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 (CT) 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 (AT) 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 CT 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 Aₜ, Cₜ, 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: Cₜ⁰,wat = -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]; Aₜ⁰ = -1.965·θ + 2332 (N = 120, σ = 12) [Millero et al., 1998]. We have chosen the mean ΔCₜ⁰ (~55 µmol kg⁻¹) of the
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 μmol 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 (CFCl₃), and CFC-12 (CF₂Cl₂) [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 Horf, 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 concentrations 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 (pCO2). An expression of the static buffering capacity of surface seawater is the Revelle factor R = [(dCO2/pCO2)/(dC/CT)], the quotient of the relative increases in pCO2 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 μmol 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 μmol kg⁻¹ only depending on the Revelle factor. Generally, low Revelle factors indicate a '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...
represents 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 T,0 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 T,0 as input. The present day disequilibrium (ΔpCO2, Eq. 1) equals the difference between pCO2,0 pres and the corresponding equilibrium pCO2,0 hist under the 1997 atmosphere (362.7 ppmv, Keeling and Whorf [1998]):

\[
ΔpCO2 = pCO2,0_{hist} - pCO2,0_{pre-ind}
\]  

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 pCO2,0 hist of surface waters (pCO2,0 hist). By subtracting the equilibrium pCO2,0 hist for the pre-industrial atmosphere (276.8 ppmv, Friedli et al. [1986]) from pCO2,0 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:

\[
'\text{excess'} \ pCO2 = pCO2,0_{hist} - pCO2,0_{pre-ind}
\]  

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 5. Plot of the calculated 'excess' $pCO_2$ 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' $pCO_2$ is of the order of 10–15 $\mu$atm 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 $pCO_2$ 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 $CO_2$ and CFCs. This is strongly reflected in the results of the comparison we present here. In general the two tracers 'excess' $CO_2$ 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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