in TSR is found to be mainly attributable to localized biases in data of $\text{O}_2$ (Section 5.3), which results in a reduced ability to determine time trends through use of this parameter. This sensitivity of the TSR approach (and likely other approaches that use $\text{O}_2$) to biases of measurements of $\text{O}_2$ illustrates the need for future more accurate determinations of the dissolved $\text{O}_2$.

Table 5

The time trends in C₇ (derived in both the non-gridded and the gridded data) and in C₇, C₇, and CFC-12 as determined within the cores of each of the four water masses SHALLOW, WDW, WSDW and WSBW. Definitions of the water mass cores are given in Table 2. Significant time trends are in bold print. Time trends in the shallow waters that are expected to be susceptible to the influence of seasonality at the surface are shown in brackets. As opposed to the underlying data of the other results in this table, the CFC data were not normalized in the WDW/uWSDW and indicate that the core of the WDW is not entirely ventilated. Rather, it shows a rate of increase of about 30% of that of the WSBW. Although this suggests that an upward correction may conceivably have to be applied to the C₇-based results, we opt not to perform this adjustment. See text Section 7.2.

<table>
<thead>
<tr>
<th>Water mass</th>
<th>C₇</th>
<th>C₇</th>
<th>C₇</th>
<th>C₇</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(μmol kg⁻¹ decade⁻¹)</td>
<td>Gridded data</td>
<td>Gridded data</td>
<td>Gridded data</td>
</tr>
<tr>
<td>SHALLOW</td>
<td>+1.846 ± 0.693</td>
<td>+2.979 ± 3.181</td>
<td>+3.878 ± 3.656</td>
<td>+0.332 ± 1.797</td>
</tr>
<tr>
<td>WDW</td>
<td>+0.086 ± 0.298</td>
<td>-0.213 ± 0.720</td>
<td>+0.340 ± 0.362</td>
<td>-0.436 ± 0.520</td>
</tr>
<tr>
<td>WSDW</td>
<td>+0.241 ± 0.318</td>
<td>+0.176 ± 0.321</td>
<td>+0.268 ± 0.613</td>
<td>-0.363 ± 0.636</td>
</tr>
<tr>
<td>WSBW</td>
<td>+1.250 ± 0.563</td>
<td>+1.151 ± 0.563</td>
<td>+0.512 ± 0.832</td>
<td>+0.445 ± 0.405</td>
</tr>
</tbody>
</table>
The atmospheric concentration histories of \( C_{\text{ant}} \) in the WSBW is clearly smaller than the time trend in measured \( C_T \) (Fig. 10A). This is further quantified in below Section 6.2. However, away from the core of the WSBW, several features of the distribution of the time trends in measured \( C_T \) are reflected in the distribution of time trends in \( C_{\text{TSR}} \). Most notably, the columnar feature adjacent to the Antarctic continental slope (see also Section 6.1) and the southernmost deepest core (66°S–69°S, >3500 m) are observed (although their magnitude is slightly smaller than the time trends observed directly in measured \( C_T \), Fig. 10A). Additionally, in both \( C_T \) and \( C_{\text{TSR}} \), a strong time trend is seen in the upper waters (<500 m) north of the diversion zone at 60°S. These results indicate that at these locations, a significant fraction of the time trends observed in measured \( C_T \) may be attributed to uptake of \( C_{\text{res}} \) at the surface of the Weddell Sea.

Lastly, a striking difference between time trends in \( C_T \) and \( C_{\text{TSR}} \) is noted that, as we will argue, may be explained by the fact that values of (and time trends determined in) \( C_{\text{TSR}} \) are insensitive to seasonality. Namely, in the upper waters near the Antarctic continent (south of 66°S and shallower than 500 m), the \( C_{\text{TSR}} \) shows a marked increase with time (about 2–3 \( \mu \text{mol kg}^{-1} \text{ decade}^{-1} \); Fig. 10D) indicating that the anthropogenic component of \( C_T \) is increasing there. This increase is not evident from in \( C_T \) or \( C_{\text{TSR}} \), which both show a negative time trend (Fig. 10A and C). Both these latter two inferred decreases are conceivably strongly influenced by the combination of strong seasonal variability in these upper waters and the unbalanced seasonal distribution of the cruises, and are indeed statistically not significant (data not shown). Because the natural seasonal variability in \( C_T \) over the 1973–2008 era is by the TSR method related to independent parameters (mainly temperature), this variability is nicely replicated in the values of \( C_{\text{TSR}} \). However, the
gradually increasing \( C_{\text{ant}} \) in these waters is not expressible in terms of an independent variable, and is therefore visible as a time trend in \( C_{\text{TSR residual}} \).

