

Comparison of two approaches to quantify anthropogenic CO₂ in the ocean: Results from the northern Indian Ocean

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Abstract. This study compares two recent estimates of anthropogenic CO₂ in the northern Indian Ocean along the World Ocean Circulation Experiment cruise I1 [Goyet *et al.*, 1999; Sabine *et al.*, 1999]. These two studies employed two different approaches to separate the anthropogenic CO₂ signal from the large natural background variability. Sabine *et al.* [1999] used the ΔC^* approach first described by Gruber *et al.* [1996], whereas Goyet *et al.* [1999] used an optimum multiparameter mixing analysis referred to as the MIX approach. Both approaches make use of similar assumptions in order to remove variations due to remineralization of organic matter and the dissolution of calcium carbonates (biological pumps). However, the two approaches use very different hypotheses in order to account for variations due to physical processes including mixing and the CO₂ solubility pump. Consequently, substantial differences exist in the upper thermocline approximately between 200 and 600 m. Anthropogenic CO₂ concentrations estimated using the ΔC^* approach average $12 \pm 4 \mu\text{mol kg}^{-1}$ higher in this depth range than concentrations estimated using the MIX approach. Below ~ 800 m, the MIX approach estimates slightly higher anthropogenic CO₂ concentrations and a deeper vertical penetration. Despite this compensatory effect, water column inventories estimated in the 0–3000 m depth range by the ΔC^* approach are generally $\sim 20\%$ higher than those estimated by the MIX approach, with this difference being statistically significant beyond the 0.001 level. We examine possible causes for these differences and identify a number of critical additional measurements that will make it possible to discriminate better between the two approaches.

1. Introduction

The first anthropogenic CO₂ estimates calculated from direct observations of total alkalinity (TA) and

total carbon dioxide (TCO₂) concentrations were presented over 20 years ago by Brewer [1978] and Chen and Millero [1979]. Variations of this approach have been pursued by a large number of investigators in many regions of the world ocean [Chen, 1982; Papaud and Poisson, 1986; Poisson and Chen, 1987; Goyet and Brewer, 1993; Goyet *et al.*, 1998]. However, the Brewer and Chen/Millero approach has not found general acceptance, since the uncertainties were generally regarded as too large [Shiller, 1981; Broecker *et al.*, 1985]. Recently, Gruber *et al.* [1996] proposed to improve this approach by introducing a “quasi-conservative” tracer, ΔC^* , in combination with the use of transient tracers to estimate ventilation ages. This approach (here-

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after referred to as the ΔC^* approach) has been applied in the Atlantic Ocean [Gruber *et al.*, 1996; Gruber, 1998] and with a slight modification in the Indian Ocean [Sabine *et al.*, 1999] with the data from the Joint Global Ocean Flux Study (JGOFS) and World Ocean Circulation Experiment (WOCE) Indian Ocean survey. More recently, Goyet *et al.* [1999] introduced a new approach based upon an optimum multiparameter mixing analysis (hereafter referred to as the MIX approach). This approach was first applied to estimate anthropogenic CO_2 along WOCE section I1 (WOCE I1) in the northern Indian Ocean across the Arabian Sea and the Bay of Bengal. Since both Goyet *et al.* [1999] and Sabine *et al.* [1999] used the same WOCE I1 data, a detailed comparison between the two approaches can be made.

This study will focus on the similarities and differences in the fundamental concepts and assumptions of the two approaches. Results from WOCE line I1 will be used to illustrate the effect that these assumptions have on the final results. In the absence of any other method for directly measuring oceanic anthropogenic CO_2 concentrations, a comparison of these two very different approaches can provide insights on the uncertainties of anthropogenic CO_2 concentrations. We first recall the fundamental concepts and hypotheses used in each approach before comparing the results and analyzing the differences.

2. Principles of the Two Approaches

Both the ΔC^* and the MIX approaches are based on the same premise that below the mixed layer depth, the anthropogenic CO_2 content of a water parcel ($\text{TCO}_2^{\text{ant}}$) can be estimated by subtracting the contribution of the biological pumps ($\Delta \text{TCO}_2^{\text{bio}}$) and of the physical processes (including mixing of the preindustrial end-member TCO_2 concentrations and the CO_2 solubility pump) ($\text{TCO}_2^{\text{phys}}$) from the measured TCO_2 (TCO_2^m). Hence

$$\text{TCO}_2^{\text{ant}} = \text{TCO}_2^m - \Delta \text{TCO}_2^{\text{bio}} - \text{TCO}_2^{\text{phys}}. \quad (1)$$

Such a separation relies on the hypothesis that the natural carbon cycle has been in a steady state before the industrial revolution and that it has remained in this steady state ever since. In the subsequent sections the treatment of the individual contributions in (1) are analyzed and compared between the two different approaches. The most fundamental equations used in the original papers are given and referenced to a common notation to facilitate the comparison.

2.1. Biological Pump Contribution

The contribution of the biological pump must include adjustments for both organic matter decomposition and calcium carbonate formation/dissolution. Both ap-

proaches examined here rely on the same assumption that below the mixed layer depth, the effect of remineralization of organic matter and calcium carbonate can be estimated from changes in dissolved oxygen and total alkalinity (TA) using constant stoichiometric ratios (i.e., Redfield ratios). Both approaches evaluate the function [Brewer, 1978]:

$$\Delta \text{TCO}_2^{\text{bio}} = R_{\text{C:O}_2} \Delta \text{O}_2 + 0.5(\Delta \text{TA} + R_{\text{N:O}_2} \Delta \text{O}_2), \quad (2)$$

where $R_{\text{C:O}_2}$ is a stoichiometric carbon to oxygen ratio, ΔO_2 is the difference between the measured dissolved oxygen (O_2^m) and a reference oxygen concentration (O_2^0), and ΔTA is the difference between the measured total alkalinity (TA^m) and a reference total alkalinity (TA^0). In the ΔC^* approach, the reference O_2^0 concentration is assumed to be the oxygen concentration in surface seawater in equilibrium with the atmosphere. The reference TA^0 concentration is estimated from an empirical fit of surface TA as a function of conservative properties.

The MIX approach uses the same equation (2) and evaluates directly the changes in oxygen (ΔO_2) and total alkalinity (ΔTA) concentrations from the optimum multiparameter mixing analysis (OMPA) (see details of this analysis in section 2.2.2, the ‘‘MIX approach,’’ on the contribution of physical processes and the solubility pump). The OMPA simultaneously quantifies the mixing coefficient of each water mass at each station for each sample. These terms (ΔO_2 , ΔTA) are introduced in the following equation:

$$\Delta \text{TCO}_2^{\text{bio}} = a \Delta \text{O}_2 + 0.5 \Delta \text{TA}, \quad (3)$$

where the coefficient a is equivalent to the sum $R_{\text{C:O}_2} + 0.5 R_{\text{N:O}_2}$.

Both approaches are susceptible to uncertainties in the reference concentrations (O_2^0 and TA^0) and to potential biases in the stoichiometric ratios. Here the primary difference between the MIX approach and the ΔC^* approach are the reference concentrations O_2^0 and TA^0 . In the MIX approach the reference concentrations are the properties of the water sources. In other words, there are several reference levels whose number depends upon the considered number of source waters. It is important to note that these water sources are not necessarily at the surface. By contrast, all O_2^0 and TA^0 concentrations in the ΔC^* approach are referenced relative to the surface ocean and are represented by functions of conservative water properties.

In summary, both approaches employ similar concepts for making the biological corrections. However, differences in certain details of the computation, like differing calculation of the changes in oxygen and total alkalinity concentrations, can lead to differences in the estimated anthropogenic CO_2 concentrations. These resulting differences will be discussed in section 4.

