

Anthropogenic CO₂ and CFCs in the North Atlantic Ocean – A comparison of man-made tracers

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Abstract. We compare estimates of the anthropogenic CO₂ content of seawater samples from the subpolar North Atlantic Ocean calculated on the basis of a back-calculation technique with measurements of the chlorofluorocarbon CFC-11. Estimated anthropogenic CO₂ concentrations are in the range 10–80 μmol kg⁻¹, while CFC-11 concentrations cover the full range from below detection limit to > 5 pmol kg⁻¹ in waters at atmospheric equilibrium. The majority of the data points show a linear correlation between anthropogenic CO₂ concentrations and CFC-11 saturation, which can only be explained by the strongly advective nature of the North Atlantic Ocean. Only deep eastern basin samples deviate from this general observation in that they show still significant concentrations of anthropogenic CO₂ where CFC-11 is no longer detectable. In order to remove the influence of the Revelle factor reflected in the anthropogenic CO₂ concentrations we have calculated 'excess' pCO₂, showing an even tighter linear correlation with atmospheric equilibrium concentrations of CFC-11.

Introduction

Since the 18th century, the increasing demands of our expanding mankind have – through burning of fossil fuels and changes in land use – raised the atmospheric concentration of CO₂ until 1997 by 30 % [Friedli *et al.*, 1986; Keeling and Whorf, 1998]. From the long-standing record of atmospheric CO₂ we know, that only less than half of all anthropogenic emissions of CO₂ remain airborne. The ocean has long since been recognized as an important sink for a significant portion of the "missing" anthropogenic CO₂ [e.g., Siegenthaler and Sarmiento, 1993]. The reliable estimation of this oceanic sink of anthropogenic CO₂ is an important step in understanding the fate of fossil-fuel CO₂.

The concepts in tracing and quantifying the anthropogenic CO₂ in the ocean are manifold. Here we compare estimates of the anthropogenic CO₂ content of seawater samples from the North Atlantic Ocean calculated on the basis of a back-calculation technique [Brewer, 1978; Chen and Millero, 1979]

with concentrations of the chlorofluorocarbon CFC-11, determined from the same samples. Only few examples of similar comparisons can be found in the literature [e.g., Chen, 1993; Goyet and Brewer, 1993; Chen *et al.*, 1995].

Methods

CO₂ system parameters/oxygen. Total dissolved inorganic carbon (C_T) was measured by extraction with subsequent coulometric titration [Johnson *et al.*, 1993] with an accuracy (precision) of 1.5 (0.5) μmol kg⁻¹. Alkalinity (A_T) was determined by potentiometric titration with an accuracy (precision) of 3.0 (1.0) μmol kg⁻¹. Oxygen samples were analyzed by modified Winkler titration [Hansen, 1999] with a precision of ±0.5 μmol kg⁻¹.

CFC-11/CFC-12. CFCs were analyzed using a purge-and-trap extraction technique in combination with gas chromatography with electron capture detection after Bullister and Weiss [1988]. The estimated precision is about 1 %.

Anthropogenic CO₂. The anthropogenic CO₂ was calculated using a back-calculation technique published independently by Brewer [1978] and Chen and Millero [1979]. The concept involves a back-calculation in the marine CO₂ system to reveal any difference between historical and contemporary preformed values of C_T as a measure of the anthropogenic CO₂ content. Although heavily criticized over the years [e.g., Shiller, 1981; Broecker *et al.*, 1985] the potential of the concept in providing direct, model-independent fossil-fuel CO₂ uptake estimates has been demonstrated by several authors [e.g., Jones and Levy, 1981; Chen, 1987; Brewer *et al.*, 1997].

The back-calculation requires quantification of changes in the marine CO₂ system due to decomposition of particulate organic matter, dissolution of particulate carbonates and mixing after a water parcel left contact with the atmosphere. This is feasible on the basis of measurements of A_T, C_T, oxygen, salinity and potential temperature (θ). A detailed description of the method and its major drawbacks can be found in Körtzinger *et al.* [1998].

