

On the penetration of anthropogenic CO₂ into the North Atlantic Ocean

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Abstract. The penetration of anthropogenic or “excess” CO₂ into the North Atlantic Ocean was studied along WOCE-WHP section A2 from 49°N/11°W to 43°N/49°W using hydrographic data obtained during the *METEOR* cruise 30-2 in October/November 1994. A backcalculation technique based on measurements of temperature, salinity, oxygen, alkalinity, and total dissolved inorganic carbon was applied to identify the excess CO₂. Everywhere along the transect surface water contained almost its full component of anthropogenic CO₂ (~62 μmol kg⁻¹). Furthermore, anthropogenic CO₂ has penetrated through the entire water column in the western basin of the North Atlantic Ocean. Even in the deepest waters (5000 m) of the western basin a mean value of 10.4 μmol kg⁻¹ excess CO₂ was calculated. The maximum penetration depth of excess CO₂ in the eastern basin of the North Atlantic Ocean was ~3500 m with values falling below 5 μmol kg⁻¹ in greater depths. These results compare well with distributions of carbontetrachloride. They are also in agreement with the current understanding of the role of the “global ocean conveyor belt” for the uptake of anthropogenic CO₂ into the deep ocean.

1. Introduction

The increasing demands of a steadily expanding mankind have raised the atmospheric concentration of CO₂ through burning of fossil fuels and changes in land use by 30% since the 18th century. From the long-standing record of atmospheric CO₂ [e.g., Keeling *et al.*, 1995] we know, that only less than half of these 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. While from a thermodynamic point of view it is clear, that in a future steady state the ocean will have absorbed of the order of 85% of the man-made CO₂, the kinetics involved make the actual uptake rather slow. With a mean ventilation time of the world ocean of 500–1000 years as the main kinetic barrier the ocean cannot keep pace with the atmospheric perturbation. As it is the ocean, which ultimately determines the atmospheric CO₂ concentration, the understanding of its role in the global carbon cycle has become a key question in discussions and predictions of a global climate change.

The concepts in tracing and quantifying the anthropogenic CO₂ in the ocean are manifold, and most of them are based on assumptions and parameterizations that are not unequivocally accepted. One of the few concepts that yield direct CO₂ uptake estimates is the calculation of the “excess” CO₂ by a protocol first independently published by Brewer [1978] and Chen and Millero [1979]. Especially Chen has presented results from this concept in a number of publications [Chen, 1982a, b, 1987,

1993; Chen *et al.*, 1990], but other authors have also published interesting applications of this technique in various parts of the world ocean [e.g., Jones and Levy, 1981; Poisson and Chen, 1987; Krumpal *et al.*, 1990; Anderson and Jones, 1991; Goyet and Brewer, 1993].

This concept (hereafter called ΔC_T⁰ method) involves a backcalculation technique to reveal any difference between historical and contemporary preformed values of the total dissolved inorganic carbon concentration (C_T) as a measure of the anthropogenic CO₂ content. It is subject to rather large uncertainties (up to 15 μmol kg⁻¹ according to Chen [1982b]) and has been heavily criticized [e.g., Shiller, 1981, 1982; Broecker *et al.*, 1985a]. However, with the improved data quality and good spatial coverage, which have been achieved in the international WOCE- and JGOFS-based CO₂ surveys, nowadays this concept is likely to produce more accurate, model-independent uptake estimates for CO₂. Modelers [Sarmiento *et al.*, 1992; Stocker *et al.*, 1994] have pointed out the possible use of such estimates for the validation of model results. In a report on building blocks of a global ocean observing system, Wallace [1995] has underlined the possible benefit from this concept in the light of the international WOCE-based CO₂ survey.

Here we show a new application of the ΔC_T⁰ method to a data set along the WOCE-WHP section A2 which has been acquired during cruise 30-2 of R/V *METEOR* from Hamburg to St. John's/Newfoundland (October 12 to November 12, 1994). We also include a brief discussion of the shortcomings of this method.

2. The ΔC_T⁰ Method

The following abbreviations are used in the description of the method. All of them (except AOU) denote concentrations

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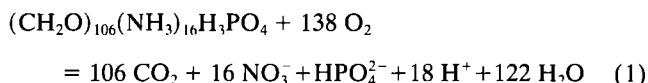
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of chemical properties (in $\mu\text{mol kg}^{-1}$) that have been normalized to a salinity of 35 to compensate for dilution and evaporation effects:

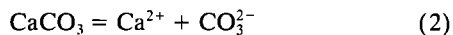
C_T	total dissolved inorganic carbon (synonyms: DIC, TCO ₂ , ΣCO_2);
A_T	total alkalinity;
$\Delta A_{T,\text{CaCO}_3}$	total alkalinity change due to dissolution of particulate carbonates;
C_T^{meas}	measured C_T ;
A_T^{meas}	measured A_T ;
$C_T^{0,\text{old}}$	calculated preformed C_T of the sampled water during its last contact with the atmosphere;
$C_T^{0,\text{pres}}$	calculated preformed C_T of present waters;
A_T^0	calculated preformed A_T ;
C_T^{ant}	anthropogenic or "excess" C_T ;
AOU	apparent oxygen utilization.

The method has been described in more detail elsewhere [e.g., Brewer, 1978; Chen and Millero, 1979; Krumgalz et al., 1990] and shall therefore only be outlined here. It involves backcalculation of the total dissolved inorganic carbon concentration (C_T) of a seawater sample to its initial (preformed, superscript zero) concentration when it was at the sea surface ($C_T^{0,\text{old}}$). As a water body sinks and loses contact with the atmosphere, any changes in C_T must result from decomposition of particulate organic matter (POM), dissolution of particulate carbonates, and mixing of water masses with different preformed values. The distinction of the contributions of these mechanisms and processes is required for the calculation of the historical preformed C_T values. This is feasible on the basis of changes in A_T , AOU, salinity and potential temperature. The difference (ΔC_T^0) between $C_T^{0,\text{old}}$ and the contemporary preformed C_T value ($C_T^{0,\text{pres}}$) is a measure of the anthropogenic CO₂ in the seawater sample. The method is principally based on two assumptions: (1) the source region of the sampled water has remained at a fixed degree of saturation (not necessarily equilibrium) with respect to the atmospheric CO₂ concentration (steady state assumption), and (2) surface seawater alkalinity has remained constant over time (i.e., the anthropogenic CO₂ invasion does not affect the surface alkalinity).