2.2. Physical Processes and Solubility Pump Contribution

The largest differences in the ΔC^* and MIX approaches lie in the evaluation of the CO_2 contributions from the physical processes including the preindustrial solubility pump. We first describe the ΔC^* approach and then the MIX method.

2.2.1. ΔC^* approach. In the ΔC^* approach the $\text{TCO}_2^{\text{phys}}$ term is separated into a preindustrial solubility equilibrium ($\text{TCO}_2^{\text{eq } 280}$) and into a component ($\Delta \text{TCO}_2^{\text{diseq}}$) representing the CO_2 disequilibrium between the preindustrial atmosphere and the surface ocean:

$$\text{TCO}_2^{\text{phys}} = \text{TCO}_2^{\text{eq } 280} + \Delta \text{TCO}_2^{\text{diseq}}. \quad (4)$$

The term $\text{TCO}_2^{\text{eq } 280}$ is the TCO_2 concentration the waters would have if they were in equilibrium with the preindustrial atmospheric CO_2 partial pressure of 280 μatm . This preindustrial equilibrium concentration can be directly computed for each sample from potential temperature, salinity, and estimated preformed TA using known thermodynamic relationships. The disequilibrium term, $\Delta \text{TCO}_2^{\text{diseq}}$, reflects the fact that due to the relatively slow gas exchange for CO_2 [Broecker and Peng, 1974], surface waters are seldom in equilibrium with the atmosphere. Once a water parcel leaves the surface ocean, the air-sea disequilibrium is preserved and can subsequently change only by mixing. Thus the $\Delta \text{TCO}_2^{\text{diseq}}$ of any water parcel represents a mixture of the air-sea disequilibria of the different end-members contributing to this water parcel. Combining (1) and (4) gives

$$\begin{aligned} \text{TCO}_2^{\text{ant}} &= \text{TCO}_2^m - \Delta \text{TCO}_2^{\text{bio}} - \text{TCO}_2^{\text{eq } 280} - \Delta \text{TCO}_2^{\text{diseq}} \\ &= \Delta C^* - \Delta \text{TCO}_2^{\text{diseq}}. \end{aligned} \quad (5)$$

The three terms to the right of the first equal sign can be explicitly calculated for each sample. These terms combined make the quasi-conservative tracer ΔC^* [Gruber *et al.*, 1996]. The estimation of the disequilibrium term is more difficult and requires two important assumptions. First it is assumed that water masses move and mix predominantly along isopycnal surfaces. The second hypothesis is that $\Delta \text{TCO}_2^{\text{diseq}}$ remained constant over time (i.e., did not change as a consequence of the CO_2 increase in the atmosphere). This assumption implies that surface water $p\text{CO}_2$ has increased at roughly the same rate as atmospheric $p\text{CO}_2$.

The $\Delta \text{TCO}_2^{\text{diseq}}$ of each end-member is then evaluated over discrete density intervals following two different methods. For deeper density surfaces the ΔC^* values far away from the outcrop region are old enough to be free of anthropogenic CO_2 . In these regions the left-hand side of (5) is zero, and $\Delta \text{TCO}_2^{\text{diseq}}$ is calculated as the mean of ΔC^* within this region and for each isopycnal interval. On shallower density surfaces, where

anthropogenic CO_2 is present over the entire isopycnal surface, $\Delta \text{TCO}_2^{\text{diseq}}$ is evaluated using ΔC^*_t :

$$\begin{aligned} \Delta \text{TCO}_2^{\text{diseq}} &= \text{mean of } \Delta C^*_t \\ &= \text{mean of } (\text{TCO}_2^m - \Delta \text{TCO}_2^{\text{bio}} - \text{TCO}_2^{\text{eq } t}), \end{aligned} \quad (6)$$

where $\text{TCO}_2^{\text{eq } t}$ is the TCO_2 in equilibrium with the atmospheric CO_2 partial pressure present at the time when the water parcel was last at the surface. This time is evaluated on the basis of transient tracers (e.g., chlorofluorocarbons or CFCs) that contain information on the ventilation age of the water parcel. The equilibrium concentration at time t ($\text{TCO}_2^{\text{eq } t}$) can be directly computed from potential temperature, salinity, and preformed alkalinity using known thermodynamic relationships. In the intermediate waters a transition from the ΔC^*_t to the ΔC^* method for estimating $\Delta \text{TCO}_2^{\text{diseq}}$ must be made. This transition can be made either as an abrupt switching of methods or as a gradual transition from one method to another. The exact method is somewhat subjective. The approach taken for the Indian Ocean estimates is discussed in section 3.1.

Once the individual $\Delta \text{TCO}_2^{\text{diseq}}$ of each end-member of an isopycnal surface has been determined, the anthropogenic CO_2 below the mixed layer can be determined according to (5). Note that there is no theoretical limit to the number of end-members considered, but in practice, a two end-member mixing model has been used for most regions [Gruber, 1998; Sabine *et al.*, 1999]. In surface waters the anthropogenic CO_2 content is calculated directly as a difference between ΔC^*_t and ΔC^* , which is equivalent to the difference between $\text{TCO}_2^{\text{eq } t}$ and $\text{TCO}_2^{\text{eq } 280}$:

$$\text{TCO}_2^{\text{ant}} = \text{TCO}_2^{\text{eq } t} - \text{TCO}_2^{\text{eq } 280}. \quad (7)$$

The ΔC^* method of separating the anthropogenic CO_2 from the large variability of TCO_2 is based on many assumptions. However, many of these assumptions can be tested against observations. Gruber [1998] shows that most of these tests support the assumptions, but nevertheless a number of caveats remain. The most important ones are the assumption that the air-sea disequilibrium has remained constant over time and that the tracer age is a good approximation of the “true” ventilation age. These caveats will be discussed in greater detail below when discussing results from the two methods.

2.2.2. MIX approach. In the MIX approach, $\text{TCO}_2^{\text{phys}}$ is calculated from the mixing coefficients (k_j) and the preanthropogenic concentration [TCO_2^0] $_j$ in each of the n water sources j .

$$\text{TCO}_2^{\text{phys}} = \sum_{j=1}^n k_j [\text{TCO}_2^0]_j \quad (8)$$

The mixing coefficients are initially quantified from conservative (C) and semiconservative (NC) tracers using an optimum multi-parameter analysis (OMPA) adapted from a method first described by *Tomczak and Large* [1989]. Briefly, this analysis solves the system of equations [*Goyet et al.*, 1999; *Coatanoan et al.*, 1999]:

$$C_m = \sum k_j C_j, \quad (9)$$

$$NC_m = \sum k_j NC_j + \Delta NC, \quad (10)$$

$$\sum k_j = 1 \text{ with all } k_j \geq 0, \quad (11)$$

where C_j and NC_j are the properties of the source waters and ΔNC denotes the nonconservative change that occurred since the individual source waters left their origin. The number of source waters considered depends on the location and on the number of independent tracers available. The system of (9)–(11) is solved by optimization of the residuals. The optimized residuals from the OMPA provide a feedback and indication on the validity of the choice of the different water sources. As mentioned above, the reference properties are those of the different water sources (surface, intermediate, and deep waters) rather than those of surface waters. In (8) the preindustrial TCO_2 concentrations of the source waters, $[\text{TCO}_2^0]_j$, are not known, except in deep waters where anthropogenic CO_2 is assumed to be zero. Only the sum $[\text{TCO}_2^0 + \text{TCO}_2^{\text{ant}}]_j$ is known within the range of spatial and temporal variability. Therefore, (8) is not explicitly used. For the calculation of each $[\text{TCO}_2^{\text{ant}}]_j$, a sigmoid function is introduced to add the additional constraint that anthropogenic CO_2 decreases with increasing distance (and consequently age) from the considered water source. Different sigmoid functions ($F_j(z)$) can be used according to the geographical location and depth of the water sources. Thus the $[\text{TCO}_2^{\text{ant}}]_j$ are determined below the wintertime mixed layer from the following equation:

$$\text{TCO}_2^m - \text{TCO}_2^{\text{bio}} = \sum_{j=1}^n k_j \left[[\text{TCO}_2^0]_j + [\text{TCO}_2^{\text{ant}}]_j F_j(z) \right] \quad (12)$$

with the constraint

$$[\text{TCO}_2^0]_j + [\text{TCO}_2^{\text{ant}}]_j = [\text{TCO}_2^w]_j + \epsilon_j, \quad (13)$$

where ϵ_j represents the uncertainty of the TCO_2 concentration in the water mass $[\text{TCO}_2^w]_j$. This uncertainty includes both the measurement uncertainty and the uncertainty caused by spatiotemporal variability.