The following equations were used here: C_T^{0,pres} = -10.38·θ + 2194 (N = 497, σ = 12), as calculated from North Atlantic Ocean surface samples measured during the R/V *Meteor* cruise 36-1 in a new semi-continuous operation mode of the coulometric titration technique [Johnson *et al.*, submitted]; A_T⁰ = -1.965·θ + 2332 (N = 120, σ = 12) [Millero *et al.*, 1998]. We have chosen the mean ΔC_T⁰ (-55 μmol kg⁻¹) of the

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deepest samples collected in the eastern basin of the North Atlantic (48°N, 13–18°W, depth ≥ 4000 m) during *Meteor* cruise 39–3 in 1997 as reference level. These samples reflect the northernmost extension of the Antarctic Bottom Water (AABW) and can be expected to be free of anthropogenic CO₂ [Körtzinger *et al.*, 1998].

The overall uncertainty of the anthropogenic CO₂ was estimated to be 10 $\mu\text{mol kg}^{-1}$. There is, however, the potential for a systematic error of the same size due to the use of summer values for the calculation of present day preformed C_T instead of winter values [Chen and Pytkowicz, 1979].

Results and Discussion

Fig. 1 shows the atmospheric history of the transient tracers anthropogenic CO₂, CFC-11 (CCl₃F), and CFC-12 (CCl₂F₂) [CFCs after S. Walker, P.K. Salameh and R.F. Weiss, personal communication] until 1996. Anthropogenic CO₂ was separated from the natural CO₂ background by subtracting pre-industrial concentrations of the middle of the 18th century (276.8 ppmv) as determined in air occluded in Antarctic ice [Friedli *et al.*, 1986] from atmospheric CO₂ concentrations between 1791 and 1997 (until 1953 from Antarctic ice cores [dito], after 1958 from direct measurements on the Mauna Loa, Hawaii [Keeling and Whorf, 1998]).

Clearly neither CFC-11 nor CFC-12 can be regarded as a potential analogue for the atmospheric evolution of anthropogenic CO₂. However, given the active mixing taking place in the North Atlantic Ocean a more or less linear correlation between CFCs and anthropogenic CO₂ was expected. Only water masses essentially formed more than 50 years ago should carry a different signature, *i.e.*, very low CFC concentrations associated with still significant concentrations of anthropogenic CO₂.

We compare calculated concentrations of the anthropogenic CO₂ with CFC-11 data from a total of approx. 1000 samples taken at 76 hydrographic stations in the North Atlantic Ocean (R/V *Meteor* cruises 39–2/4, Fig. 2). Near-zonal section of anthropogenic CO₂ (Fig. 3, top) and CFC-11 saturation with respect to the 1996 atmosphere (Fig. 3 bottom, calculated after Warner and Weiss [1985]) across the North Atlantic Ocean show a striking similarity. CFC saturation was chosen instead of concentration to remove the effect of the temperature-dependent solubility of CFC-11 in seawater, which otherwise obscures the pure ventilation information contained in the CFC distribution.

Major features, visible in both sections, are: Lower Deep Water (LDW) in the deep eastern basin carrying the signature of Antarctic Bottom Water (AABW) with lowest concentra-

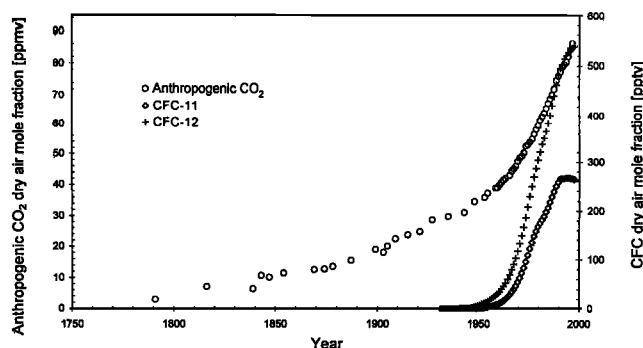


Figure 1. Evolution of the atmospheric concentrations of anthropogenic CO₂, CFC-11 and CFC-12.