6.2. Time trends determined in water mass cores.

Fig. 12 and Table 5 present the determined time trends in the four water masses defined in Table 2 (SHALLOW, WDW, WSDW, WSBW). On the one hand the time trends of \( C_T \) in the WSBW are quite small and non-significant at \( +0.241 \pm 0.318 \) and \( +0.176 \pm 0.321 \text{ mol kg}^{-1} \text{ decade}^{-1} \) for the gridded and non-gridded data, respectively. On the other hand, the time trends of \( C_T \) in the WSBW are sizable and significant at \( +1.151 \pm 0.563 \) and \( +1.250 \pm 0.563 \text{ mol kg}^{-1} \text{ decade}^{-1} \) for the gridded and non-gridded data, respectively. These values resemble the results shown for the WSBW in the section plot of the time trends in \( C_T \) (Fig. 10A), providing confidence that the results are robust. No significant trends in (gridded or non-gridded) \( C_T \) are found in the three overlying water masses, although there is a hint at increase in the shallow waters (\( < 200 \text{ m} \)), notwithstanding seasonality and the upwelling character of the SHALLOW water mass at the defined 58°S–63°S latitude (Table 2).

The time trends in \( C_{\text{TSR}} \) (deemed to represent influences on \( C_T \) of natural variability) are not significantly different from zero in the three deeper water masses. This is deemed to confirm that there are no systematic time trends of hydrographic or biogeochemical origin over the 35 yr. The variability in \( C_T \) in the upper waters (Fig. 12; top panels of leftmost two columns), that likely is a result of uneven distribution of sampling in various seasons, is partly reproduced by \( C_{\text{TSR}} \), suggesting that seasonality indeed obscures conceivable trends in \( C_T \) there.

The time trend of \( C_{\text{TSR residual}} \) (deemed to represent the time trend of \( C_{\text{ant}} \)) in the WSBW equals about one-third of that observed in measured \( C_T \): \( 0.445 \pm 0.405 \text{ mol kg}^{-1} \text{ decade}^{-1} \). This difference was also observed in the section plots of trends (Fig. 10A and D; text Section 6.1) and will be further discussed in text Section 7.3. The time trends in the other three water masses are not significantly different from 0. Finally, no increase in \( C_{\text{TSR residual}} \) is observed in the upper waters, suggesting very little penetration of \( C_{\text{ant}} \) into the upwelling waters.

6.3. Determined \( C_{\text{TSR residual}} \)

The section of \( C_{\text{ant}} \) derived using the TrOCA method (Fig. 13) resembles the distribution of the concentration of (and trends in) CFC-12 (Fig. 8). Specifically, the low values in the WDW (circa 10 \text{ mol kg}^{-1}) and higher concentrations in two distinct bottom water cores (circa 16 \text{ mol kg}^{-1}) are clearly discernible in both properties. These values are in general accordance with earlier
6.4. The carbonate system of the Weddell Gyre in a high-CO2 world.

Significant decreasing time trends are observed for all calculated parameters of the carbonate system ([CO$_3^{2-}$], pH, $\Theta_{arb}$ and $\Omega_{A}$) in the shallow waters ($<200$ m; Table 2) and the WSBW (Fig. 14). For the shallow waters these trends exceed beyond the expected strong influence of seasonality there. In the WSBW, the time trend in the concentration of carbonate ion is $-0.7 \pm 0.3$ mol kg$^{-1}$ decade$^{-1}$, which equates to almost $-1\%$ per decade. Orr et al. (2005) used a set of ocean carbon cycle models to predict the global evolution of [CO$_3^{2-}$] for the 2000–2100 era under a ‘business-as-usual’ scenario for anthropogenic emissions of CO$_2$. For the surface waters of the Southern Ocean, they computed an approximately linear trend of about $-5$ mol kg$^{-1}$ decade$^{-1}$ (their Fig. 7). The fact that we observe a time trend in $C_T$ would be overestimated by about 25% (i.e., $+1.5$ instead of $+1.2$ mol kg$^{-1}$ decade$^{-1}$). We are confident, however, that any remaining bias in the GEOSECS is of limited influence on our results. Some justification for the used correction of $-0.6$ mol kg$^{-1}$ is found in the literature. Peng and Wanninkhof (2010) determined corrections for $C_T$ for individual GEOSECS stations in the Atlantic Ocean. Their results indicate that $C_T$ at the stations that are used in this study should be corrected by between $0 \pm 4$ mol kg$^{-1}$ (their Fig. 5) and $-2 \pm 4$ mol kg$^{-1}$ (their Fig. 7). The fact that we observe a time trend in $C_T$ also in the waters that were not sampled by GEOSECS (Figs. 5 and 10A) is an additional indication that the derived results are robust and not an artifact of GEOSECS bias.