The formation/decomposition of particulate organic matter in the ocean can be described according to the Redfield-Ketchum-Richards model [Redfield et al., 1963] by the following well-known equation (1):



The stoichiometry of the dissolution of particulate carbonates is represented by



The apparent oxygen utilization (AOU) of a sample can be calculated after

$$\text{AOU} = \text{O}_2^{\text{sat}} - \text{O}_2^{\text{meas}} \quad (3)$$

in which O_2^{sat} is the saturation concentration of oxygen calculated after Weiss [1970] at the potential temperature Θ and salinity S of the sample and O_2^{meas} is its measured oxygen concentration.

The total change in A_T (ΔA_T) resulting from dissolution of particulate carbonates ($\Delta A_{T,\text{CaCO}_3}$) and remineralization of

POM is then given by (4). The AOU factor of (1–18)/138 represents the release of 1 mol HPO_4^{2-} and 18 moles H^+ per consumption of 138 moles O_2 during the remineralization process according to (1). Both products are relevant for the alkalinity change as they are included in the definition of alkalinity after Dickson [1981]. This effect is also known as "nitrate correction" and can be regarded as an in situ titration of alkalinity:

$$\Delta A_T \equiv A_T^{\text{meas}} - A_T^0 = \Delta A_{T,\text{CaCO}_3} + 1-18/138 \text{ AOU} \quad (4)$$

The total chemically and biologically mediated change in C_T (ΔC_T) is given by

$$\Delta C_T \equiv C_T^{\text{meas}} - C_T^{0,\text{old}} = 0.5 \Delta A_{T,\text{CaCO}_3} - 106/138 \text{ AOU} \quad (5)$$

and thus, by combining (4) and (5),

$$C_T^{0,\text{old}} = C_T^{\text{meas}} - 0.5(A_T^{\text{meas}} - A_T^0) - 0.83 \text{ AOU} \quad (6)$$

The variables C_T^{meas} , A_T^{meas} , and AOU are known from measurements. Hence the final requirement to calculate $C_T^{0,\text{old}}$ is a knowledge of A_T^0 . Under the assumption that A_T is not affected by the invasion of anthropogenic CO₂ we do not have to differentiate between historical and contemporary A_T^0 values. Values for A_T^0 can thus be derived from contemporary measurements. Several authors [e.g., Edmond, 1974; Chen and Pytkowicz, 1979] have reported linear correlations between the potential temperature Θ and salinity normalized values of surface A_T and C_T . The linear regressions calculated from our data set are given by

$$A_T^0 = -0.55 \cdot \Theta + 2327 \quad \text{s.d.} \pm 9.0 \quad (7)$$

$$C_T^{0,\text{pres}} = -10.25 \cdot \Theta + 2195 \quad \text{s.d.} \pm 7.6 \quad (8)$$

The $C_T^{0,\text{hist}}$ value of any given sample is thus calculated from measured values of C_T , A_T , oxygen, Θ , and S with the use of (3), (6), and (7). Equation (8) is then required to compute $C_T^{0,\text{pres}}$ values at the potential temperature Θ of the sample. Any difference (ΔC_T^0) between the two C_T^0 values reveals the anthropogenic imprint of the sampled water (9) if the above assumptions are valid:

$$\Delta C_T^0 = C_T^{0,\text{old}} - C_T^{0,\text{pres}} \quad (9)$$

The expected range of ΔC_T^0 surface values for North Atlantic Central Waters can be approximated from a knowledge of the rise of the atmospheric CO₂ concentration since the onset of the industrial revolution (280 ppmv) to the present (360 ppmv), the pre-industrial C_T of surface seawater and the Revelle or buffer factor $R = (d\text{pCO}_2/\text{pCO}_2)/(dC_T/C_T)$ [Sundquist et al., 1979]. We used our C_T measurements and parallel continuous measurements of the surface water partial pressure of CO₂ (pCO_2) to calculate the Revelle factor along WOCE-WHP section A2. For this purpose we computed the alkalinity from measured (i.e., nonnormalized) C_T/pCO_2 data pairs at each station using the constants of Goyet and Poisson [1989] and Weiss [1974]. Measured C_T and calculated A_T data were then normalized to a salinity of 35. Finally, the pCO_2 was computed from each of these salinity normalized C_T/A_T data pairs for the mean surface seawater temperature of 17.35 °C. We calculated a mean Revelle factor of 8.8 ± 0.4 along the transect from a linear regression of $\ln \text{pCO}_2$ (at $S = 35$, $T = 17.35$ °C) versus $\ln C_T$ (at $S = 35$). The pre-industrial C_T of surface waters in the central North Atlantic Ocean was assumed to be 2000 $\mu\text{mol kg}^{-1}$. The increase in C_T of surface

water can then roughly be estimated assuming a constant Revelle factor after

$$\Delta C_T = \frac{80 \mu\text{atm}}{280 \mu\text{atm}} \frac{2000 \mu\text{mol kg}^{-1}}{8.8} = 65 \mu\text{mol kg}^{-1}$$

However, this approximation ignores the fact that the Revelle factor itself is not constant over the atmospheric CO₂ rise but increases with the $p\text{CO}_2$. A more realistic calculation with a variable Revelle factor would therefore yield even slightly higher ΔC_T values. Based on this simplistic approach the ΔC_T^0 values (9) can be expected to range between zero for fully equilibrated contemporary surface seawater and $-65 \mu\text{mol kg}^{-1}$ for uncontaminated old waters.