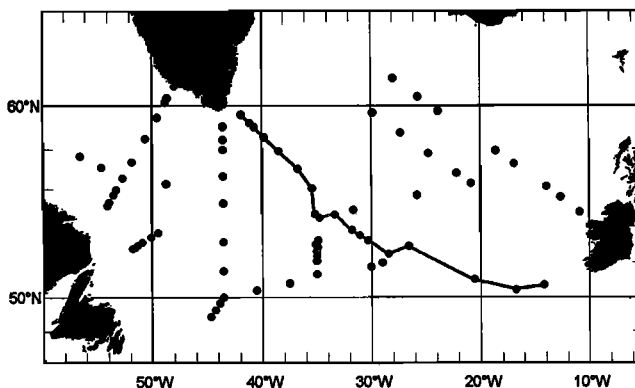


Figure 2. Location of 76 hydrographic stations where CFC-11, alkalinity (A_T), total dissolved inorganic carbon (C_T) and dissolved oxygen were measured (cruises 39–2 and 39–4 of the German R/V *Meteor*). Also shown is the location of the near-zonal section referred to in the text and Fig. 3.

tions of anthropogenic trace gases; recently formed Labrador Sea Water (LSW) in the western basin (around 40°W) with sign of high ventilation down to about 2000 m depth; the Denmark Strait Overflow Water (DSOW) derivative in the deep western basin (around 3000 m depth) lying against the lower part of the Greenland Slope and the derivative of the remotely formed Iceland Scotland Overflow Water (ISOW) sloping against the Mid-Atlantic Ridge in the western basin (around 35–40°W) with sign of lower ventilation centered around 2800–3000 m depth. Less clear but still visible is the spreading of the LSW across the Mid-Atlantic Ridge into the Eastern North Atlantic at depths between 1000 and 1500 m.

We plotted anthropogenic CO₂ vs. CFC-11 saturation (Fig. 4). When comparing the uptake of anthropogenic CO₂ with that of a chemically inert tracer like CFC-11 we have to recall the buffer chemistry of CO₂ in the ocean. The net equilibrium uptake of anthropogenic CO₂ is not only a function of the atmospheric CO₂ increase but also of the marine CO₂ system itself. It is the speciation within the marine CO₂ system which determines the equilibrium uptake of CO₂ for a given increase of the atmospheric CO₂ partial pressure ($p\text{CO}_2$). An expression of the static buffering capacity of surface seawater is the buffer or Revelle factor $R = [(dp\text{CO}_2/p\text{CO}_2)/(dC_T/C_T)]$, the quotient of the relative increases in $p\text{CO}_2$ and C_T at equilibrium and constant temperature, salinity and alkalinity [Sundquist *et al.*, 1979].

The Revelle factor can be calculated based on a knowledge of the speciation of the CO₂ system in seawater, which in turn is given by a combination of any two CO₂ system parameters. We have computed Revelle factors from measured surface C_T and A_T for all stations. The resulting range of the present-day (pre-industrial) Revelle factor for the whole data set is 9.8–12.4 (8.7–11.0) yielding full anthropogenic CO₂ signals of 75–48 $\mu\text{mol kg}^{-1}$ for the observed atmospheric CO₂ increase of 85.8 ppmv between the 1750s and 1997. Accordingly, a CFC saturation of 100 % in surface waters fully equilibrated with respect to both anthropogenic trace gases corresponds to a range of anthropogenic CO₂ concentrations of 48–75 $\mu\text{mol kg}^{-1}$ only depending on the buffer factor. Generally, low Revelle factors are indicative of ‘southern component’ water originating in the sub-tropical gyre, while high Revelle factors reflect ‘northern component’ water of high latitude provenance.

The two dotted lines in Fig. 4 represent upper and lower limits based on the observed extremes of the Revelle factor

