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Different oceanic features of anthropogenic CO₂ and CFCs

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Abstract The relationship between CFC-11 and anthropogenic CO₂ ($\Delta\text{DIC}_{\text{ant}}$) concentrations in the world ocean are evaluated based on a simple off-line tracer ventilation model. Since the different solubility characteristics of CFC-11 and $\Delta\text{DIC}_{\text{ant}}$ cause major differences in their oceanic uptake features, indicating different uptake pathways, a care should be taken while assessing $\Delta\text{DIC}_{\text{ant}}$ in the oceans relying on CFC-11 concentrations. Evidence will be provided that CFC-11 storage occurs mainly in colder, high latitude regions, whereas the warmer, low latitude regions of the world ocean play an important role in both storing and absorbing anthropogenic CO₂. This can be caused by an increased CO₂ uptake or by a reduced CO₂ release to the atmosphere at lower latitudes, both as a result of increasing atmospheric CO₂ concentrations.

Introduction

Trace gases such as chlorofluorocarbons (CFCs) and carbon dioxide (CO₂) have a considerable impact on the earth's climate system. Via air–sea exchange the oceans partly buffer anthropogenic emissions of such gases to the atmosphere, thereby controlling their atmospheric concentrations and also diminishing possible deleterious effects on the earth's climate. The concentrations of the chemically and biologically inert transient CFC tracers have proved to be a useful tool in investigating ocean circulation (e.g. Rhein 1994; Doney et al. 1997; Sy et al. 1997), since their input functions are well known via

their atmospheric time history. Transient tracer data have been used in various studies to evaluate and improve the capability of global ocean general circulation models (GCMs) (e.g. England 1995; Robitaille and Weaver 1995; England and Hirst 1997; England and Holloway 1998). GCMs, in turn, are an essential tool for assessing oceanic uptake of trace gases on a global scale, since oceanic field data have not yet achieved the necessary high-density data coverage. Moreover, GCMs have been applied in various studies to assess the oceanic uptake of anthropogenic CO₂ ($\Delta\text{DIC}_{\text{ant}}$) which cannot be measured directly (e.g. Sarmiento et al. 1992; Thomas et al. 2001; see Wallace 2001 for review).

Information on ocean ventilation gained from transient tracer data has been used to quantify the oceanic uptake of $\Delta\text{DIC}_{\text{ant}}$ on a regional scale (e.g. Gruber 1998; Thomas and Ittekkot 2001). It might also be a tempting approach to derive the oceanic uptake of CO₂ directly from transient tracer data, for example from CFCs, since both show at some least similarities in their atmospheric time history over the last decades of the past century (Fig. 1a, inset). In this study the different oceanic characteristics of CFC-11 and $\Delta\text{DIC}_{\text{ant}}$ will be evaluated in detail, employing an off-line ventilation experiment. Evidence will be provided that firstly the CFC-storage occurs mainly in colder waters, whereas the temperate regions of the world ocean play an important role in storing $\Delta\text{DIC}_{\text{ant}}$, and that secondly the uptake of both tracers might follow different routes.

Methodology

As recently shown for CO₂, the oceanic penetration by anthropogenic trace gases can be linked to their atmospheric time history via an age spectrum for water masses (Thomas et al. 2001). The age spectrum resolves the composition of a water mass with regard to the ages of the constituent components and can thus be seen as a relative measure of ocean ventilation. Accordingly, any observed water mass, i.e. point in the world ocean, can be described as a composite of individually aged contributions. Each of those contributions is thus characterised by a particular gas concentration (c_{age}) which can be related to the atmospheric gas con-