Positive values of the anthropogenic CO₂ content can be derived by defining a reference level ($\Delta C_T^{0,\text{ref}}$) which is usually (with respect to anthropogenic CO₂) uncontaminated deep water [Poisson and Chen, 1987]:

$$C_T^{\text{ant}} = \Delta C_T^0 - \Delta C_T^{0,\text{ref}} \quad (10)$$

As mentioned earlier, the method is subject to a number of uncertainties, some of which shall be discussed briefly. The stoichiometric coefficients in (1) after Redfield *et al.* [1963] are a matter of debate and evidence has been shown that the C/P and O/P ratios (and thus the relevant C/O ratio) have to be revised to some extent [Broecker *et al.*, 1985b; Takahashi *et al.*, 1985a; Anderson and Sarmiento, 1994]. The coefficients applied to AOU in (4) to (6) are based on the “classical” Redfield ratios. Broecker *et al.* [1985a] have proposed a “best correct estimate” of 0.72 ± 0.08 for the C/O ratio, which is in perfect agreement with a value of 0.722 ± 0.05 for 10 stations widely scattered in the Pacific Ocean [Chen and Pytkowicz, 1979]. The corresponding AOU coefficient is 0.78, instead of 0.83 for the original Redfield stoichiometry. This revised value of 0.78 was used for the AOU coefficient in the present work. Equation (6) is then modified to become

$$C_T^{0,\text{old}} = C_T^{\text{meas}} - 0.5(A_T^{\text{meas}} - A_T^0) - 0.78 \text{ AOU} \quad (6')$$

For the calculation of AOU an oxygen saturation of 100% is usually assumed. This is, however, seldom exactly the case in the natural environment. Typical deviations of 1–3% are known with maximum values reaching 10% and more. For a typical oxygen saturation concentration of $300 \mu\text{mol kg}^{-1}$ an error of 2% corresponds to $6 \mu\text{mol kg}^{-1}$ in AOU. With an AOU factor of 0.78 this translates into an error of roughly $4 \mu\text{mol kg}^{-1}$ in $C_T^{0,\text{old}}$. This is small as compared to the observed range of ΔC_T^0 .

The mixing problem is generally handled in a rather simplistic manner. Salinity normalization of all properties (except AOU) provides a means of correcting for salinity-proportional mixing effects, while the empirical temperature relationships (7) and (8) compensate for mixing of waters with differing preformed values. The latter correction neglects the fact, that for dissolved gases the mixing line is not exactly linear, with the error, however, introduced by this being comparatively small.

The production of the North Atlantic Deep Water (NADW) is far from being a simple, fully understood process. It is impossible to identify a single source region for the purpose of establishing valid temperature correlations for normalized surface C_T and A_T . Instead, the NADW is produced by a complex series of processes which to some extent take place in deep convection areas in the Norwegian Sea north of Iceland but to a major extent occur as entrainment in the overflow waters

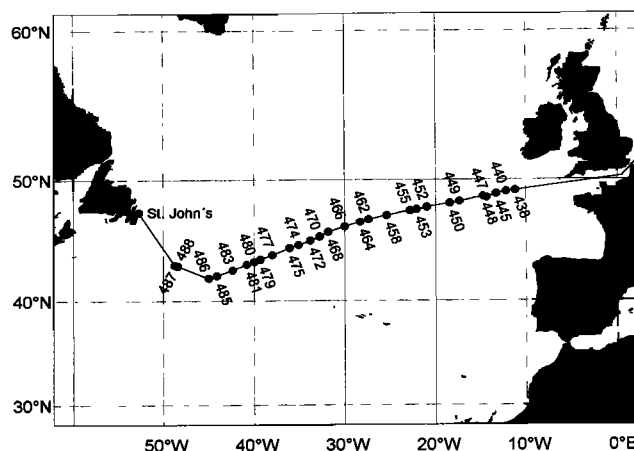


Figure 1. Ship track of R/V *METEOR* cruise 30-2 from Hamburg to St. John's/Newfoundland (October/November 1994) along WOCE-WHP section A2. Only the 28 stations are shown, where measurements of total dissolved inorganic carbon and alkalinity were performed. Nutrient and oxygen concentrations were measured at 24 additional stations. The surface seawater $p\text{CO}_2$ was continuously monitored along the entire cruise track.

south of the sills and as deep convection in the Irminger and Labrador Seas [Schmitz and McCartney, 1993; Dickson and Brown, 1994]. Chen and Pytkowicz [1979] emphasized that a possible summer-winter incompatibility of the data sets introduced a potential systematic error of up to $15 \mu\text{mol kg}^{-1}$ when temperature correlations based on summer data are used.

A formal evaluation of the overall error of this backcalculation technique is almost impossible. We think that an error of $15 \mu\text{mol kg}^{-1}$ given by Chen and Pytkowicz [1979] is certainly an upper limit. In this work the probability of systematic errors is very low as all calculations are based entirely on this internally consistent data set and on differences of the CO₂ system parameters (ΔA_T , ΔC_T) only. We have carried out two important checks on the validity of our calculated C_T^{ant} values using other published data. For this purpose we run the whole backcalculation with different temperature correlations: (1) for $C_T^{0,\text{pres}}$ and A_T^0 after Chen *et al.* [1990], and (2) for A_T^0 only based on the revised TTO-NAS data set [Brewer *et al.*, 1986]. The results are presented in the Results and Discussion section. On the basis of these checks of the temperature correlations and judged from the scatter within each basin (standard deviation of $6.9 \mu\text{mol kg}^{-1}$) we think that our results are probably good to better than $\pm 10 \mu\text{mol kg}^{-1}$.

3. Sampling and Analysis

Dissolved oxygen and nutrients were measured in ~ 1400 samples (52 stations) and C_T and A_T in ~ 700 samples (28 stations) along the WOCE-WHP section A2 during cruise 30-2 of R/V *METEOR* from Hamburg to St. John's/Newfoundland (October 12 to November 12, 1994). Figure 1 shows the cruise track as well as the location of all stations where CO₂ system parameters were determined. Samples were drawn from Niskin bottles according to a standard operating procedure for the parameters of the oceanic CO₂ system [Department of Energy, 1994]. The C_T and A_T samples were not poisoned with mercury chloride as they were stored at 4°C in the dark and analyzed within 12 hours after sampling. Furthermore, the partial pres-