The constants of the sigmoids and the values of $[\text{TCO}_2^{\text{ant}}]_j$ are estimated iteratively to minimize the residuals of (12) randomly around zero. These residuals represent the sum of the uncertainties of each term of the equation, thus including the uncertainties of the TCO_2^m , $\Delta \text{TCO}_2^{\text{bio}}$, k_j , $F_j(z)$, and $[\text{TCO}_2^{\text{ant}}]_j$. Finally, $\text{TCO}_2^{\text{ant}}$ is calculated throughout the water column from the following equation:

$$\text{TCO}_2^{\text{ant}} = \sum_{j=1}^n k_j [\text{TCO}_2^{\text{ant}}]_j F_j(z) \quad (14)$$

The MIX approach explicitly accounts for the effect of water sources mixing and relies on the assumption that the properties of each water sample can be considered as representing the properties of a mixture of n discrete source water types [*You and Tomczak*, 1993]. The results of the MIX approach are sensitive to uncertainties and potential biases in the specification of source water characteristics. We take the influence of random uncertainties into account by computing the mean solution for each mixing coefficient from 30 perturbation experiments. These experiments are performed by adding random deviations to the measured data and tracer characteristics of each water source and computing the solution as in the standard case. The residuals from the OMPA used to quantify the mixing coefficients k_j (equations (9)–(11)) and those from (12) provide a certain feedback on the validity of the choice of the water sources and on the uncertainties of the results. A more detailed discussion of potential biases and the influence they may have on the results is given below in section 3.1 in reference to the specific application of the MIX approach to the WOCE I1 data.

3. Application in the Northern Indian Ocean along WOCE I1 Cruise

3.1. Specific Hypotheses

Sabine et al. [1999] applied the ΔC^* approach to data from the entire Indian Ocean as sampled by the WOCE/JGOFS global survey. The values of the ΔC^* were calculated using a carbon to oxygen ratio of -0.688 and a nitrogen to oxygen ratio of -0.094 [*Anderson and Sarmiento*, 1994]. Preformed alkalinity was estimated from an empirical fit of surface TA in the Indian Ocean as a function of salinity, potential temperature, and the conservative tracer PO ($\text{PO} = \text{O}_2 + 170 \text{ PO}_4$). The air-sea disequilibria, $\Delta \text{TCO}_2^{\text{diseq}}$, were then determined in isopycnal intervals of thickness 0.05 over three main layers in the water column: (1) the subsurface layer ($25.95 < \sigma_\theta < 27.25$), where the $\Delta \text{TCO}_2^{\text{diseq}}$ concentration was estimated using the mean of ΔC^*_t within each isopycnal interval; (2) the intermediate layer ($27.25 < \sigma_\theta < 27.5$), where the $\Delta \text{TCO}_2^{\text{diseq}}$ concentration was estimated using a weighted average of the mean of ΔC^* and the mean of ΔC^*_t within each isopycnal interval; and (3) the deeper layer ($\sigma_\theta > 27.5$), where the $\Delta \text{TCO}_2^{\text{diseq}}$ concentration was estimated using the mean of ΔC^* within each isopycnal interval. In these three main layers the anthropogenic CO_2 concentrations were calculated according to (5). In the surface layer, at lower densities ($\sigma_\theta < 25.95$; \sim upper 150 m), anthropogenic CO_2 was calculated following (7).

Along the section WOCE I1, two end-members on each density interval were considered in the Arabian Sea and one end-member on each density interval in the Bay of Bengal. In addition, a term of denitrification was also introduced throughout the water column for the $\text{TCO}_2^{\text{bio}}$ calculation [Sabine et al., 1999]. The $\Delta\text{TCO}_2^{\text{bio}}$ term in (2) assumes that the remineralization of carbon in the interior of the ocean occurs in proportion to the oxygen consumption based on the stoichiometry of oxic remineralization. For some regions of the Arabian Sea, however, oxygen depletion can be quite extensive at relatively shallow depths [Sen Gupta et al., 1976; Deuser et al., 1978; Naqvi and Sen Gupta, 1985]. In areas where the waters become suboxic, denitrification can significantly alter the dissolved carbon to oxygen ratio since inorganic carbon is added to seawater without an accompanying loss of oxygen [Naqvi and Sen Gupta, 1985; Anderson and Dyrssen, 1994]. The dissolved carbon generated by denitrification shows up as high ΔC^* values. Following the methods of Gruber and Sarmiento [1997], the denitrification signal was estimated using N^* . The N^* tracer is a quasi-conservative tracer that can be used to identify nitrogen excess or deficits relative to phosphorus. The N^* values were converted from nitrogen units to $\mu\text{mol C kg}^{-1}$ based on a denitrification carbon to nitrogen ratio of 106:–104 [Gruber and Sarmiento, 1997] and subtracted from ΔC^* throughout the Indian Ocean. This correction has no effect on the majority of the Indian Ocean but can be as large as $15 \mu\text{mol kg}^{-1}$ in the Arabian Sea. For the WOCE I1 section, this correction was generally less $3\text{--}4 \mu\text{mol kg}^{-1}$ at intermediate depths (400–1000 m) in the Arabian Sea and $2\text{--}3 \mu\text{mol kg}^{-1}$ in the Bay of Bengal.

In the MIX approach [Goyet et al., 1999], (9)–(11) and (12)–(13) were solved for samples below 200 m. This depth was assumed to be at or below the wintertime mixed layer depth. For the stoichiometric factor a in (3), a value of -0.78 was adopted [Brewer, 1978]. The magnitude of this stoichiometric factor is thus slightly larger than the corresponding value of -0.74 ($-0.688 + 0.5(-0.094)$) used by Sabine et al. [1999]. Eight water sources were characterized using potential temperature, salinity, oxygen, TA, and literature. Three surface source waters were included: Bengal Bay Surface Water (BBSW), Red Sea Surface Water (RSSW), and Arabian Sea Water (ASW). Three source waters are originating at intermediate depths: Bengal Bay Intermediate Waters (BBIW), Red Sea Water (RSW), and Indian Intermediate Waters (IIW). Last, two deep water sources were considered: Deep Indian Water (DIW) and Bottom Water (BW). Four different sigmoid functions were used according to geographical location and depth of the water sources (1 for ASW and RSSW, 1 for BBSW, 1 for RSW and IIW, and 1 for BBIW). Since most of the denitrification occurs in the northern part of the Arabian Sea, north of 12°N [Naqvi, 1994], this pro-

cess is not expected to strongly affect waters along the WOCE I1 cruise track and therefore was not included in this application. The low N^* corrections found by Sabine et al. [1999] for WOCE I1 further supports this assumption. After the mixing coefficients and the anthropogenic TCO_2 concentrations of the source waters had been determined, the anthropogenic CO_2 content was determined throughout the water column from (14).

3.2. Results

Figure 1 shows the mean profiles of the anthropogenic CO_2 concentrations estimated by the two approaches along the three main sections of the WOCE I1 cruise. The error bars represent the variability of the results within the depth intervals (20 m in the upper 250 m; 100 m for full water column profiles) and zonal intervals (from 43°E to 59°E in the Gulf of Aden, from 51°E to 76°E in the Arabian Sea, and from 81°E to 97°E in the Bay of Bengal).