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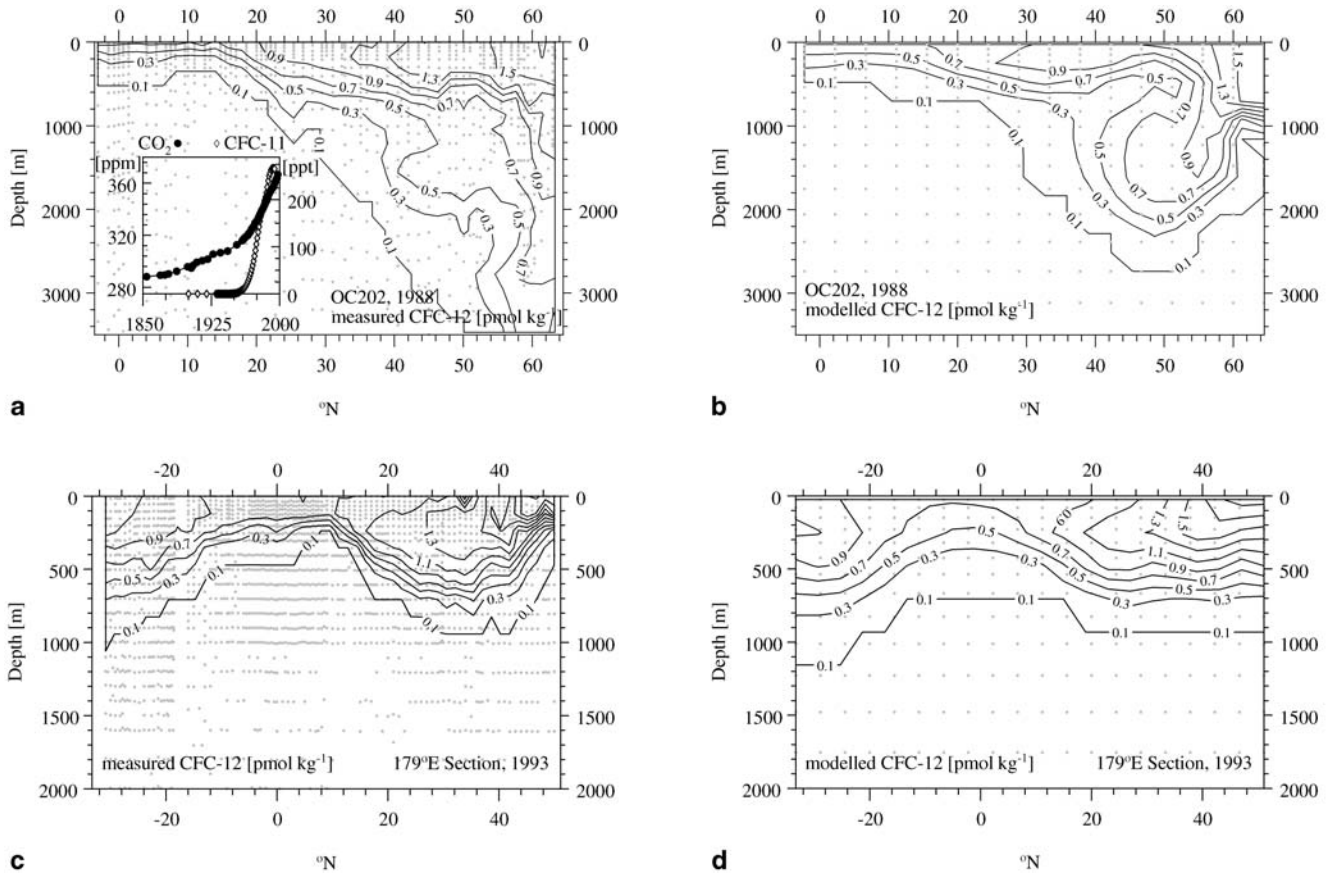


Fig. 1 Modelled CFC-12 concentrations vs. observations along the OC202 section at approx. 20°W (**a**, **b**) for the year 1988 (Doney et al. 1997) and along 179°E (**c**, **d**) for the year 1993 obtained from the WOCE data base. *Inset* in **a**: time history of the atmospheric concentrations of CFC-11 (after England and Holloway 1998) and CO₂ (Friedli et al. 1986; Keeling and Whorf 1999)

centration via the age of the contribution. The integration of all contributions over the time scale relevant for the corresponding gas and weighted according to the age composition by the factor f_{age} , provides the overall concentration (c_{gas}) in a water mass:

$$c_{\text{gas}} = \int_0^{\infty} c_{\text{age}} f_{\text{age}} dt \quad (1)$$

In order to estimate the concentrations of the anthropogenic trace gases CFC-11 and $\Delta\text{DIC}_{\text{ant}}$, two different schemes have to be applied. Since the beginning of the 1930s CFCs have been entering a previously CFC-free ocean and no chemical metabolism has to be considered. Thus, the oceanic uptake of CFC can be directly estimated using Henry's law. The concentrations of a gas (i) in oceanic surface waters (C_i , in mol kg⁻¹) can be described by its partial pressure (X_i , in atm) above seawater and its solubility constant (for CFCs, see Warner and Weiss 1985) (K_i , in mol kg⁻¹ atm⁻¹):

$$c_i = K_i X_i \quad (2a)$$

In contrast, $\Delta\text{DIC}_{\text{ant}}$ is a minor contributor to the manifold higher background concentrations of dissolved inorganic carbon (DIC) in the water column. The equilibrium reactions of the carbonate system, the so-called oceanic CO₂-buffer, have to be considered as well as the background DIC and/or alkalinity. At any given temperature (T), salinity (S) and alkalinity (A_T) an in-

crease in the $p\text{CO}_2$ causes an increase in DIC, that is $\Delta\text{DIC}_{\text{ant}}$, defined by the equilibrium reactions of the marine carbonate system. This DIC change has been computed for a wide range of T , S , A_T and $p\text{CO}_2$ conditions and a subsequent multiparameter-analysis allows the description of the concentrations of $\Delta\text{DIC}_{\text{ant}}$ (in $\mu\text{mol kg}^{-1}$) as a function of T (in °C), S and atmospheric $p\text{CO}_2$ (in ppm) (for details, see Thomas et al. 2001; Thomas and Ittekkot 2001):

$$\Delta\text{DIC}_{\text{ant}} = -199.6 + 0.89S + 0.42T + 0.60p\text{CO}_2 \quad (2b)$$

Note that as a consequence of the equilibrium reactions at a given change in the $p\text{CO}_2$, the oceanic $\Delta\text{DIC}_{\text{ant}}$ is higher at high than at low temperatures and the uptake of $\Delta\text{DIC}_{\text{ant}}$ thus shows a positive temperature coefficient. Taking into account the ventilation history of water masses and the time history of the atmospheric partial pressures of CFC-11 and CO₂ ($X_{\text{CFC-11}}$, X_{CO_2}) (Fig. 1a, inset), the corresponding concentrations of a water mass can be obtained for any given time, T and S characteristics:

$$c_{\text{CFC-11}} = \int_0^{\infty} K_{\text{CFC-11}} X_{\text{CFC-11}} f_{\text{age}} dt \quad (3a)$$

$$\Delta\text{DIC}_{\text{ant}} = \int_0^{\infty} \left[-199.6 + 0.89S + 0.42T + 0.60p\text{CO}_2 \right] f_{\text{age}} dt \quad (3b)$$