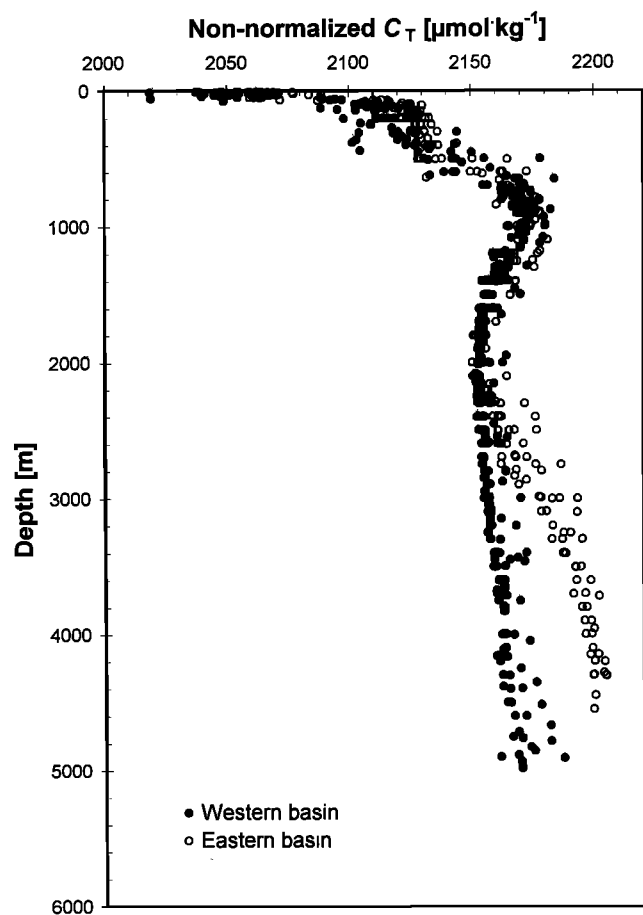


Figure 2. Plot of nonnormalized total dissolved inorganic carbon (nonnormalized C_T) versus depth of ~ 700 samples from 28 stations along WOCE-WHP section A2.

tures of CO₂ ($p\text{CO}_2$) in surface seawater and overlying air were continuously monitored with high spatial resolution (< 500 m) throughout the cruise.

C_T was measured with a coulometric titration system often referred to as "SOMMA" [Johnson *et al.*, 1993; DOE, 1994]. Determination of A_T was carried out by potentiometric titration with a closed titration cell, similar to the technique described by Bradshaw and Brewer [1988] and Millero *et al.* [1993]. Oxygen samples were analyzed by modified Winkler titration after Grasshoff [1983]. The measurement of $p\text{CO}_2$ was carried out with a newly designed continuous $p\text{CO}_2$ monitoring system based on equilibration at ambient pressure and nondispersive infrared detection of CO₂ [Körtzinger *et al.*, 1996]. The estimated accuracies (precisions) of the analyses are ± 1.5 (± 0.5) $\mu\text{mol kg}^{-1}$ for C_T , ± 6 (± 3) $\mu\text{mol kg}^{-1}$ for A_T and ± 1 (± 2) μatm for $p\text{CO}_2$. The precision of oxygen analyses is ± 0.5 $\mu\text{mol kg}^{-1}$.

4. Results and Discussion

Figures 2 and 3 show plots of nonnormalized values of C_T and A_T versus depth for 700 samples from 28 stations along WOCE-WHP section A2. The C_T profiles differ markedly between the two basins east and west of the Mid-Atlantic Ridge. While all profiles coincide in a narrow range of 2152 ± 3 $\mu\text{mol kg}^{-1}$ at 1800 m depth, they split into two distinct branches

below. C_T increases only slightly with depth in the western branch but more strongly by ~ 50 $\mu\text{mol kg}^{-1}$ in the eastern branch. Although less distinct this pattern is similarly present in A_T profiles, which show a generally smaller variability and somewhat larger scatter. The same applies to profiles of salinity normalized values of C_T and A_T as well as nutrient concentrations, which for brevity are omitted here. A plot of AOU values (calculated after (3)) for all 1400 samples from 52 stations is presented in Figure 4. Again, the two branches are clearly obvious.

Temperature correlations for C_T and A_T were calculated from surface samples along the transect. Figure 5 shows plots of (salinity normalized) C_T and A_T versus potential temperature. The temperature relationships shown in (7) and (8) are linear regressions of these data.

ΔC_T^0 values calculated after (3), (6'), (7)–(9) reach a constant level of about -62.7 $\mu\text{mol kg}^{-1}$ only in the eastern basin at depths below 3500 m. This is indicative of water, which has not yet been in contact with anthropogenic CO₂ and coincides with the northernmost traces of Antarctic Bottom Water (AABW). The average ΔC_T^0 value for the upper 300 m of the water column is -2.4 $\mu\text{mol kg}^{-1}$. The surface to bottom difference of ΔC_T^0 values of 60.3 $\mu\text{mol kg}^{-1}$ indicates that these surface waters have taken up of the order of 93% of their full component of excess CO₂ (assuming a full signal of 65 $\mu\text{mol kg}^{-1}$). In the western basin the anthropogenic CO₂ has penetrated through the entire water column down to the seafloor

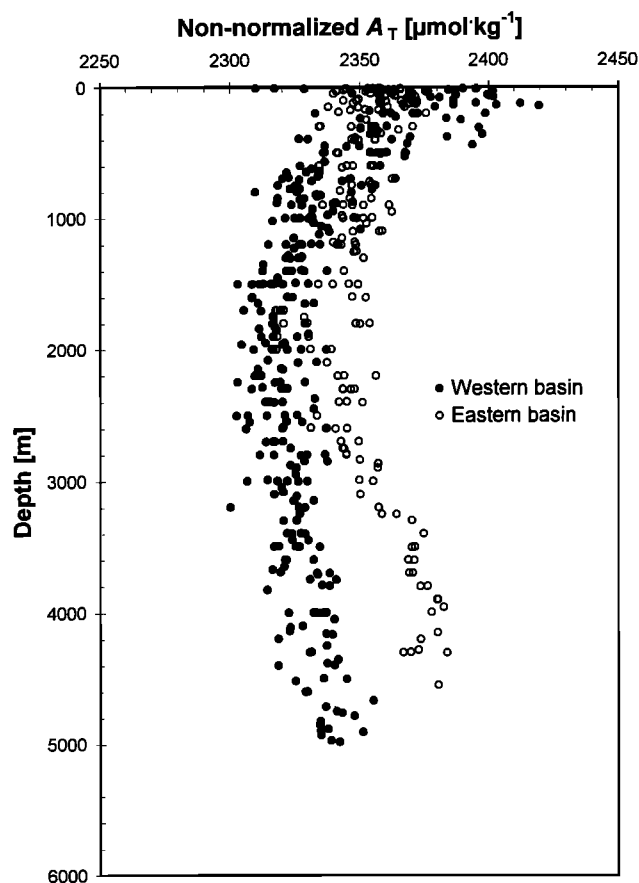


Figure 3. Plot of nonnormalized total alkalinity (nonnormalized A_T) versus depth of ~ 700 samples from 28 stations along WOCE-WHP section A2.

with a mean ΔC_T^0 value of $-52.3 \mu\text{mol kg}^{-1}$. This value is $10.4 \mu\text{mol kg}^{-1}$ higher than in the eastern basin. Generally, ΔC_T^0 values show larger scatter close to the surface, which must partly be due to the more variable oxygen saturation and biological effects.