7.1. GEOSECS bias

The GEOSECS (1973) data are so far in the past compared to the 1984–2008 era of the other cruises that a conceivably remaining bias in the GEOSECS data will have excessive leverage in the linear regression. For example, if these data would, after the WDW normalization, still be $2$ mol kg$^{-1}$ too low, time trends in $C_T$ would be overestimated by about 25% (i.e., $+1.5$ instead of $+1.2$ mol kg$^{-1}$ decade$^{-1}$). We are confident, however, that any remaining bias in the GEOSECS is of limited influence on our results. Some justification for the used correction of $-0.6$ mol kg$^{-1}$ is found in the literature. Peng and Wanninkhof (2010) determined corrections for $C_T$ for individual GEOSECS stations in the Atlantic Ocean. Their results indicate that $C_T$ at the stations that are used in this study should be corrected by between $0 \pm 4$ mol kg$^{-1}$ (their Fig. 5) and $-2 \pm 4$ mol kg$^{-1}$ (their Fig. 7). The fact that we observe a time trend in $C_T$ also in the waters that were not sampled by GEOSECS (Figs. 5 and 10A) is an additional indication that the derived results are robust and not an artifact of GEOSECS bias.

7.2. Effects of WDW normalization

The absence of the trends in $C_T$ in the WDW (Fig. 12, second row, first two columns) indicates that the normalization of values in the WDW was valid and effective. However, the spread that was observed in the WDW before normalization may have contained an obscured real-world trend. The detection of trends of CFC-12 hints at the slow but definite ventilation of this water mass. The trend in CFC-12 in the WDW is $0.041 \pm 0.025$ pmol kg$^{-1}$ decade$^{-1}$, versus $0.138 \pm 0.032$ pmol kg$^{-1}$ decade$^{-1}$ in the WSBW (see Table 5, Fig. 9). Translated to the results for $C_{int}$, this suggests that the real-world trends in WSBW and WDW

Fig. 14. Time trends in the cores of four water masses (SHALLOW, WDW, WSDW, WSBW; see Table 2), determined using ordinary least squares regression, of the calculated values of (A) the carbonate ion concentration [CO$_3^{2-}$]; (B) the concentration of hydroxide ion ([OH$^{-}$]), expressed as in situ pH (see text section 6.4); (C) the saturation state $\Omega$ of aragonite; (D) the saturation state $\Omega$ of calcite. Trends in (A) in mol kg$^{-1}$ decade$^{-1}$, trends in (B, C and D) in units of decade$^{-1}$. For the last two panels (C and D), values of $\Omega$ below 1 indicate that the seawater is undersaturated with respect to the aragonite or calcite crystalline state of CaCO$_3$, respectively. See Sections 5.8 and 6.4 for details. All results are based on data that were adjusted for consistency in WDW/μWSDW.
conceivably may be as large as \( +1.65 \) and \( +0.49 \mu mol \ kg^{-1} \ decade^{-1} \), respectively. However, the trend in non-adjusted data of \( C_t \) in the WSBW (excluding the strongly outlying data of ANT-V/2&3 and AJAX) is \( 1.1 \pm 1.0 \mu mol \ kg^{-1} \ decade^{-1} \), (i.e., less clearly resolved, but of similar slope as the adjusted data). Therefore, although we acknowledge the possibility that real-world trends in the WSBW might be up to 30% higher than the \( +1.2 \pm 0.6 \mu mol \ kg^{-1} \ decade^{-1} \), we opt not to perform such an upward correction of our results.