In the Arabian Sea and the Bay of Bengal, both methods estimate very similar concentrations in the upper ocean, above 150 m. These concentrations are very close to what can be expected from thermodynamic considerations assuming that these surface waters had tracked closely the atmospheric CO_2 increase. The two methods also estimate relatively similar values below ~ 800 m where the concentrations are small (less than $10 \mu\text{mol kg}^{-1}$). However, substantial differences exist in the depth range from 200 to 600 m. This difference is a consequence of the estimation of a completely different vertical gradient by the two approaches. In the upper 600 m, the ΔC^* approach estimates a decrease in anthropogenic CO_2 concentration by $\sim 70\%$, while the MIX approach estimates nearly a 90% decrease. Around $\sim 600\text{--}800$ m, the anthropogenic CO_2 concentrations from the ΔC^* approach sharply decrease to reach the MIX anthropogenic concentrations. In contrast, the MIX approach estimates a smooth decrease with depth, similar to salinity and density, throughout the water column. Below 800 m, a more detailed inspection of Figure 1 reveals that the results from the MIX approach are slightly higher and tend to indicate a deeper vertical penetration of anthropogenic ΔCO_2 than those from the ΔC^* approach.

Figure 2 illustrates that the large difference between the two approaches found in the midthermocline extends over all sections of the WOCE I1 cruise. The differences attain largest values in the western part of the Gulf of Aden section and decrease toward the east in the Arabian Sea. The smallest differences are found in the eastern Arabian Sea. The differences are relatively constant at intermediate depths along the Bay of Bengal section. These sections also show more clearly that the MIX approach tends to estimate slightly higher anthropogenic CO_2 concentration in the depth range

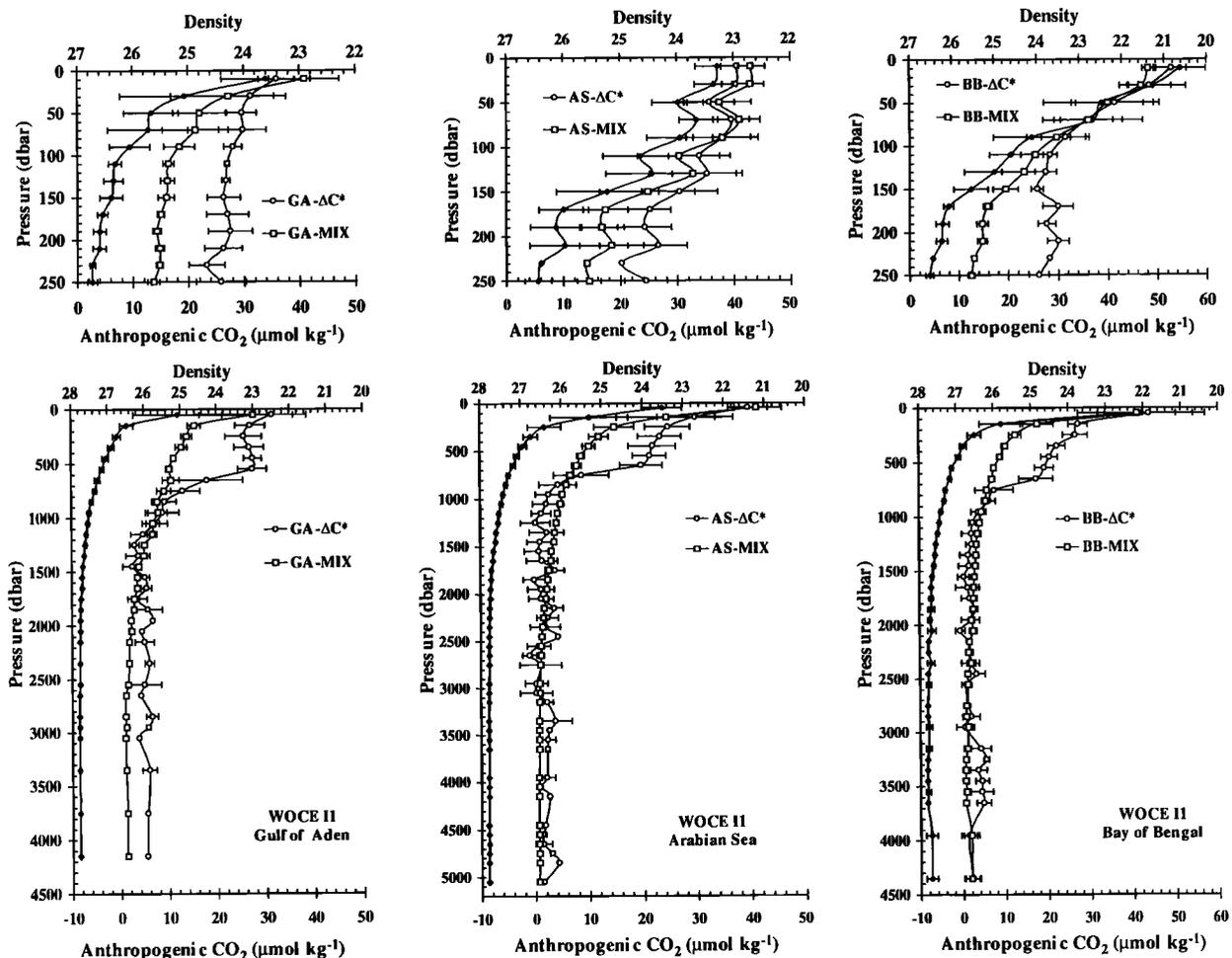


Figure 1. Average vertical distribution of density and anthropogenic CO₂ ($\mu\text{mol kg}^{-1}$) estimated by the ΔC^* approach (circles) and the MIX approach (squares) for the three basins, the Gulf of Aden (GA), the Arabian Sea (AS), and the Bay of Bengal (BB). These averages were calculated over 20 dbar intervals above 250 dbar and over 100 dbar intervals below. The error bars represent the variability of the anthropogenic CO₂ concentration over the calculated pressure ranges and zonal sections.

from ~ 800 to 2000 m in the Arabian Sea and the Bay of Bengal, and from 1000 to 1500 m in the Gulf of Aden, where anthropogenic CO₂ concentrations range from 10 to 0 $\mu\text{mol kg}^{-1}$.

To quantify the effect of these differences on the estimated water column inventories, the anthropogenic CO₂ concentrations were vertically integrated at each station. To do so, the anthropogenic CO₂ concentrations were first converted to units of mol m^{-3} . The data at each station were then fitted with a one-dimensional quasi-cubic Hermite interpolation [International Mathematical and Statistical Library, 1980]. Finally, the interpolated data were integrated between the surface and 3000 m. Stations without enough data to generate a reasonable fit (e.g., fewer than four points or not sampled evenly enough to constrain the curve down to 3000 m) were excluded from consideration. As a result,

only a limited number of stations far from the strait of Bab el Mandeb were used for the section in the Gulf of Aden.