The average value of $-62.7 \mu\text{mol kg}^{-1}$ for uncontaminated eastern basin samples below 3500 m was chosen as reference level to calculate C_T^{ant} according to (10). This reference level was assumed to be also valid for the western basin, where for obvious reasons no reference level of uncontaminated water can be defined. Figure 6 shows the resulting distribution of C_T^{ant} in the North Atlantic Ocean along WOCE-WHP section A2. It demonstrates the deeper penetration of anthropogenic CO₂ in the western basin, where even in the deepest waters a mean value of $10.4 \mu\text{mol kg}^{-1}$ of excess CO₂ was found. Although we do not claim accuracy at this level, even the existence of the Deep Western Boundary Current (DWBC) can be inferred from the C_T^{ant} data (Figure 6).

As a first cross-check the calculation was repeated with temperature correlations for C_T^{pres} and A_T^0 after *Chen et al.* [1990], which are based on measurements during a *HUDSON* cruise in the Norwegian and Greenland Seas in 1982. In contrast to our data these samples cover a range of low temperatures between -2 and 8°C . The differences between the C_T^{ant} values calculated after the two sets of temperature correlations [$C_T^{\text{ant}}(\text{METEOR}) - C_T^{\text{ant}}(\text{HUDSON})$] are small ranging from $-3 \mu\text{mol kg}^{-1}$ at 5000 m to $5 \mu\text{mol kg}^{-1}$ at 1500 m, thus nearly

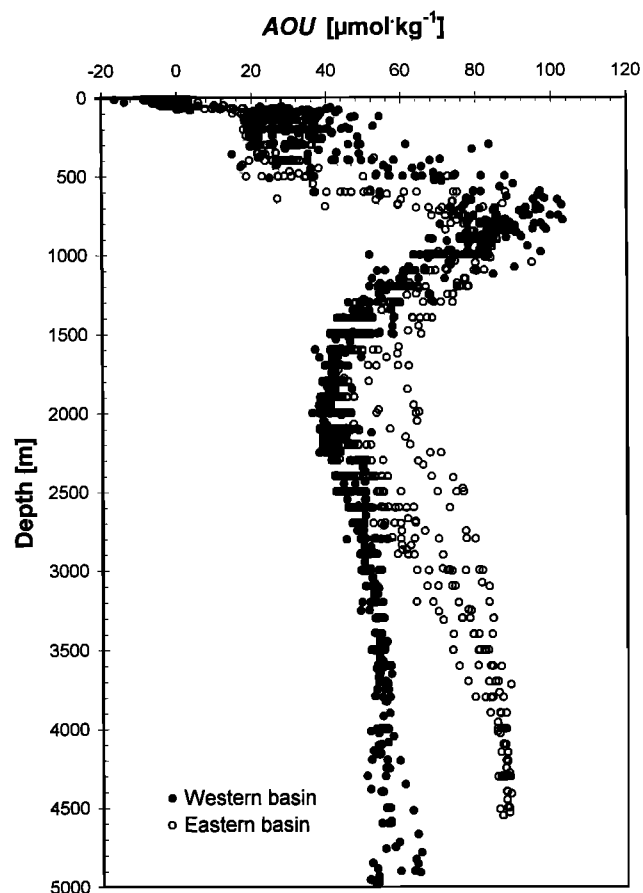


Figure 4. Plot of the apparent oxygen utilization (AOU) versus depth of ~ 1400 samples from 52 stations along WOCE-WHP section A2.

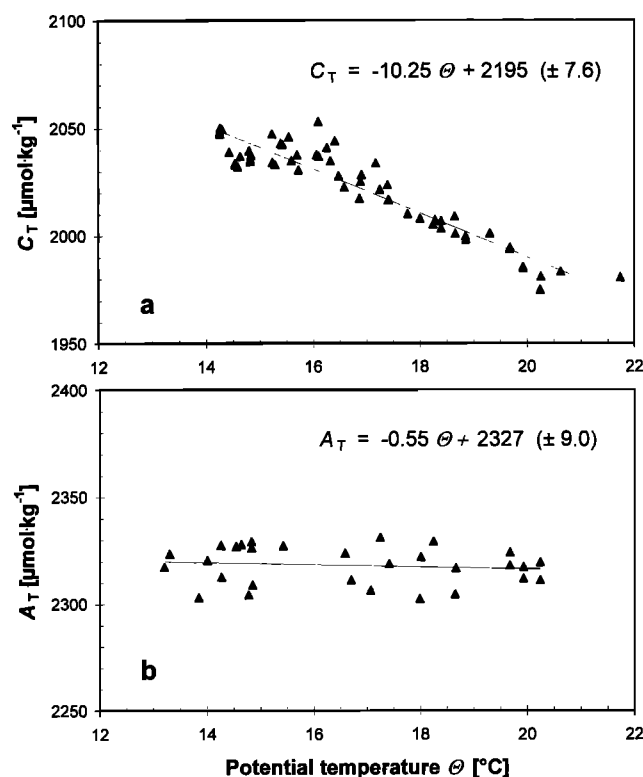


Figure 5. Plots of (salinity normalized) (a) C_T and (b) A_T versus potential temperature θ from surface samples along WOCE-WHP section A2. Linear regression lines according to (7) and (8) are also shown.

compensating over this depth interval (Figure 7a). In contrast the temperature correlations after *Chen et al.* [1990] are clearly not valid in the upper 1500 m of the water column as they yield ΔC_T^0 values between -50 and $-80 \mu\text{mol kg}^{-1}$. This would mean that the upper part of the water column and especially the mixed layer contained virtually no (or even negative values of) excess CO₂, which is clearly not the case. In part this discrepancy is probably due to the fact that the temperature correlations after *Chen et al.* [1990] were established for cold surface waters and are not applicable at the much higher temperatures ($>10^\circ\text{C}$) of the upper 500 m of the water column. Judged from this very good agreement for waters below 1500 m and given the fact that the Norwegian and Greenland Seas are not the source area for the major part of the NADW, we found the use of our own temperature correlations over the full depth profile justified. This also eliminates a potential systematic offset (e.g., from potentiometric determination of C_T during the *HUDSON* cruise) between the two data sets, which could cause strong biases in the backcalculation.