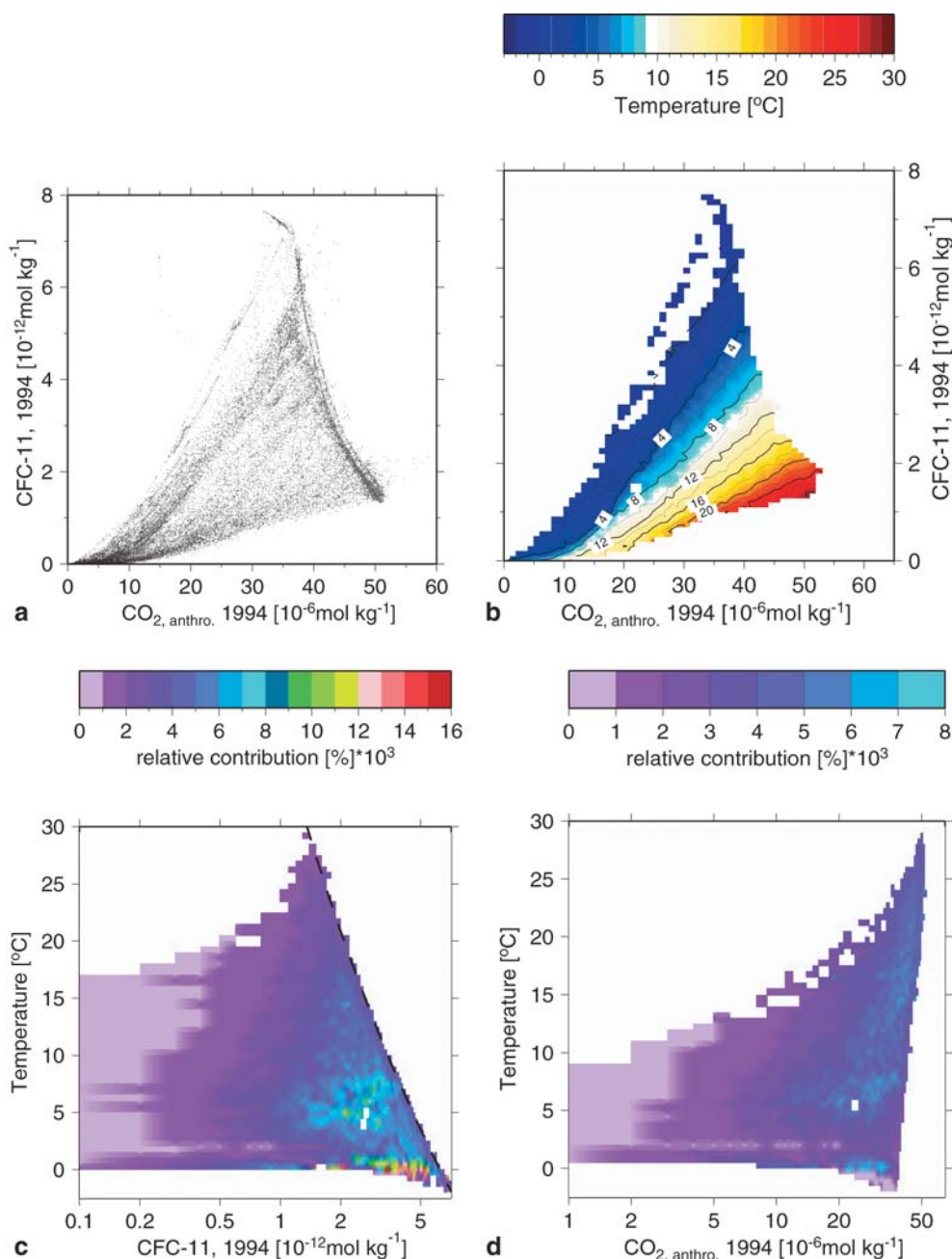
The concentrations of both CFC-11 and $\Delta\text{DIC}_{\text{ant}}$ have been computed for the year 1994 applying age spectra which were obtained from a global ocean GCM. The GCM, which includes the effect of ice coverage, has been validated with reference to observational radiocarbon and chlorofluorocarbon data (for de-

tails, see England and Hirst 1997; England and Rahmstorf 1999; Thomas et al. 2001). A comparison of the CFC concentrations obtained using the age-spectra approach and field observations (Fig. 1a–d) for two north to south sections in the Atlantic and Pacific oceans, respectively, reveals good agreement except for the known problems of the GCM itself in describing the North Atlantic Deep Water formation (see above references for details). It should be recalled that the age-spectra approach requires the assumption of a constant CO_2 air–sea disequilibrium with time (for details, see Thomas et al. 2001). This assumption might not necessarily hold true for both deep water formation and upwelling regions; however, any changes in the disequilibrium are yet to be assessed as well as a corresponding bias of the age-spectra calculations. A recent in-depth validation of the age-spectra approach for assessing the uptake of both $\Delta\text{DIC}_{\text{ant}}$ and CFCs supports the general applicability of the approach (Hall et al. 2002).

Results and discussion

The relationship between the oceanic CFC and $\Delta\text{DIC}_{\text{ant}}$ concentrations shows no obvious pattern (Fig. 2a). A more detailed analysis (Fig. 2b) provides striking evidence that the different temperature coefficients of the solubility of CFC-11 and CO_2 are mainly responsible for the observed complex relationship. It is obvious from Fig. 2b that for certain narrow temperature ranges a simple relationship between CFC-11 and $\Delta\text{DIC}_{\text{ant}}$ uptake might be obtained. This confirms recent results by Körtzinger et al. (1999) referring to CFC-11 field data and a field-data-based $\Delta\text{DIC}_{\text{ant}}$ estimate for the North Atlantic Ocean. Whilst a simple relationship might hold true