7.3. Attribution of trends

We show a distinct and unambiguous increase in \( C_t \) in the WSBW of about \( 1.2 \pm 0.6 \mu mol \ kg^{-1} \ decade^{-1} \). This trend is only partly consistent with the significant time trend in \( C_{\text{residual}}^{\text{TSR}} \) (about \( 0.4 \pm 0.4 \mu mol \ kg^{-1} \ decade^{-1} \)), deemed representative of an increase of \( C_{\text{ant}} \) over time. However, there is no significant time trend in the WSBW of \( C_T \) \( (0.512 \pm 0.832 \mu mol \ kg^{-1} \ decade^{-1}) \), implying that there are no clear systematic trends of biogeochemical and/or hydrographic origin over the 35 yr that would explain the remainder of the observed time trend in \( C_t \). In order to more satisfyingly attribute the observed time trend in \( C_t \) to either natural variability or accumulation of anthropogenic \( \text{CO}_2 \), we consider below the alternative lines of evidence, and eventually opt to ascribe the entire increase of \( C_t \) (i.e., \( 1.2 \pm 0.6 \mu mol \ kg^{-1} \ decade^{-1} \)) for accumulation of anthropogenic \( \text{CO}_2 \) in the WSBW.

From an absence of trends in (IWDW/ruWSDW-normalized) \( \text{NO}_3, \text{PO}_4 \) and \( \text{O}_2 \), we rule out enhanced remineralization as cause of the observed trend in \( C_t \). Due to the limited accuracy of the \( A_t \) data and the lack of time trends in \( A_t^{\text{AMR}} \) (Section 5.4) no such statement can be made for the influence of \( \text{CaCO}_3 \) dissolution, but the rate of that process and the variability therein may be considered to be too small to suggest an explanation (Sabine et al., 2002). Alternatively, part of the time trend in \( C_t \) in the WSBW might be the result of a changing formation process of the water mass. In order to explain the observed increasing temperature of the WSBW, Fahrbach et al. (2004) suggest that increases in the penetration of CDW into the Weddell Sea and in the amount of entrainment of (CDW-derived) WDW during the convective formation of WSBW from Ice Shelf Water (ISW) would increase the temperature of the WSBW. Lenton et al. (2009) provide a tentative mechanism for this increased penetration of CDW involving anthropogenically driven changes in atmospheric circulation. Such increased entrainment of WDW would inevitably also increase the \( C_t \) of the WSBW and can be quantified as follows. The WSBW is considered to be a mixture of Ice Shelf Water and near-continental slope WDW (ISW: \( \theta = -1.85 \, ^\circ\text{C} \), salinity-normalized \( C_t = 2250 \mu mol \ kg^{-1} \); WDW: \( \theta = 0.25 \, ^\circ\text{C} \), salinity-normalized \( C_t = 2285 \mu mol \ kg^{-1} \)), with a gradient of the mixing line of \( 16.7 \mu mol \ kg^{-1} \cdot ^\circ\text{C}^{-1} \) (Hoppema et al., 1998). This gradient multiplied with the observed time trend of \( \theta \) in the WSBW of \( +0.015 \pm 0.006 \, ^\circ\text{C} \ decade^{-1} \) (comparable to the trend observed by Fahrbach et al., 2004) yields a time trend of \( C_t \) of \( 0.25 \pm 0.10 \mu mol \ kg^{-1} \ decade^{-1} \). In other words, an increase in the amount of WDW entrained by ISW during the formation of WSBW may at most explain \( \sim 20\% \) of the observed trend in \( C_t \).

Overall, we reckon that the observed increase of \( C_t \) in the WSBW at a rate of about \( 1.2 \pm 0.6 \mu mol \ kg^{-1} \ decade^{-1} \) may best be completely ascribed to a true invasion of anthropogenic \( \text{CO}_2 \) into the deep Weddell Gyre. This attribution is at least partly supported by the significant time trend in \( C_{\text{residual}}^{\text{TSR}} \) (\( 0.4 \pm 0.4 \mu mol \ kg^{-1} \ decade^{-1} \)). More importantly, the strong spatial correlation of the increase of \( C_t \) and the increase of CFC-12 (Fig. 11), is most convincing. However, the given rate of \( 1.15 \pm 0.56 \mu mol \ kg^{-1} \ decade^{-1} \) is deemed to be an upper limit, because natural variability of hydrography may account for a part of the trend (\( 0.25 \pm 0.10 \) to \( 0.5 \pm 0.8 \mu mol \ kg^{-1} \ decade^{-1} \), as suggested above by the mixing consideration and the TSR approach, respectively).