For the second cross-check we used a temperature correlation for A_T^0 which was calculated from surface samples of the revised TTO-NAS data set [*Brewer et al.*, 1986]. As shown in Figure 7b the resulting differences of the calculated C_T^{ant} values [$C_T^{\text{ant}}(\text{METEOR}) - C_T^{\text{ant}}(\text{TTO-NAS})$] are very small over the depth interval from 1500 to 5000 m ranging from $-0.2 \mu\text{mol kg}^{-1}$ at 5000 m to $0.7 \mu\text{mol kg}^{-1}$ at 1500 m. Above 1500 m the differences increase toward $7 \mu\text{mol kg}^{-1}$ yielding a total difference in the water column inventory of C_T^{ant} (see calculation below) of only $\sim 5\%$ if calculated with TTO-NAS alkalinity

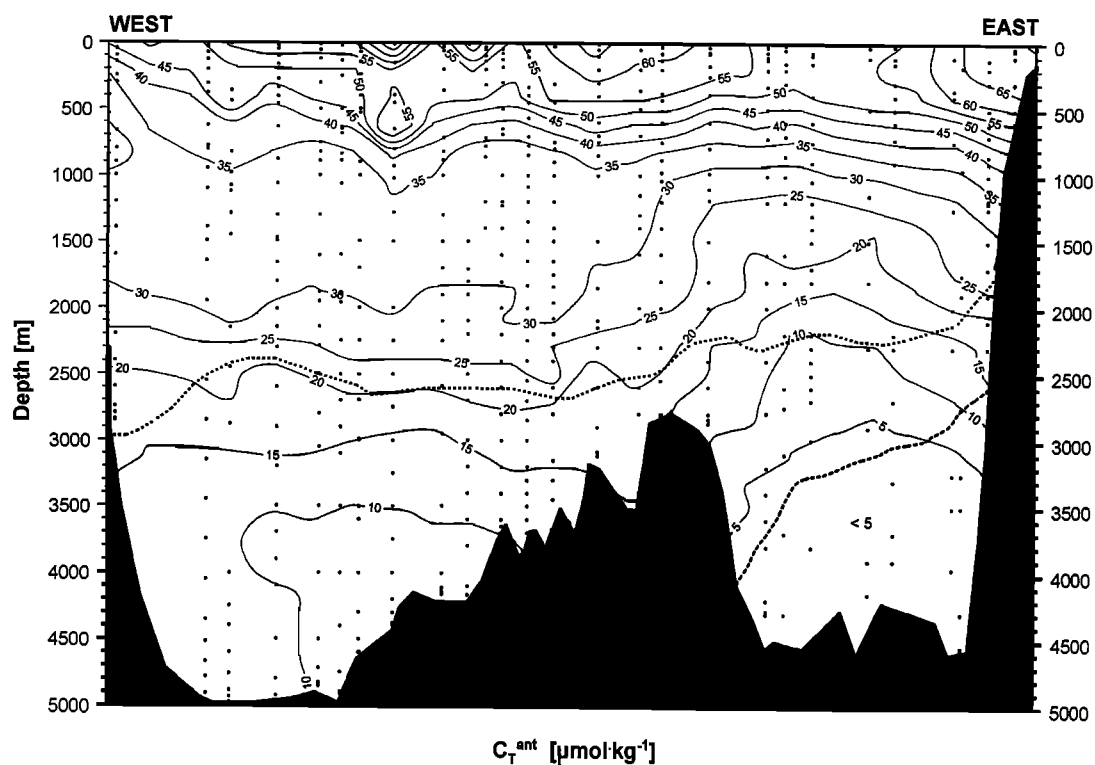


Figure 6. Section of the anthropogenic CO₂ (C_T^{ant}) across the North Atlantic Ocean along WOCE-WHP section A2. The dotted lines represent the distribution of carbon tetrachloride as obtained during the same cruise (H. Rose, personal communication, 1995). The shallow line is the 2.0 $\mu\text{mol kg}^{-1}$ isopleth, the deeper one the 0.5 $\mu\text{mol kg}^{-1}$ isopleth.