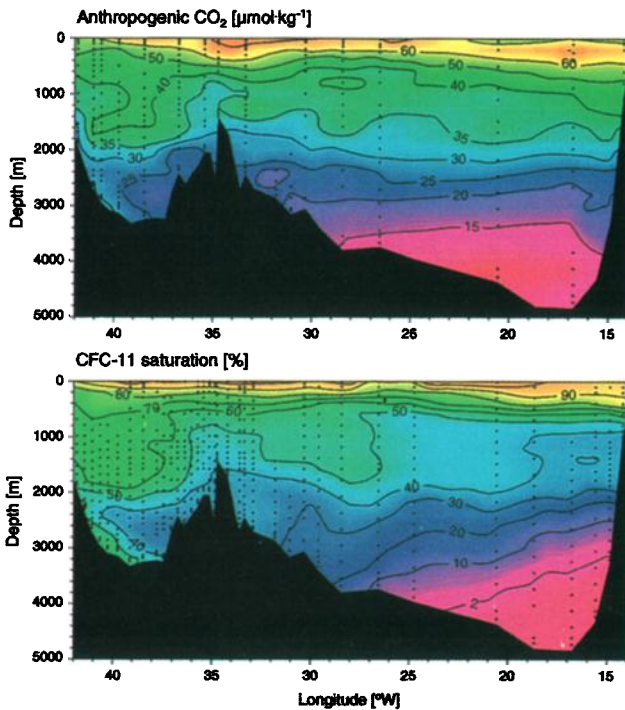


Figure 3. Sections of anthropogenic CO₂ (top) and CFC-11 saturation (with respect to the 1996 atmosphere, bottom) in the North Atlantic Ocean. See Fig. 2 for location.

and assuming a direct proportionality between anthropogenic CO₂ and CFCs over the full concentration range. Thus, if we further assume the calculated surface water Revelle factors to be representative of the whole water column in the sampled area of the North Atlantic Ocean, all data points should fall between these two lines. This is the case for the vast majority of the data points. In detail, Fig. 4 shows no general tendency towards one of the extremes at CFC-11 saturation < 55 %. From 55–85 % CFC saturation a trend parallel to the low limit line ('northern component') is observed. This saturation range is mainly representative of the 1000–2000 m depth range of the LSW spreading (see also Fig. 3). In contrast, for CFC saturation > 85 % a slight trend towards the high limit line can be seen indicating the more dominant share of 'southern component' water in the upper 200 m

Values for surface water reveal higher scatter. They also show CFC-11 supersaturation by up to 10 %. The range in the anthropogenic CO₂ concentration of surface waters (with CFC-11 saturation > 100 %) of 35–80 μmol kg⁻¹ is an artifact of the back-calculation. In surface water we observe the largest deviations of measured C_T values from the present day preformed values ΔC_T^{0,pres}, although by theory they should be identical. These deviations are due to biological activity, which is reflected in C_T but at same time cannot equally be seen in oxygen, as it is much more rapidly exchanged with the atmosphere. As a result, the AOU-based quantification of photosynthesis and respiration do not work adequately in surface waters in the presence of significant biological activity.

Nevertheless most data points show a direct proportionality between the two tracers. The only exception are a couple of samples from the deep eastern basin, which can be seen above the upper limit line as a trend pointing towards 12 μmol kg⁻¹ of anthropogenic CO₂ at 0 % CFC saturation. These samples

represent LDW as an AABW derivative with the highest water mass age in the whole area. It is here, where we have the only clear indication of the different atmospheric input functions of anthropogenic CO₂ and CFCs being reflected in sampled waters of the subpolar North Atlantic Ocean.

The influence of the Revelle factor can be removed by converting calculated 'excess' CO₂ concentrations into 'excess' pCO₂. This was carried out using the software package of *Lewis and Wallace* [1995] with the carbonic acid dissociation constants after *Mehrbach et al.* [1973]. These have been shown to yield most consistent results when calculating pCO₂ from C_T and A_T [*Johnson et al.*, submitted]. We used ΔC_T^{0,pres} and A_T⁰ to compute the present day preformed pCO₂^{0,pres} of all samples. Historical preformed pCO₂^{0,hist} was calculated using C_T^{0,hist} and A_T⁰ as input. The present day disequilibrium (ΔpCO₂, Eq. 1) equals the difference between pCO₂^{0,pres} and the corresponding equilibrium pCO₂^{Eq,pres} under the 1997 atmosphere (362.7 ppmv, *Keeling and Whorf* [1998]):

$$\Delta p\text{CO}_2 = p\text{CO}_2^{0,\text{pres}} - p\text{CO}_2^{\text{Eq,pres}} \quad (1)$$

Assuming an the same degree of saturation of present day surface waters as in the pre-industrial situation (which is an implicit and necessary assumption of the back-calculation technique) we have also applied these disequilibrium values to the historical preformed values of pCO₂^{0,hist} to get the corresponding equilibrium pCO₂ of surface waters (pCO₂^{Eq,hist}). By subtracting the equilibrium pCO₂^{Eq,pre-ind} for the pre-industrial atmosphere (276.8 ppmv, *Friedli et al.* [1986]) from pCO₂^{Eq,hist} values we get the 'excess' pCO₂ (Eq. 2), which is equivalent to the change of the atmospheric pCO₂ since pre-industrial times as preserved in a given sample:

$$\text{'excess' } p\text{CO}_2 = p\text{CO}_2^{\text{Eq,hist}} - p\text{CO}_2^{\text{Eq,pre-ind}} \quad (2)$$