7.4. Comparing the time trend of \( C_{\text{ant}} \) with other estimates

Hoppema et al. (2001), following the method of Poisson and Chen (1987), report a ‘negligible’ increase in \( C_{\text{ant}} \) between 1973 and 1998 from a comparison of cruise data from the mid-1990s with data of GEOSECS and AJAX. Although no significant change was determined, the authors concluded from statistical considerations that the increase of \( C_{\text{ant}} \) in the WSBW is almost certainly smaller than \( 2 \mu mol \ kg^{-1} \ decade^{-1} \). That upper limit estimate is in agreement with the \( 1.2 \pm 0.6 \mu mol \ kg^{-1} \ decade^{-1} \) found in the present study. Another recent determination of \( A_{\text{ant}} \) in the Weddell Sea, also along the 0°-meridian, relies on the eMLR method (Frisi et al., 2005; see text Section 3.2.3) to derive an increase of \( C_{\text{ant}} \) between the two cruises ANT-X/4 (1992) and ANT-XXIV/2 (2008) (Hauck et al., 2010). The magnitude of the reported increases over 16 yr is similar to our findings. However, for individual water masses significant discrepancies exist with our results. Firstly, in the WSDW, the reported pronounced increase (\( \sim 1.5 \rightarrow 2.0 \mu mol \ kg^{-1} \) over 16 yr), is incompatible with the about fivefold smaller and non-significant time trend in \( C_T \) found in our study (\( 0.2 \pm 0.3 \mu mol \ kg^{-1} \ decade^{-1} \), Fig. 12, Table 5). Moreover, we do not find a significant time trend of \( C_{\text{residual}}^{\text{TSR}} \) (\( -0.4 \pm 0.6 \mu mol \ kg^{-1} \ decade^{-1} \), Fig. 12, Table 5) either, representative of \( C_{\text{ant}} \). In favor of the findings of Hauck et al., one might argue that the procedure of WDW normalization performed in the present study has inadvertently also removed the trend in the WSDW. However, that argument is mutually exclusive with our concurrent finding of a significant positive trend in \( C_T \) in the WSBW (about \( +1.2 \pm 0.6 \mu mol \ kg^{-1} \ decade^{-1} \)), where Hauck et al. report an increase that is significantly smaller than \( 1 \mu mol \ kg^{-1} \) over 16 yr. On the other hand, the reported low increase in the WSDW does coincide with our TSR-based results for \( C_{\text{residual}}^{\text{TSR}} \) (WSBW + \( 0.4 \pm 0.4 \mu mol \ kg^{-1} \ decade^{-1} \)). However, we do not hold this resemblance to demonstrate the veracity of the results of either study, mainly in light of the fact that the two studies indicate different water masses to dominate the storage of \( C_{\text{ant}} \) (namely, WSDW in the study of Hauck et al., and WSBW in the present study). Instead, the discrepancies between the two studies may be due to the fact that the used datasets are not the same. Specifically, although Hauck et al. (2010) showed the overall quality of the used data to be satisfactory, we have chosen to exclude the southerly deep \( C_T \) measurements (south of 63°S and deeper than 1500 m) of the ANT-X/4 (1992) cruise, which we consider to be erroneously high by up to \( 7 \mu mol \ kg^{-1} \) on the basis of a regression versus \( \theta \) (see above Section 5.1). The exclusion we performed (and the additional exclusion of \( C_T \) measurements of AJAX, 1983) is corroborated by the distribution of time trends in our remaining dataset of actually measured \( C_T \) (Fig. 10A), which closely resembles the distribution of time trends of CFC-12 in the deep region of the Weddell Gyre (Section 6.1; Fig. 8C), comprising the WSDW and WSBW. In the study of Hauck et al., the presence of a bias in part of the data may have led to increased uncertainty (but not necessarily inaccuracy) in the applied eMLR and the results derived from it. Additionally, the low number of samples qualifying as WSBW in the study of Hauck et al. (Fig. 5) may have affected their results obtained for this water mass.

7.5. The concentration of \( C_{\text{ant}} \) derived from the observed decadal time trend

The Transient Steady State approach (Tanhua et al., 2007; Section 3.1.5) implies that the per decade increase in \( C_{\text{ant}} \)
represents a fraction of about 0.2 ± 0.03 of the total concentration of \( C_{\text{ant}} \) (i.e., \( C_{\text{ant}} \) [\( \mu \text{mol kg}^{-1} \]) = 5.1 \Delta C_{\text{ant}} \) [\( \mu \text{mol kg}^{-1} \text{ decade}^{-1} \}); notice the informal use of units in this expression). Assuming that the time trend of \( C_{\text{ant}} \) in the WSBW equals that of \( C_T \) (i.e., about 1.2 ± 0.6 \( \mu \text{mol kg}^{-1} \text{ decade}^{-1} \)), we infer a \( C_{\text{ant}} \) of 6 ± 3 \( \mu \text{mol kg}^{-1} \). We will take 1995 as the year for which this estimate is valid, that is, slightly more recent than the midpoint of the 1973–2008 period. The error bound of this estimate is not formally determined, due to several assumptions inherent to the taken approach. Nonetheless, the estimate may serve as a rough guide to assess the validity of our study versus various other estimates of \( C_{\text{ant}} \) previously reported by other investigators.