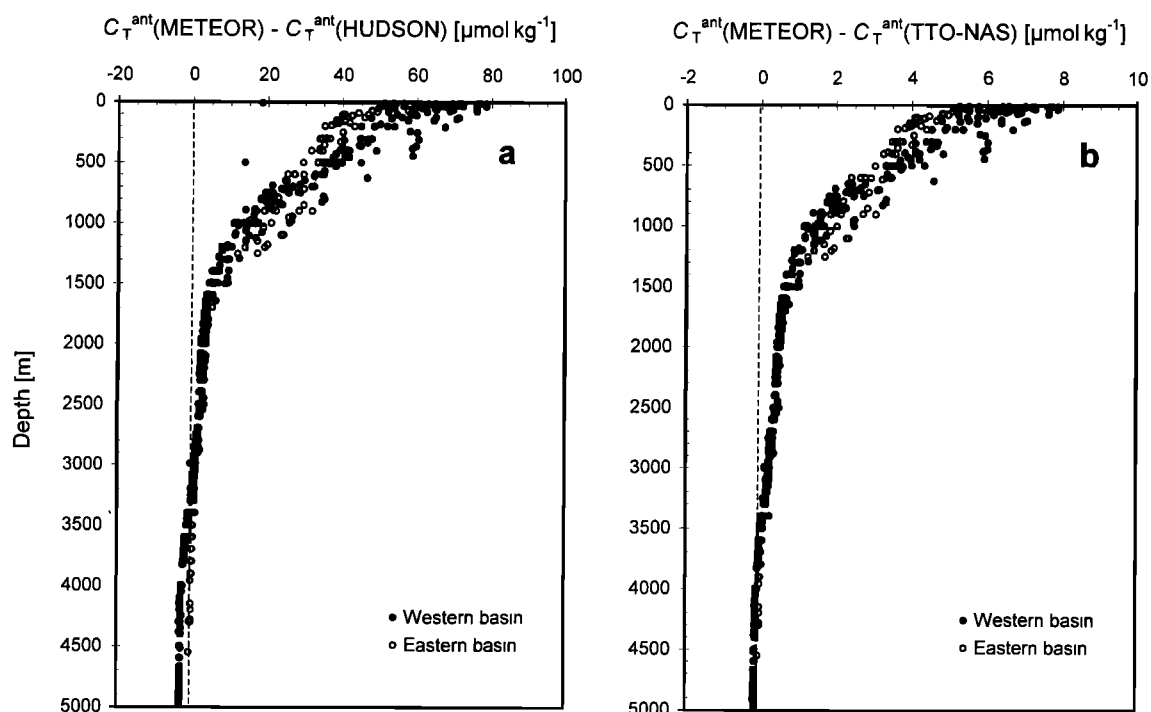


Figure 7. Plots of the differences (a) $C_T^{\text{ant}}(\text{METEOR}) - C_T^{\text{ant}}(\text{HUDSON})$ and (b) $C_T^{\text{ant}}(\text{METEOR}) - C_T^{\text{ant}}(\text{TTO-NAS})$ versus depth for all stations along WOCE-WHP section A2.

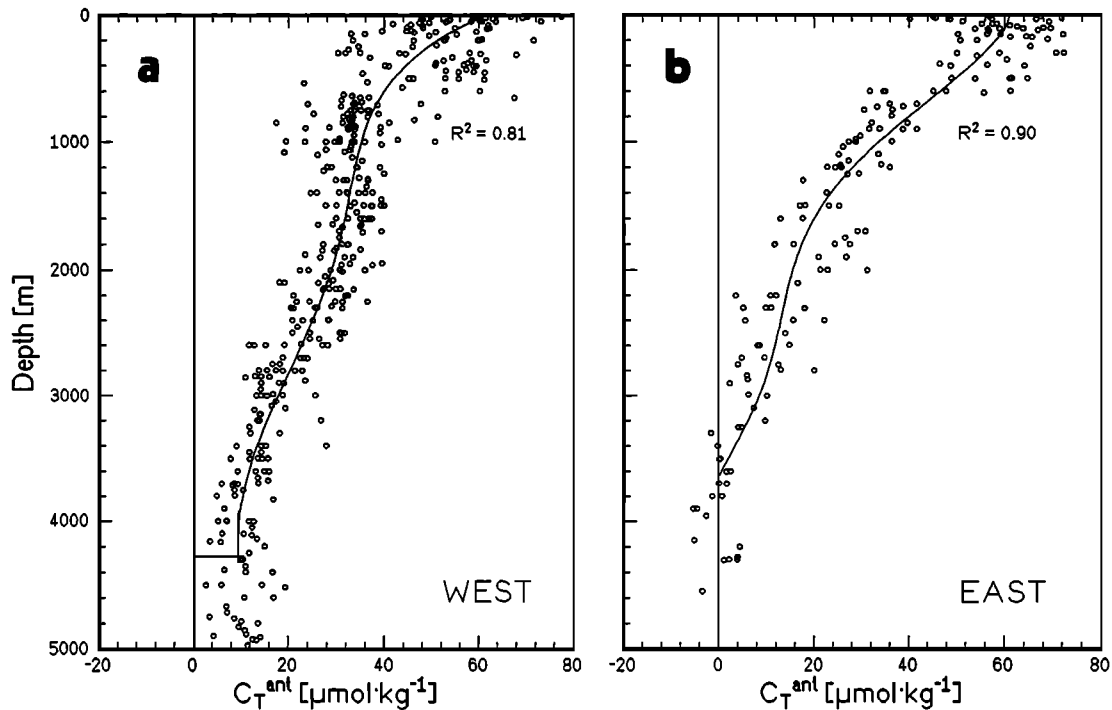


Figure 8. Cumulated depth profiles of C_T^{ant} for the (a) western and (b) eastern basin of the North Atlantic Ocean along WOCE-WHP section A2. The plot also shows the third-order polynomial least squares fit functions calculated for each basin.

data. Again, we gained confidence in our results from this very good agreement with this much larger data set.

In Figure 6 we included two contours (dotted lines) of the carbontetrachloride (CCl_4) distribution as determined from measurements during the same cruise (H. Rose, University of Bremen, personal communication, 1995). The atmospheric input function of CCl_4 closely resembles that of excess CO_2 and it has been proposed as a potential analog for the distribution of excess CO_2 [Krysell and Wallace, 1988; Wallace et al., 1994]. The equilibrium concentrations of CCl_4 in seawater under the 1994 atmosphere (~ 130 pptv) at the potential temperatures of the two contour lines (3.1°C at 2.0 pmol kg^{-1} and 2.6°C at 0.5 pmol kg^{-1}) are ~ 8.7 , respectively, 8.9 pmol kg^{-1} (calculated using Henry's law constants after Hunter-Smith et al. [1983]). These contour lines therefore account for 23% (2.0 pmol kg^{-1}) and 6% (0.5 pmol kg^{-1}) of the equilibrium concentrations of CCl_4 . The calculated concentrations of C_T^{ant} at the depths of these CCl_4 contours account for almost the same fractions of the estimated full anthropogenic CO_2 signal of $65\text{ }\mu\text{mol kg}^{-1}$, i.e., $\sim 25\%$ ($16\text{ }\mu\text{mol kg}^{-1}$) and 6% ($4\text{ }\mu\text{mol kg}^{-1}$).