Fig. 2 **a** Scatter plot of CFC-11 vs. $\Delta\text{DIC}_{\text{ant}}$ for all oceanic values. **b** The contours indicate the corresponding temperature levels associated with the CFC-11 vs. $\Delta\text{DIC}_{\text{ant}}$ plot. **c** Relationship between dissolved CFC-11 and temperature for the entire world ocean. The *plot* shows the relative contributions of water masses characterised by both CFC-11 concentrations and temperatures to the entire oceanic CFC-11 inventory. The *dashed line* indicates the CFC-11 saturation concentration at $S=35$ for the year 1994 highlighting the physical control of the CFC-11 uptake. Concentrations $<0.1 \text{ pmol kg}^{-1}$ are not shown. **d** The same for $\Delta\text{DIC}_{\text{ant}}$ and temperature. Note that an identical *colour scale* has been applied to both $\Delta\text{DIC}_{\text{ant}}$ and CFC-11 from zero to $8 \times 10^{-3}\%$. Concentrations lower than $1 \text{ } \mu\text{mol kg}^{-1}$ are not shown.



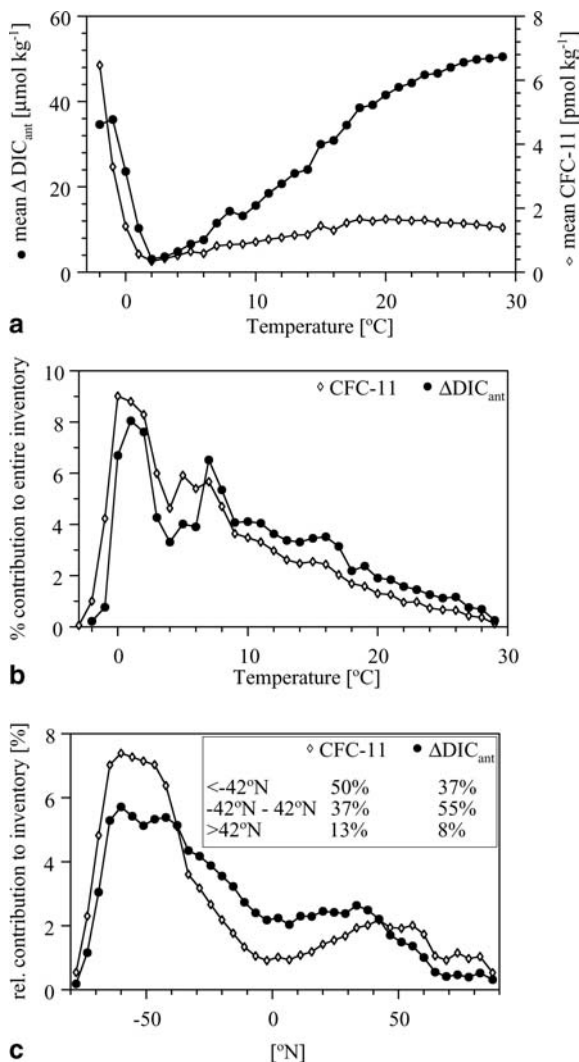


Fig. 3 **a** Volume-weighted ocean-wide mean concentrations of $\Delta\text{DIC}_{\text{ant}}$ and CFC-11 integrated over 1°C -bins. **b** The relative contributions of CFC-11 and $\Delta\text{DIC}_{\text{ant}}$ integrated over 1°C -bins to the corresponding entire oceanic inventory. **c** Global distribution of the CFC-11 and $\Delta\text{DIC}_{\text{ant}}$ inventories integrated over longitudinal $\approx 4.5^{\circ}$ -belts. *In the box*, the contributions of the area south of 42°S , between 42°S and 42°N and north of 42°N are given. Note that between 42°S and 42°N 55% of $\Delta\text{DIC}_{\text{ant}}$ but only 37% of CFC-11 is stored

for a narrow range of temperature at a given time of observation, extrapolation over the entire ocean temperature range appears to be questionable. Moreover, the different atmospheric time histories of CFC-11 and CO_2 (Fig. 1a, inset) cause relationships between oceanic CFC-11 and $\Delta\text{DIC}_{\text{ant}}$ concentrations which vary with time. As discussed below, the oceanic concentrations of CFC-11 and $\Delta\text{DIC}_{\text{ant}}$ show also individual regional patterns. Any obtained uptake relationship between the two tracers thus depends on the time and the location of the observation.