Table 6 lists the \( C_{\text{ant}} \) estimates derived in this study, as well as various estimates of the concentration of \( C_{\text{ant}} \) in the Weddell Gyre that were obtained by other investigators (Poission and Chen, 1987; Lo Monaco et al., 2005b; Waugh et al., 2006; Vázquez-Rodríguez et al., 2009). Poission and Chen (1987), using a back-calculation approach (Section 3.1.1), reported a concentration of \( C_{\text{ant}} \) in the deep Weddell Sea (for 1984) of circa 6 ± 5 \( \mu \text{mol kg}^{-1} \), which is in agreement with the results of this study. However, several estimates of \( C_{\text{ant}} \) in the WSBW that have been derived using the \( \Delta C^* \) method are close to zero (Sabine et al., 2004; Waugh et al., 2006; Vázquez-Rodríguez et al., 2009). On the other hand, results from application of the TTD approach (e.g., Waugh et al., 2006; Vázquez-Rodríguez et al., 2009) are generally somewhat higher than our results. Both authors report estimates of \( C_{\text{ant}} \) in the WDW and the (largely WSDW-derived) AABW at 30 E of about 9 \( \mu \text{mol kg}^{-1} \). These estimates are significantly higher (WDW) or slightly higher (AABW) than the results obtained in the present study (0 and 6 ± 3 \( \mu \text{mol kg}^{-1} \), respectively). On the other hand, by assuming an undersaturation of dissolved oxygen of 12%, Lo Monaco et al. (2005a, 2005b) used the \( C_T \) method to determine a \( C_{\text{ant}} \) concentration in 1996 of circa 22 \( \mu \text{mol kg}^{-1} \) in the core of the AABW at 30 E. This estimate is very significantly higher than what is obtained in our study using the Transient Steady State method.

Results of the applications of the TrOCA method agree fairly well between the different studies, which is not surprising given the strict definition and application of the method. However, all TrOCA-based estimates for the WSBW (or AABW) (all around 15 \( \mu \text{mol kg}^{-1} \)) are higher than results obtained by our study or by studies employing the TTD or \( \Delta C^* \) methods.

Obviously, the highest of the above discussed, previously published estimates of \( C_{\text{ant}} \) for the WSBW/AABW presented in Table 6, are incompatible with the results of this study. We here assume the central argument of the Transient Steady State method to be valid. That is, the exponential accumulation of \( C_{\text{ant}} \) in the atmosphere and the ocean surface will lead to exponentially increasing concentrations in the ocean interior (Tanhua et al., 2007). The time trends in \( C_{\text{ant}} \) that would therefore necessarily be associated with high concentrations of \( C_{\text{ant}} \) (for example, a \( C_{\text{ant}} \) of ~20 \( \mu \text{mol kg}^{-1} \)) requires a trend in \( C_{\text{ant}} \) of ~4 \( \mu \text{mol kg}^{-1} \text{ decade}^{-1} \) are irreconcilable with the observed time trends in measured \( C_T \) (about +1.2 ± 0.6 \( \mu \text{mol kg}^{-1} \text{ decade}^{-1} \)). Moreover, the trends in \( C_T \) observed in our study are deemed to represent an upper limit of the trend in \( C_{\text{ant}} \) (see text Section 7.3), which further reduces the likelihood that the highest previously published estimates of \( C_{\text{ant}} \) in Table 6 are accurate.

### 7.6. The rate of increase of the inventory of \( C_{\text{ant}} \) of the deep Weddell Gyre

The determined time trend in the concentration of \( C_{\text{ant}} \) along the section may be spatially extrapolated and integrated to obtain