Figure 3 shows the corresponding water column inventories for the two approaches. The vertically integrated concentrations from the ΔC^* approach are on average 20% higher than those from the MIX approach. A Wilcoxon Signed Rank test [Huber, 1981; Launer and Wilkinson, 1979] on the results ($N = 94$; $W = 3197$; $Z = 6.03$), indicates that the difference between the two sets of estimates is highly significant. The difference between these integrated concentrations would be slightly larger if there were not a compensatory effect of the deeper vertical penetration of anthropogenic CO₂ estimated by the MIX approach and if the negative values from the ΔC^* method were reduced to zero. Figure 3 also demonstrates that there is more variability in

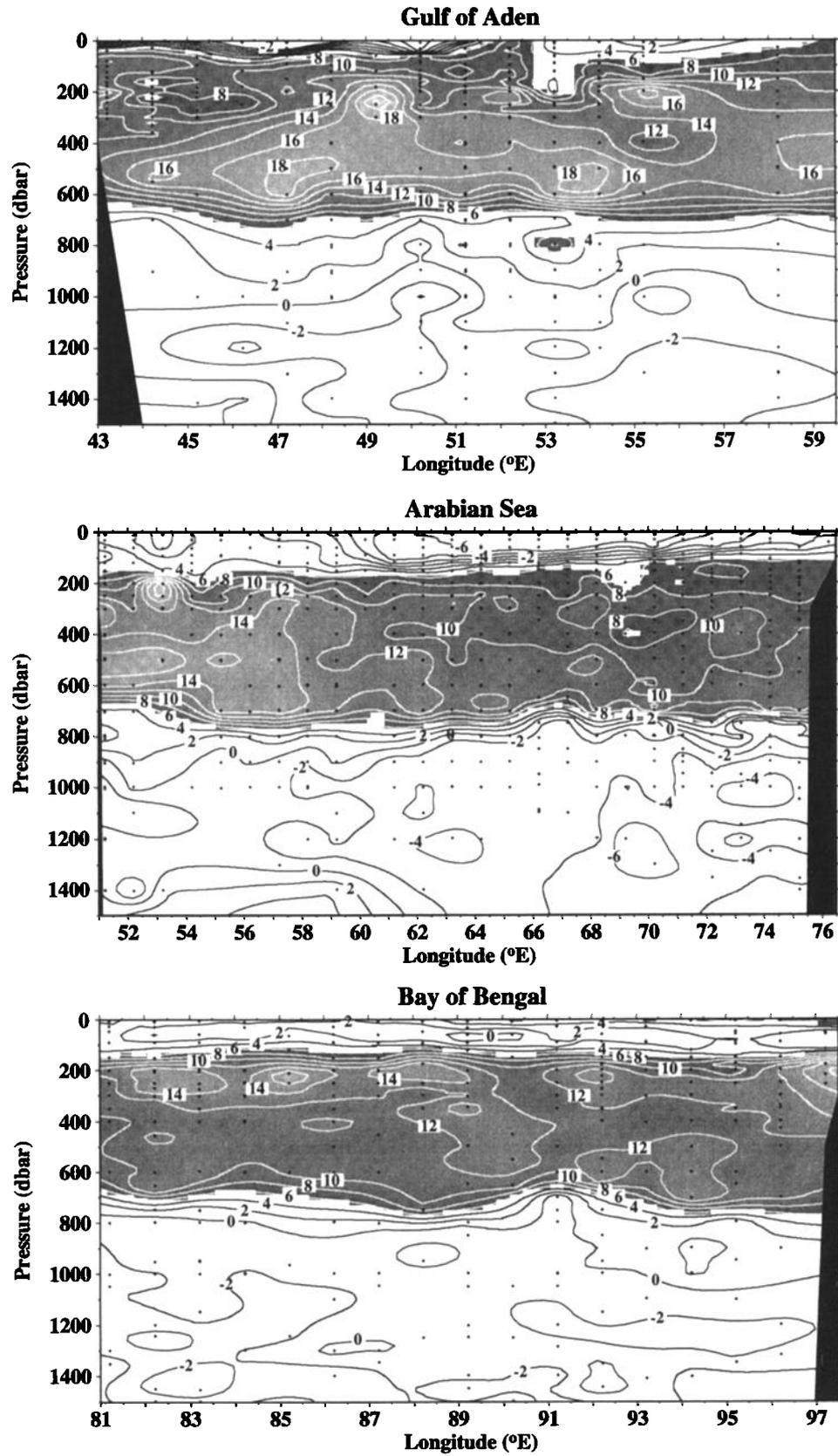


Figure 2. Zonal sections of the difference ($\mu\text{mol kg}^{-1}$) between the anthropogenic CO₂ calculated from the ΔC^* approach and the MIX approach along the three sections of the WOCE II cruise.

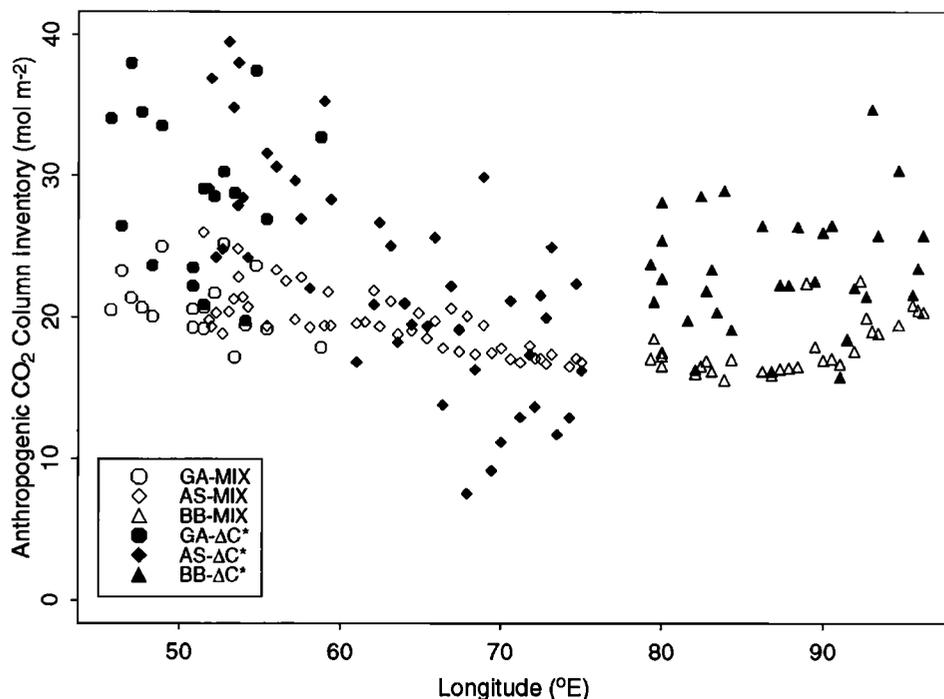


Figure 3. Vertically integrated anthropogenic CO_2 concentrations as a function of longitude. The anthropogenic CO_2 concentrations are integrated at each station where enough data were available over the 0–3000 m depth range. The solid symbols are the estimates by the ΔC^* approach, and the open symbols are the estimates by the MIX approach. The circles, rhombs, and triangles represent the Gulf of Aden, the Arabian Sea, and the Bay of Bengal, respectively.

the ΔC^* vertical integrals. This variability results from scatter in the vertical profiles and larger zonal variations in the ΔC^* values along the three different sections. For instance, in the Arabian Sea (west of about 78°E), the ΔC^* approach estimates a strong decrease of the inventories toward the east with a slope of -0.61 ± 0.09 , whereas the MIX method estimates a significantly smaller slope of -0.18 ± 0.03 for the same region. In the Bay of Bengal the slopes are 0.17 ± 0.16 and 0.19 ± 0.05 for the ΔC^* and the MIX methods, respectively.

4. Discussion

The results presented in Figures 1–3 demonstrate that these two independent approaches used to detect anthropogenic CO_2 in the oceans yield relatively similar results in the upper 150 m of the Arabian Sea and the Bay of Bengal. However, these two approaches estimate very different distributions of anthropogenic CO_2 concentrations below this depth, especially in the thermocline in the depth range between 200 and 600 m. Lacking any direct means to verify the estimated anthropogenic CO_2 distributions, it is not possible to identify which estimated distribution is closer to the “true” distribution. However, we can attempt to identify the reasons why the two methods yield such different distri-

butions and which assumptions and parameters are the most weakly constrained. In addition, we can also attempt to develop specific hypotheses that can be tested with additional data in the future that may allow a more conclusive assessment of the two methods. We will start this section with a discussion of the differences that arise from differing estimation of the contributions from the biological pump and then proceed to address the contributions from the physical processes and the solubility pump.