The relationships of the oceanic CFC-11 and $\Delta\text{DIC}_{\text{ant}}$ concentrations with temperature are used to analyse the individual uptake characteristics in detail. At highest temperatures the highest CFC-11 concentrations – represent-

ing the solubility maximum in the surface waters – show a negative gradient versus temperature (Fig. 2c). This expected feature is caused by the decreasing solubility of CFC-11 (as for most gases) with increasing temperatures. The recently ventilated water masses in the deep-water formation areas are represented by low temperatures and high CFC-11 concentrations. The very cold waters ($\approx 0^{\circ}\text{C}$) are from the southern high latitude regions, whereas waters with $T \approx 5^{\circ}\text{C}$ are from either the Southern or Northern hemisphere. A contrasting feature is obtained for $\Delta\text{DIC}_{\text{ant}}$ concentrations (Fig. 2d). For $\Delta\text{DIC}_{\text{ant}}$ the relative contributions of the above mentioned colder waters of $\approx 0^{\circ}\text{C}$ and $\approx 5^{\circ}\text{C}$ are less than those of the warmer waters, notably at temperatures above $\approx 15^{\circ}\text{C}$.

The volume-weighted ocean-wide mean concentrations of $\Delta\text{DIC}_{\text{ant}}$ and CFC-11 as a function of temperature make the differences in gas uptake even more evident (Fig. 3a). For both $\Delta\text{DIC}_{\text{ant}}$ and CFC-11, the minimum mean concentrations are found at water temperatures of approximately 2°C and can be assigned to the deep ocean waters which have not recently been ventilated. For CFC-11 the mean concentrations increase only slightly with increasing temperature, whilst the coldest water masses carry the highest concentrations. The ocean-wide mean $\Delta\text{DIC}_{\text{ant}}$ concentrations increase significantly above 2°C , revealing even higher means in warm waters than in the coldest waters found in deep water formation areas. The minimum mean concentrations for both $\Delta\text{DIC}_{\text{ant}}$ and CFC-11 concentrations are generated by integrating contaminated cold surface waters with the large quantities of less or uncontaminated old deep waters of the world ocean. This feature is also evident from Fig. 2c, d, revealing both lowest and highest concentrations at low temperatures. These rather “volumetric” considerations have been discussed in detail by England and Hirst (1997). $\Delta\text{DIC}_{\text{ant}}$ shows lower relative contributions than CFC-11 at lower temperatures, but higher ones at higher temperatures (Fig. 3b). Consequently, the main $\Delta\text{DIC}_{\text{ant}}$ storage is located at lower latitudes, whereas the main CFC-11 storage occurs at higher latitudes (Fig. 3c). Caldeira and Duffy (2000) argued that the $\Delta\text{DIC}_{\text{ant}}$ uptake occurs at deep-water formation areas at high latitudes, whereas the main $\Delta\text{DIC}_{\text{ant}}$ storage is located at lower latitudes. Assuming the same uptake regions for CFC-11 and $\Delta\text{DIC}_{\text{ant}}$, similar storage characteristics for both anthropogenic tracers are to be expected despite their different solubility characteristics. However, the different latitudinal distributions of the CFC-11 and $\Delta\text{DIC}_{\text{ant}}$ inventories imply that the low latitude, warm water regions play a more important role for the $\Delta\text{DIC}_{\text{ant}}$ uptake and storage than for the CFC-11 and that the uptake of both tracers in part follows different pathways.

Conclusions

The oceanic concentrations of the anthropogenic trace gases $\Delta\text{DIC}_{\text{ant}}$ and CFC-11 reveal an unequivocal relationship which is mainly caused by their different solu-

bility characteristics. Evidence has been provided for the important role of warmer waters in both taking up and storing $\Delta\text{DIC}_{\text{ant}}$. The positive temperature gradient of $\Delta\text{DIC}_{\text{ant}}$ is likely to serve as an explanation for the different CFC-11 and $\Delta\text{DIC}_{\text{ant}}$ storage features and caution should be exercised when assessing $\Delta\text{DIC}_{\text{ant}}$ in the oceans relying on CFC-11 concentrations.