<table>
<thead>
<tr>
<th>Source</th>
<th>( C_{\text{ant}} ) estimate (( \mu \text{mol kg}^{-1} ))</th>
<th>Nominal year</th>
<th>Longitude of section</th>
<th>Method</th>
<th>Remarks</th>
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<td><strong>Warm Deep Water</strong></td>
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<td></td>
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<td></td>
<td></td>
</tr>
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<td>~6</td>
<td>1996</td>
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<td>( C_T ) (assuming ( O_2 ) saturation)</td>
<td>From their Fig. 5A</td>
</tr>
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<td>Lo Monaco et al. (2005a)</td>
<td>~9</td>
<td>1996</td>
<td>30 E</td>
<td>( C_T ) (assuming 12% ( O_2 ) undersaturation)</td>
<td>From their Fig. 5B</td>
</tr>
<tr>
<td>Sabine et al. (2004)</td>
<td>~0</td>
<td>1996</td>
<td>30 E</td>
<td>( \Delta C^* )</td>
<td>From GLODAP data product</td>
</tr>
<tr>
<td>Lo Monaco et al. (2005b)</td>
<td>~6</td>
<td>1996</td>
<td>30 E</td>
<td>( \Delta C^* ) (assuming 12% ( O_2 ) undersaturation)</td>
<td>From their Fig. 4C</td>
</tr>
<tr>
<td>Waugh et al. (2006)</td>
<td>~0</td>
<td>1996</td>
<td>30 E</td>
<td>( \Delta C^* )</td>
<td>From their Fig. 6B</td>
</tr>
<tr>
<td>Vázquez-Rodríguez et al. (2009)</td>
<td>~1</td>
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<td>30 E</td>
<td>TTD</td>
<td>From their Fig. 4</td>
</tr>
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<td>30 E</td>
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<td>Lo Monaco et al. (2005b)</td>
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<td>TrOCA</td>
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</tr>
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<td>30 E</td>
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</tr>
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<td>0 E</td>
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</tr>
<tr>
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<td>0 E</td>
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<td>0 E</td>
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<td>From their Fig. 5A</td>
</tr>
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<td>Lo Monaco et al. (2005a)</td>
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<td>1996</td>
<td>30 E</td>
<td>( C_T ) (assuming ( O_2 ) saturation)</td>
<td>From their Fig. 5B</td>
</tr>
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<td>30 E</td>
<td>( \Delta C^* )</td>
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<td>~18</td>
<td>1996</td>
<td>30 E</td>
<td>( \Delta C^* ) (assuming 12% ( O_2 ) undersaturation)</td>
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<td>30 E</td>
<td>( \Delta C^* )</td>
<td>From their Fig. 6B</td>
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<tr>
<td>Vázquez-Rodríguez et al. (2009)</td>
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<td>1996</td>
<td>30 E</td>
<td>( \Delta C^* )</td>
<td>From their Fig. 4</td>
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<td>30 E</td>
<td>TTD</td>
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<td>Vázquez-Rodríguez et al. (2009)</td>
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<td>30 E</td>
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<td>30 E</td>
<td>TrOCA</td>
<td>From their Fig. 4A</td>
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<td>TrOCA</td>
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<td>0 E</td>
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a first estimate of the time trend of the inventory of $C_{\text{ant}}$ in the deep (below 3000 m) Weddell Gyre over the period of this study (i.e., 1973–2008), as follows. The mean rate of increase in $C_T$ (taken to represent an upper bound to rate of increase of $C_{\text{ant}}$, see Section 7.3) of all grid points along the section between 70°S and 55°S and below 3000 m depth is $0.9 \pm 0.4 \mu\text{mol} \text{kg}^{-1} \text{decade}^{-1}$. Assuming this rate of increase of the concentration to be representative of the deep Weddell Gyre as a whole (here taken as west of 20°E and deeper than 3000 m, and thus having a volume of approximately $11 \times 10^6 \text{km}^3$), the rate of increase of the inventory of $C_{\text{ant}}$ in the deep (below 3000 m) Weddell Gyre is calculated to be $12 \pm 6 \times 10^3 \text{gC yr}^{-1} \text{(TgC yr}^{-1}\text{), which is about 0.15} \pm 0.07\% \text{of the current rate of anthropogenic emissions. Please note that this rate of local storage of $C_{\text{ant}}$ does not include the additional $C_{\text{ant}}$ transferred into other oceans with the north-eastward spreading AABW. Moreover, the storage of $C_{\text{ant}}$ in the shallower layers (typically < 200 m), that actually have the highest $C_{\text{ant}}$ component, could not be included in this approximation due to seasonal variability.}

The calculated rate of storage of $C_{\text{ant}}$ in the deep Weddell Gyre appears to be compatible with the results of Anderson et al. (1991), who estimated an export of $C_{\text{ant}}$ from the continental shelf into the deep Weddell Gyre of $8–16 \times 10^6 \text{TgC year}^{-1}$ from observations in the Filchner Depression in the southern Weddell Sea in 1988–1989. The latter rate of export would on the one hand include the transfer with AABW into other oceans, yet on the other hand, just as in our study exclude the shallower layers.