4.1. Biological Pump Contribution

Both approaches use very similar concepts for the determination of the biological contribution. However, one difference arises from the fact that *Goyet et al.* [1999] employed a stoichiometric coefficient a (see equation (3)) of -0.78 , whereas *Sabine et al.* [1999] used a corresponding coefficient of -0.74 . *Gruber* [1998] and *Sabine et al.* [1999] showed that the ΔC^* method is sensitive to the exact choice of this stoichiometric coefficient and that the changes are most pronounced in the oxygen minimum zones of the intermediate waters. Since the largest biological corrections occur in the depth range, where the two methods disagree the most, it is important to examine the effect of this difference. When *Sabine et al.* [1999] increased this sto-

ichiometric coefficient to -0.83 , the WOCE cruise II anthropogenic CO_2 estimates dropped, on average, by $\sim 11.1 \mu\text{mol kg}^{-1}$ in the depth range from 200 to 600 m, whereas the estimated anthropogenic CO_2 concentrations changed only little elsewhere. Assuming that this change is about twice of that expected for the change from -0.74 to -0.78 , we expect that the ΔC^* approach would yield estimates that are $\sim 5 \mu\text{mol kg}^{-1}$ lower in the midthermocline if *Sabine et al.* [1999] had used the same stoichiometric coefficient as *Goyet et al.* [1999]. Alternatively, had *Goyet et al.* [1999] used the lower stoichiometric coefficient of *Sabine et al.* [1999], their estimate would have been higher, although by a much smaller amount since the MIX approach is less sensitive to changes in the coefficient a . This is a consequence of having to apply smaller corrections for the biological pump. Present uncertainties with regard to the exact choice of the stoichiometric coefficient for the remineralization reactions of organic carbon are too large to specify which value of the stoichiometric coefficient is more appropriate to use [*Anderson and Sarmiento*, 1994]. Despite the fact that the use of the same coefficient would bring the two estimates in better agreement with each other, the use of a slightly different stoichiometric ratio is far from sufficient to explain the entire difference. This is further supported by the fact that there is no observable correlation between the Apparent Oxygen Utilization (AOU) and the difference in anthropogenic CO_2 concentrations between the two methods. Other differences related to the contributions from the physical processes and the solubility pump must also contribute to the different anthropogenic CO_2 estimates.

4.2. Physical Processes and Solubility Pump Contribution

The two methods use two rather different strategies for estimating the contribution from the physical processes. Both methods make a number of assumptions. However, the assumptions used in the MIX approach are independent of the assumptions used in the ΔC^* approach. This provides an opportunity to examine the consequences of applying the results of one method to the other. We will follow this backward calculation approach by first applying the MIX results to the ΔC^* results and then vice versa.

Let us suppose for the moment that the anthropogenic CO_2 estimates of the MIX approach are correct. How much do we have to change the parameters in the ΔC^* approach to generate the MIX anthropogenic CO_2 estimates? We identified in section 2.2.1 that the two most sensitive assumptions in the ΔC^* method are the reliability of the air-sea disequilibrium values determined from data in the interior of the ocean and that the tracer age is a good approximation for the “true” ventilation age. The air-sea disequilibria im-

plied by the MIX results can be estimated by taking the MIX anthropogenic CO_2 estimates and solving (5) for $\Delta\text{TCO}_2^{\text{diseq}}$. The air-sea disequilibria inferred from the MIX approach are on average $\sim 12 \mu\text{mol kg}^{-1}$ more positive than those estimated by the ΔC^* method over the entire potential density range from sigma-theta 26.0 to 27.0. The MIX $\Delta\text{TCO}_2^{\text{diseq}}$ also imply that waters with potential densities from 26.0 to 26.9 are supersaturated with respect to the atmosphere when they leave the surface, whereas the ΔC^* method suggests that these water masses are close to saturation or undersaturated when they were last in contact with the atmosphere. The $\Delta\text{TCO}_2^{\text{diseq}}$ corresponds to a certain air-sea CO_2 partial pressure difference ($\Delta p\text{CO}_2$), which is a well observable quantity. The difference of $\sim 12 \mu\text{mol kg}^{-1}$ in $\Delta\text{TCO}_2^{\text{diseq}}$ is equivalent to $\sim 20 \mu\text{atm}$ in $\Delta p\text{CO}_2$ for surface waters of the same density. This is well above the measurement precision, and therefore a complete spatio-temporal characterization of the $\Delta p\text{CO}_2$ distribution should be able to discriminate between the two estimates. The available compilation of observed $\Delta p\text{CO}_2$ [*Takahashi et al.*, 1997, 1999] indicates the existence of slightly undersaturated waters in wintertime in the density range from 26.0 to 26.9 but with a large amount of scatter. However, this compilation rests on very limited observations of waters in wintertime. Therefore the available data at present are insufficient to reject any of the two estimates.

The anthropogenic CO_2 estimates from the ΔC^* method rely heavily on the assumption that the tracer inferred age is a good approximation of the true ventilation age. The $p\text{CFC}$ age is only equal to the true age if the water parcel was in equilibrium with the atmosphere at the time of entrainment and if the water is transported along density surfaces without mixing (“piston flow”). Since the characteristic gas exchange time for CFC is of the order of a few weeks [*Broecker and Peng*, 1974], much shorter than the average residence time of waters near the surface, the first assumption is very reasonable for most regions of the surface oceans. The exceptions are the upwelling regions and the polar waters [*Wallace and Lazier*, 1988; *Doney and Bullister*, 1992; *Roether et al.*, 1993]. However, the waters ventilating the midthermocline in the northern Indian Ocean are not formed in such regions [*You and Tomczak*, 1993]. Substantial undersaturations of CFCs may also occur when a water mass is subducted [*Rintoul and Bullister*, 1999]. Resulting apparent age of the water mass is then different from the “real” age. The second requirement of no mixing is almost never met in the ocean [*Ledwell et al.*, 2000]. The effects of mixing depend upon whether all of the components in the mixture contain CFCs or whether one component is older, CFC free water. In addition, the magnitude of the blurring effect of the $p\text{CFC}$ age depends also on the relative importance of advective transport versus dif-

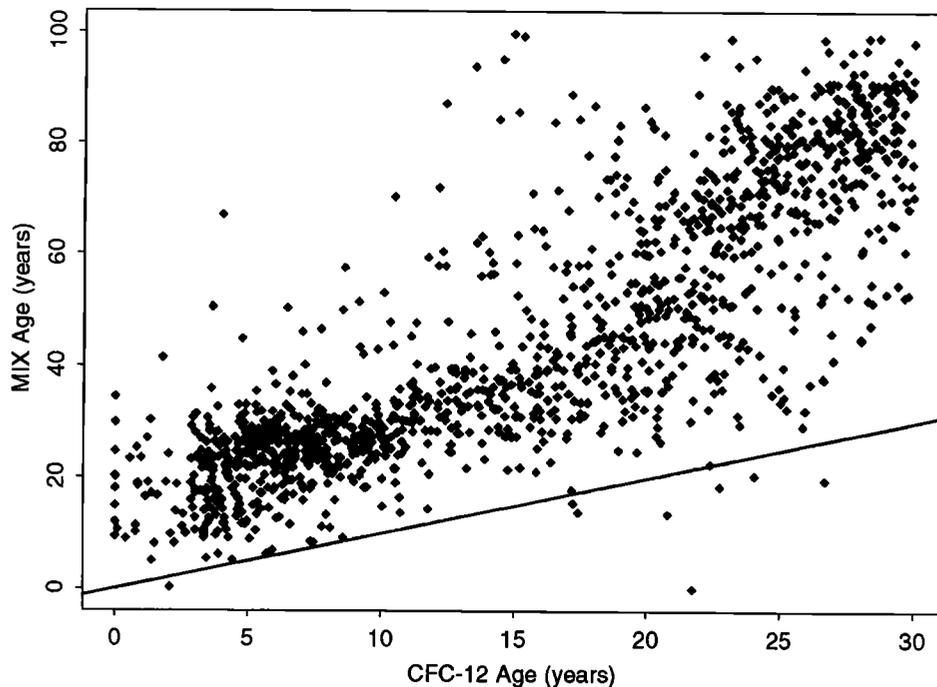


Figure 4. Plot of the estimated water age using the $\text{TCO}_2^{\text{ant}}$ results from the MIX approach in the Bay of Bengal (MIX age) versus the estimated water age from the CFC-12 data. The MIX age has been computed by inserting the MIX anthropogenic CO_2 estimates into the ΔC^* equations.