$\Delta\text{DIC}_{\text{ant}}$ uptake can be caused by either CO_2 flux into the ocean or by reduced CO_2 release to the atmosphere – i.e. net uptake – which is likely to occur at lower latitudes. This net CO_2 sink might even gain more relevance in the future, since the accelerating increase in atmospheric CO_2 reduces the $p\text{CO}_2$ air–sea gradient and thereby the CO_2 release to the atmosphere. Both the latter enhanced $\Delta\text{DIC}_{\text{ant}}$ storage and the decreasing atmospheric CFC concentrations (Fig. 1a, inset) might even force the differences between the oceanic features of $\Delta\text{DIC}_{\text{ant}}$ and CFCs in the future. This, however, has not been considered in the present study and needs further investigation.

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References

- Caldeira K, Duffy PB (2000) The role of the southern ocean in uptake and storage of anthropogenic carbon dioxide. *Science* 287: 620–622
- Doney SC, Jenkins WJ, Bullister JL (1997) A comparison of ocean tracer dating techniques on a meridional section in the eastern North Atlantic. *Deep-Sea Res* 44:603–626
- England MH (1995) Using chlorofluorocarbons to assess ocean climate models. *Geophys Res Lett* 22:3051–3054
- England MH, Hirst AC (1997) Chlorofluorocarbon uptake in a World Ocean model. 2. Sensitivity to surface thermohaline forcing and subsurface mixing parameterisation. *J Geophys Res* 102:15709–15731
- England MH, Holloway G (1998) Simulations of CFC content and water mass age in the deep North Atlantic. *J Geophys Res* 103:15885–15901
- England MH, Rahmstorf S (1999) Sensitivity of ventilation rates and radiocarbon uptake to subgrid-scale mixing in ocean models. *J Phys Oceanogr* 29:2802–2827
- Friedli H, Löttscher H, Oeschger H, Siegenthaler U, Stauffer B (1986) Ice core record of $^{13}\text{C}/^{12}\text{C}$ ratio of atmospheric CO_2 in the past two centuries. *Nature* 324:237–238
- Gruber N (1998) Anthropogenic CO_2 in the Atlantic Ocean. *Global Biogeochem Cycles* 12:165–191
- Hall TM, Haine, TWN, Waugh DW (2002) Inferring the concentrations of anthropogenic carbon in the ocean from tracers. *Global Biogeochem Cycles* 16
- Keeling CD, Whorf TP (1999) Atmospheric CO_2 records from sites in the SIO air sampling network. In: *Trends: a compendium of data on global change*. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tenn.
- Körtzinger A, Rhein M, Mintrop L (1999) Anthropogenic CO_2 and CFCs in the North Atlantic Ocean: a comparison of man-made tracers. *Geophys Res Lett* 26:2065–2068
- Rhein M (1994) The deep western boundary current: tracers and velocities. *Deep-Sea Res* 41:263–281
- Robitaille DY, Weaver AJ (1995) Validation of sub-grid scale mixing schemes using CFCs in a global ocean model. *Geophys Res Lett* 22:2917–2920
- Sarmiento JL, Orr JC, Siegenthaler U (1992) A perturbation simulation of CO_2 uptake in an ocean general circulation model. *J Geophys Res* 97:3621–3645
- Sy A, Rhein M, Lazier JRN, Koltermann KP, Meincke J, Putzka A, Bersch M (1997) Surprisingly rapid spreading of newly formed intermediate waters across the North Atlantic Ocean. *Nature* 386:675–679
- Thomas H, Ittekkot V (2001) Determination of anthropogenic CO_2 in the North Atlantic Ocean using water mass ages and CO_2 equilibrium chemistry. *J Mar Syst* 27:325–336
- Thomas H, England MH, Ittekkot V (2001) An off-line 3D model of anthropogenic CO_2 uptake by the oceans. *Geophys Res Lett* 28:547–550
- Wallace DWR (2001) Ocean measurements and models of carbon sources and sinks. *Global Biogeochem Cycles* 15:3–10
- Warner MJ, Weiss RF (1985) Solubilities of chlorofluorocarbons 11 and 12 in water and seawater. *Deep-Sea Res* 32:1485–1497