We plotted calculated 'excess' pCO₂ vs. equilibrium CFC-11 mole fraction in dry air, calculated with the solubility after *Warner and Weiss* [1985] assuming 100 % saturation (Fig. 5). This figure also contains two extremes of the relationship between these two man-made tracers: (1) the pure atmospheric build-up history of these tracers, which can only be preserved in the ocean if no mixing is going on, and (2), on the other extreme, a linear mixing line between pre-industrial

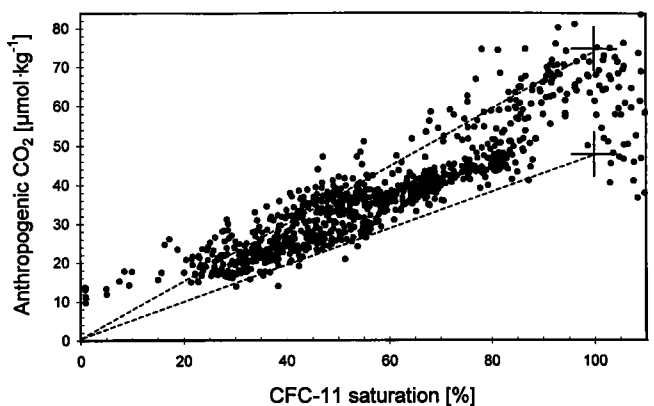


Figure 4. Plot of anthropogenic CO₂ vs. CFC-11 saturation (with respect to the 1996 atmosphere). The dotted lines represent the theoretical relationship if anthropogenic CO₂ and CFC-11 are directly proportional as spanned by the observed extremes of the Revelle factor in surface water.

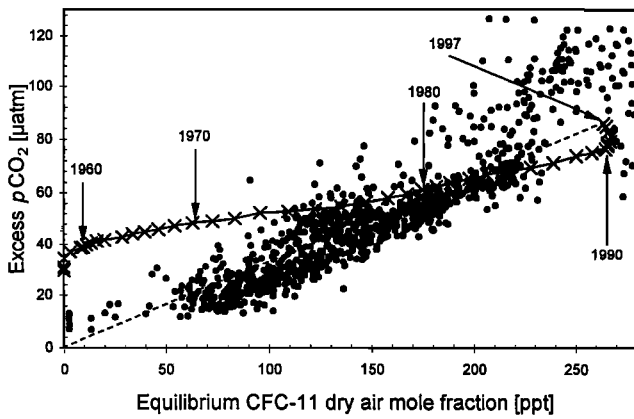


Figure 5. Plot of the calculated 'excess' $p\text{CO}_2$ vs. the atmospheric equilibrium concentration of CFC-11. Also shown is the history of the evolution of these two man-made tracers in the atmosphere (x).

atmospheric conditions (*i.e.*, both tracers are absent) and present day fully equilibrated surface waters representing a vigorous mixing between old and young water masses. The majority of the data indicate a rapid mixing in the North Atlantic, which is indeed a well-known fact.

The overall uncertainty of the 'excess' $p\text{CO}_2$ is of the order of 10–15 μatm not including a possible systematic error. The artifact due to near-surface biological activity not accounted for by the AOU is almost twice as large for $p\text{CO}_2$ as for C_T .

Summary

We know that the subpolar North Atlantic Ocean is dominated by advection of recently formed water masses, carrying a relatively large burden of anthropogenic CO₂ and CFCs. This is strongly reflected in the results of the comparison we present here. In general the two tracers 'excess' CO₂ and CFC-11 show a linear correlation throughout most of the observed concentration range. Deviations from this general picture can be explained either by the relatively large water mass age in the deep eastern basin or by artifacts of the back-calculation procedure in surface waters. These findings are consistent with the current understanding of the hydrography of the North Atlantic Ocean. Although the method employed here is not without caveats and shortcomings, as, for example, the rather simplistic treatment of water mass mixing, the general agreement found here and the detail contained in the patterns is a quieting observation. Further development addressing the well-known weak points of the method bear the potential to make it a more powerful tool.

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