fusive transport [Thiele and Sarmiento, 1990; Beining and Roether, 1996; Warner et al., 1996; Doney et al., 1997]. Modeling studies showed that for typical values of advective velocities and diffusivities, the difference between true and tracer age is usually less than 10% for ages less than 20 years [Doney et al., 1997; Karstensen and Tomczak, 1998]. Doney et al. [1997] also showed that CFC ages for waters younger than ~30 years are within 20% of tritium-helium ages (which are considerably less sensitive to mixing effects). In the case where young waters are mixed with CFC-free water, the $p\text{CFC}$ age of the older waters can be substantially biased toward younger ages since the age of the CFC-free component is only defined as >50 years old [Roether et al., 1993].

The region where mixing and $p\text{CFC}$ ages are most likely to be a problem for the estimates considered here is in the western Gulf of Aden associated with the RSW. The depth range of the largest discrepancy between the two estimates of anthropogenic CO_2 within the gulf is coincident with the RSW depth range. Mecking and Warner [1999] recently showed that the RSW enters the Gulf of Aden with CFC saturations of 70% at Bab al Mandeb. Entrainment of surrounding waters rapidly decreases the CFC saturations to near 20% once the RSW reaches its depth of neutral buoyancy. In Mecking and Warner's two end-member mixing model, the RSW with $p\text{CFC}$ -12 age of 12 years mixes with a background profile where the $p\text{CFC}$ -12 age is ~38 years. The result-

ing $p\text{CFC}$ -12 age of the mixture was 27 years. Since the $p\text{CFC}$ age estimates used for three ΔC^*_t calculations assume no mixing, the $p\text{CFC}$ based ventilation age for the RSW would be older than the true ventilation age of the waters. This would result in a bias toward lower anthropogenic CO_2 values. In other words, if a true ventilation age were used, the differences between the two estimates would be even larger in this region.

To determine if water mass age uncertainty can account for the difference between the two methods in the Bay of Bengal, we made a second backward calculation. The Bay of Bengal $\text{TCO}_2^{\text{ant}}$ from the MIX approach was assumed to be correct and was used in (5) and (6) to estimate the water age. Figure 4 shows this calculated age (referred to as MIX age) as a function of the $p\text{CFC}$ age. For $p\text{CFC}$ ages less than 15–20 years, the MIX age is generally ~15 years older. Thus the MIX age would imply that a water parcel containing a CFC concentration equivalent to 1985 (10 years old) had actually last seen the atmosphere in 1970 (25 years old).

For $p\text{CFC}$ ages older than 15–20 years, the difference between the $p\text{CFC}$ age and the MIX age increases significantly but with a lot of scatter. Water with a $p\text{CFC}$ age close to 30 years would have a MIX age between 45 and 90 years. Is it possible that the $p\text{CFC}$ ages are systematically underestimated by this amount? Strong mixing by diffusion leads indeed to an underestimation of the $p\text{CFC}$ age, but the magnitude is thought to be much smaller, particularly at ages less than 15 years.

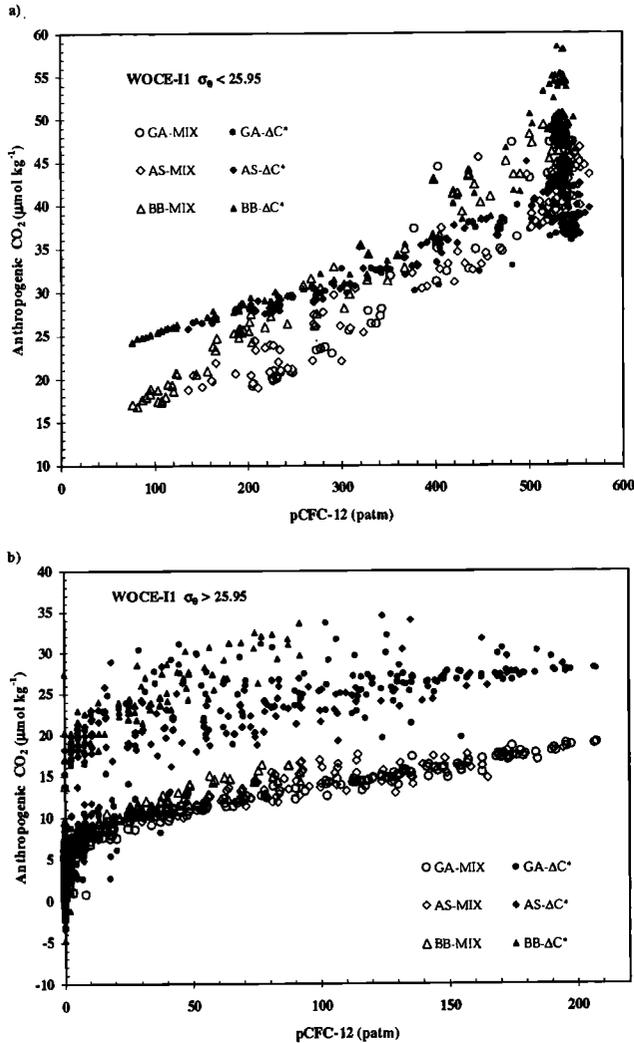


Figure 5. Anthropogenic CO_2 ($\mu\text{mol kg}^{-1}$) versus $p\text{CFC-12}$ (patm) in (a) the upper layer ($\sigma_\theta < 25.95$) and (b) the lower layer ($\sigma_\theta > 25.95$) of the WOCE I1 sections. The circles, rhombs, and triangles represent the Gulf of Aden, the Arabian Sea, and the Bay of Bengal, respectively. The filled symbols are the estimates by the ΔC^* approach, and the open symbols are the estimates by the MIX approach.

This leads to the conclusion that either the $p\text{CFC}$ ages are much more biased toward younger ages than generally thought or that the anthropogenic CO_2 concentrations estimated by the MIX approach are too low and hence the MIX ages are too old. However, it is important to note that this conclusion is based on the assumption that all the other hypotheses used in the ΔC^* method are correct, including that the air-sea disequilibria have remained constant over time. Gruber *et al.* [1996] showed that the global average disequilibrium has decreased by $\sim 5 \mu\text{mol kg}^{-1}$ as a result of the anthropogenic CO_2 transient in the atmosphere. Including this effect would decrease the MIX ages by ~ 5 years in the range of 0–15 years and by ~ 7 years in the range

of 15–30 years. Even though this effect is therefore too small to explain the discrepancy, it may explain part of it.