We calculated third-order polynomial least squares fits for the cumulated C_T^{ant} depth profiles of each basin (Figure 8), which represent the data of the individual basins reasonably well ($R^2 = 0.90$ for the eastern and 0.81 for the western basin). The standard deviation of the calculated C_T^{ant} values from the polynomial fit is $6.9\text{ }\mu\text{mol kg}^{-1}$ for each basin. Identical values for C_T^{ant} are obtained from the polynomials at the surface ($61.2\text{ }\mu\text{mol kg}^{-1}$). The polynomials were integrated over the mean basin depths along WOCE-WHP section A2. The resulting specific inventories of anthropogenic CO_2 are $118 \times 10^6\text{ mol km}^{-2}$ in the western basin and $89 \times 10^6\text{ mol km}^{-2}$ in the eastern basin.

Some authors have also tried to estimate the pre-industrial

atmospheric $p\text{CO}_2$ ($p\text{CO}_2^0$) from the preformed values C_T^{old} and A_T^0 of samples which do not carry a detectable anthropogenic CO_2 signal [e.g., Poisson and Chen, 1987]. Broecker et al. [1985a] were particularly critical of such attempts because of the large uncertainties associated with the method. We calculated a mean $p\text{CO}_2^0$ value of $231 \pm 30\text{ }\mu\text{atm}$ for anthropogenically uncontaminated samples below 3500 m in the eastern basin, using the dissociation constants for carbonic acid after Goyet and Poisson [1989]. The two different sets of temperature correlations (Chen et al. [1990] and this work) yield virtually identical results (difference $0.9\text{ }\mu\text{atm}$). Although the uncertainty of this estimate is as high as $30\text{ }\mu\text{atm}$ as a result of the estimated errors associated with the preformed C_T^{old} and A_T^0 values, it indicates that the source region for the deep waters of the eastern basin was characterized by undersaturation of the order of $50 \pm 30\text{ }\mu\text{atm}$ with respect to the CO_2 content of the pre-industrial atmosphere ($\sim 280\text{ ppmv}$). This inferred undersaturation is in general agreement with wintertime $p\text{CO}_2$ measurements in the North Atlantic Ocean, mainly in the Greenland and Norwegian Seas [e.g., Takahashi et al., 1985b, 1995]. Therefore a reliable estimation of the pre-industrial atmospheric $p\text{CO}_2$ by this method is impossible since the assumption of equilibrium in surface waters is rarely justified and may even be totally wrong in certain areas especially during wintertime. The mean value of $p\text{CO}_2^0$ in the western basin ($>3500\text{ m}$) is $247 \pm 30\text{ }\mu\text{atm}$. This is higher than in the same depth of the eastern basin by $16\text{ }\mu\text{atm}$, and the difference corresponds to 20% of the atmospheric CO_2 rise between 1750 and 1994 ($\sim 80\text{ }\mu\text{atm}$). C_T^{ant} values of $10.4\text{ }\mu\text{mol kg}^{-1}$ in these waters account for roughly the same portion (16%) of the full anthropogenic signal.

Our results are consistent with earlier results of the back-calculation technique mainly based on GEOSECS data [Chen,

1982b, 1987] if the time lag of more than 20 years is accounted for. In a recent paper, *Gruber et al.* [1996] show results for the Atlantic Ocean from an improved method for detecting anthropogenic CO₂. While their reference year is 1982, the principle patterns of anthropogenic CO₂ in the North Atlantic Ocean are very similar. For example, penetration of anthropogenic CO₂ at 30°N is deeper in the western basin. Generally, the absolute value of excess CO₂ after *Gruber et al.* [1996] are somewhat lower than ours. Surface values in the latitude belts between 30°N and 50°N only range between 40 and 50 μmol kg⁻¹. Furthermore, detectable levels of excess CO₂ below 3500 m are only present north of 50°N in contrast to our results at 45°N. In general, the depth profiles of *Gruber et al.* [1996] show greater similarity to our profiles of the eastern basin. The difference between the results are to some extent due to the 12-year time difference between 1982 and 1994, which witnessed the steepest increase in atmospheric and thus also oceanic inventories of anthropogenic CO₂. The horizontal averaging in latitude belts also obscures some of the information contained in the zonal sections of *Gruber et al.* [1996]. Although there remain some quantitative discrepancies, we find the overall agreement encouraging. As there is no obvious reason for our results to be significantly biased high, we feel that in previous studies the uptake of anthropogenic CO₂ into the North Atlantic Ocean has been underestimated to some extent.

5. Conclusions

The penetration depths of anthropogenic CO₂ reported here are in full agreement with earlier results mainly based on GEOSECS data [*Chen*, 1982b, 1987]. Nowhere in the world ocean has such a deep penetration of anthropogenic CO₂ been found. Significant areas of bottom sediments in the Western North Atlantic are already exposed to the deepest extension of the anthropogenic CO₂ perturbation. Therefore the dissolution of carbonate minerals as the final long-term step of the equilibration with the perturbed atmosphere must already have started in these areas.

A comparison with data of the distribution of carbontetrachloride determined during the same cruise shows a remarkable agreement with very similar patterns in the two basins. It remains an important step to investigate the correlation between volatile halocarbons of anthropogenic origin (CCl₄, CFCs) and the excess CO₂ in the North Atlantic Ocean.

The present findings fit into the broad picture and the general patterns of the thermohaline circulation with the downward moving limb of the "Great Ocean Conveyor" being located in the North Atlantic Ocean. The North Atlantic Ocean can be regarded as a transit region for excess CO₂: Surface waters on their northbound way from the warm to the cold surface ocean consecutively take up excess CO₂, which is subjected to export to the deep ocean when the North Atlantic Deep Water is formed. This so-called "solubility pump" is a major process in dislocating the anthropogenic CO₂ from the surface ocean to the deep, where it is separated from the atmosphere for periods of several centuries. Our estimate of the specific anthropogenic CO₂ inventory can be explained by uptake of anthropogenic CO₂ through the surface of the area as well as by waters advected from the south, which carry a higher anthropogenic CO₂ content than deep waters leaving southward down below. While the broad picture is consistent with the present understanding of the role of the North Atlan-

tic, a thorough estimation of a basin-wide inventory of the anthropogenic CO₂ would need more data, especially from meridional transects in the North Atlantic Ocean. Modification of the original backcalculation technique as for example proposed by *Gruber et al.* [1996] carry the potential to improve the reliability of the method significantly.

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