8. Conclusions

Time trends in the concentration of $C_T$ were determined directly from measured values along the 0°-meridian in the Weddell Gyre in the Southern Ocean. A significant positive trend in $C_T$ of $+1.2 \pm 0.6 \mu\text{mol} \text{kg}^{-1} \text{decade}^{-1}$ is determined in the WSBW. The determined time trends in back-calculated preformed $C_T$ ($C_T^\text{TSR}$) appear affected by inaccuracies of the oxygen data. Within the observed trend in $C_T$, we attempted to separate the contributions of natural variability and the uptake of anthropogenic CO$_2$ from the atmosphere, by use of a novel MLR-based technique: Time Series Residuals (TSR). In the taken approach, trends in the residuals ($C_{\text{TSR}}^{\text{TSR}}$) of an MLR encompassing all data of 10 cruises are assumed to represent the anthropogenic component of the observed trends in $C_T$, whereas trends in the MLR-predicted $C_T$ values ($C_T^{\text{TSR}}$) are assumed to reflect natural variability in $C_T$. Use of this approach regretfully did not allow for a convincing attribution of the observed time trend in measured data of $C_T$ to either natural variability or uptake of anthropogenic CO$_2$ from the atmosphere.

However, the significant resemblance between the spatial distributions of time trends determined in $C_T$ and CFC-12 provides compelling evidence that the results reflect genuine changes in $C_T$ of the deep Weddell Gyre that are propagated from the surface into the interior. From a consideration of the formation process of the WSBW and observed temperature changes of that water mass, we rule out a strong influence on the observed time trend in $C_T$ of variable entrainment of WDW into the forming WSBW, thereby strengthening the case for an anthropogenic (rather than a hydrographic) origin of the observed increases in $C_T$ in the deep Weddell Gyre. If indeed assuming the trend in $C_{\text{ant}}$ to equal the trend in $C_T$ (i.e., the trend in $C_{\text{ant}}$ equals about $+1.2 \pm 0.6 \mu\text{mol} \text{kg}^{-1} \text{decade}^{-1}$), and further assuming an exponential buildup of $C_{\text{ant}}$ in the deep ocean (as in the atmosphere and surface ocean), we calculate a total concentration of $C_{\text{ant}}$ in the WSBW of $6 \pm 3 \mu\text{mol} \text{kg}^{-1}$ for the year 1995. This estimate is significantly lower than estimates obtained with the TrOCA method, but higher than what is generally obtained using the $\Delta C^\text{TSR}$ method. Results from investigators using the TTD method compare more favorably with our estimate. Extrapolating the determined rate of increase of the concentration of $C_{\text{ant}}$ to the deep Weddell Gyre as a whole (below 3000 m, west of 10°E), we obtain a rate of increase of the inventory of $C_{\text{ant}}$ of about $12 \pm 6 \text{TgC yr}^{-1}$ for 1995, or about 0.15% of current anthropogenic emissions to the atmosphere. This case study of the Weddell Gyre demonstrates the value of the direct determination of time trends of $C_T$ in the deep ocean.

9. Recommendations for future research

While we arguably have been successful in using historical data of $C_T$ to determine time trends in the deep Weddell Sea, we experienced difficulties in separating the natural and anthropogenic components of the observed changes, whether with the proposed TSR method or the classical $C_T^\text{TSR}$ approach. In part, this was due to uncertainties about the accuracy of the ancillary parameters required for such an exercise. Dataset compilation efforts like GLODAP and CARINA may to some extent eliminate systematic cruise biases of these properties. Nevertheless it has become obvious that further improvement of the original measurements is needed in future cruises. Variable biases of up to 3% are quite common in the used datasets of nutrients and dissolved O$_2$, while in fact the state-of-the-art does permit an order of magnitude lower uncertainty (i.e., circa 0.2%), approaching what is common nowadays. Furthermore, it will be crucial for further constraining the oceanic uptake and storage of anthropogenic CO$_2$ on decadal time scales, both locally in the Weddell Gyre and in the ocean at large.

Acknowledgments

The diligent work performed by the officers, crew and scientists that participated in the many expeditions of which results are used in this study is immensely appreciated. Without this measurement effort, sustained over more than three decades already, this work would not have been possible. The excellent cooperation with the officers, crew and scientific party during PFS Polarstern expedition ANT-XXIV/3 is specifically acknowledged. Valuable suggestions by two anonymous reviewers have helped to substantially improve this manuscript.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.dsr2.2011.08.007.