So far we have assumed that the anthropogenic CO_2 estimates of the MIX approach are correct and investigated the consequences on the estimation of the air-sea disequilibrium and water mass age. Alternatively, let us suppose for the moment that the ΔC^* estimates are correct and examine the consequences for the assumptions in the MIX approach. The most critical assumption in the MIX approach is the accurate determination of the source water properties. The anthropogenic CO_2 concentration in each source water is estimated from the separation of the observed TCO_2 concentration of the considered source water into a preindustrial and an anthropogenic TCO_2 component. Along WOCE I1 and in the depth range from 200 to 600 m, the water mass structure is primarily determined by the mixing of the three surface and intermediate water sources. Since the anthropogenic CO_2 concentrations of the three surface source waters are rather close to those estimated by the ΔC^* method, the least constrained way for the MIX method to match the ΔC^* without generating large residuals is by increasing the TCO_2 characteristics of the three intermediate source waters. Consequently, we have increased TCO_2 in each of the three intermediate water sources by $25 \mu\text{mol kg}^{-1}$ (~ 10 times larger than the accuracy of the TCO_2 measurement). The results of the anthropogenic CO_2 concentrations in the 200–800 m depth range were not significantly affected (less than $1 \mu\text{mol kg}^{-1}$ difference). Only the residuals were increased by a factor of 2. Increasing the initial value of the anthropogenic CO_2 concentration in the intermediate waters by $10 \mu\text{mol kg}^{-1}$ also did not significantly affect the results of anthropogenic CO_2 concentrations in the 200–600 m depth range (less than $1 \mu\text{mol kg}^{-1}$ difference).

These sensitivity tests reveal the robustness of the MIX results and indicate that not just one but several water source properties would have to be modified to approach the ΔC^* results. Yet changing other characteristics of the intermediate water properties results in large residuals and leads to unrealistic water mass distributions. It is also important to point out that none of these changes were able to reproduce the sharp decrease between 600 and 800 m estimated by the ΔC^* method. Below the upper layer the MIX method estimates smooth anthropogenic CO_2 concentration-depth profiles very similar to the smooth density-depth profiles.

4.3. Comparison With CFC

The CFCs are of particular interest for studying the invasion of anthropogenic CO_2 into the oceans because they are inert anthropogenic gases with atmospheric time histories relatively similar to that of atmospheric CO_2 . In addition, the CFC play a crucial role for de-

termining the air-sea disequilibria in the ΔC^* method. It is therefore very instructive to examine the two anthropogenic CO_2 estimates in relation to the CFCs. It is important to note that despite similar atmospheric histories, there also exist three important differences between the two tracers. First, emissions of CFC-11 and CFC-12 started only in the 1930s, whereas atmospheric CO_2 began to increase significantly already at the beginning of the 19th century. Second, the two gases have very different characteristic air-sea gas exchange timescales. CFCs have an e -folding time for reaching equilibrium of a few weeks while the CO_2 e -folding time is ~ 1 year [Broecker and Peng, 1974]. Third, CFCs are much more soluble in cold waters than in warm waters, whereas warm, low-latitude waters can take up more anthropogenic CO_2 than cold, high-latitude waters [Chen, 1993]. The temperature effect of the CFCs can be eliminated by computing the partial pressure of the CFCs (i.e., by dividing the CFC concentration by the solubility). Because of these differences, one cannot expect a simple correlation between anthropogenic CO_2 and CFCs.

Figure 5 shows the estimated anthropogenic CO_2 concentrations versus CFC-12 partial pressure for the upper layers ($\sigma_\theta < 25.95$, \sim upper 250 m) and the lower layers ($\sigma_\theta > 25.95$). As noted previously, both methods estimate similar anthropogenic CO_2 concentrations in near surface waters, i.e., waters having a $p\text{CFC-12}$ of more than 500 patm (corresponding to 1991). The $\text{TCO}_2^{\text{ant}}$ estimates of both approaches decrease with decreasing $p\text{CFC-12}$ but at distinctly different slopes. Waters having a $p\text{CFC-12}$ of 100 patm (corresponding to 1968) are estimated to contain $\sim 16 \pm 3 \mu\text{mol kg}^{-1}$ in the case of the MIX method, whereas these waters are estimated to contain $\sim 27 \pm 6 \mu\text{mol kg}^{-1}$ in the case of the ΔC^* method. This difference of $\sim 11 \mu\text{mol kg}^{-1}$ between the two anthropogenic CO_2 estimates remains as CFC-free waters are approached (Figure 5b). The large systematic difference in the anthropogenic CO_2 versus $p\text{CFC-12}$ trends imply two different underlying hypotheses for the uptake of anthropogenic CO_2 by the ocean. If the MIX anthropogenic CO_2 estimates are correct, then the waters at intermediate $p\text{CFC-12}$ levels contain $\sim 11 \mu\text{mol kg}^{-1}$ less anthropogenic CO_2 than one expects from thermodynamic considerations with the assumption that waters follow isopycnal surfaces without mixing. This would indicate that these intermediate waters were not able to track the atmospheric perturbation. This conclusion hinges on the validity of the assumption that mixing does not affect the CFCs in a different manner than anthropogenic CO_2 . The blurring effect of mixing depends on the curvature of the atmospheric time history [Karstensen and Tomczak, 1998]. The curves of atmospheric CO_2 and CFCs have a similar curvature until 1992 as a consequence of the recent reductions of CFC emissions and the resulting slowing down of the atmospheric increase

of CFCs since 1992 [Intergovernmental Panel on Climate Change, 1995]. Since both anthropogenic CO_2 and CFC have very similar atmospheric time histories, we do not expect substantial deviations in the sensitivity of these two transient tracers with regard to nonlinear effects from mixing.

In contrast to the MIX results, the ΔC^* based estimates indicate that with the assumption of no mixing along isopycnal surfaces, the intermediate waters contain approximately the anthropogenic CO_2 expected from thermodynamic considerations and thus were able to track the atmospheric perturbation. These two hypotheses can be tested by determining the rate of change in TCO_2 in the outcrop regions of these intermediate waters. These outcrop regions lie in the South Indian Ocean between $\sim 30^\circ$ and 50°S , except for RSW as discussed above. Sabine *et al.* [1999] determined the average rate of change in TCO_2 in the Indian Ocean for the period between 1978 and 1995 by comparing carbon data from the Geochemical Ocean Section Study with the WOCE/JGOFS data. The rate of increase inferred from this independent approach is consistent with the assumption that surface waters in the low latitudes remained in equilibrium with the atmospheric CO_2 increase. Lacking data south of 35°S , the possibility cannot be rejected that the TCO_2 increase in the surface ocean south of 35°S is lagging behind the atmosphere.

It is interesting to note that anthropogenic CO_2 estimates from the ΔC^* approach exhibit in the upper waters a tight relationship with $p\text{CFC-12}$ independent of geographical region and with little scatter, whereas the scatter increases markedly at $p\text{CFC-12}$ below 100 patm , as indicated in Figure 5b. This is not surprising since in the upper ocean the ΔC^* results are almost directly determined from the $p\text{CFC-12}$, whereas at greater depth, the estimates increasingly rely on the ΔC^* concentrations of very old waters. In contrast, the results from the MIX approach show different $p\text{CFC-TCO}_2^{\text{ant}}$ relationships in the upper waters depending upon the different ocean areas, thus suggesting differences in the relative importance of the combined effects of air-sea gas exchange, horizontal mixing, and biochemical processes in the different ocean basins. In the lower layers, the situation reverses, and the results of the MIX approach show tighter correlations than the ΔC^* approach. Additional studies with different greenhouse gases such as that of Rehder *et al.* [1999], with methane and CFCs, are now necessary to quantify the relative influence of the various processes involved in the penetration of anthropogenic CO_2 in the oceans.

Figure 6 shows that the two methods yield rather different relationships between the vertically integrated anthropogenic CO_2 concentrations and the vertically integrated CFC-12 concentrations. The anthropogenic CO_2 estimates of the MIX method result in a tight relationship with a small slope, whereas the estimates of the ΔC^* approach indicate a slope that is about twice

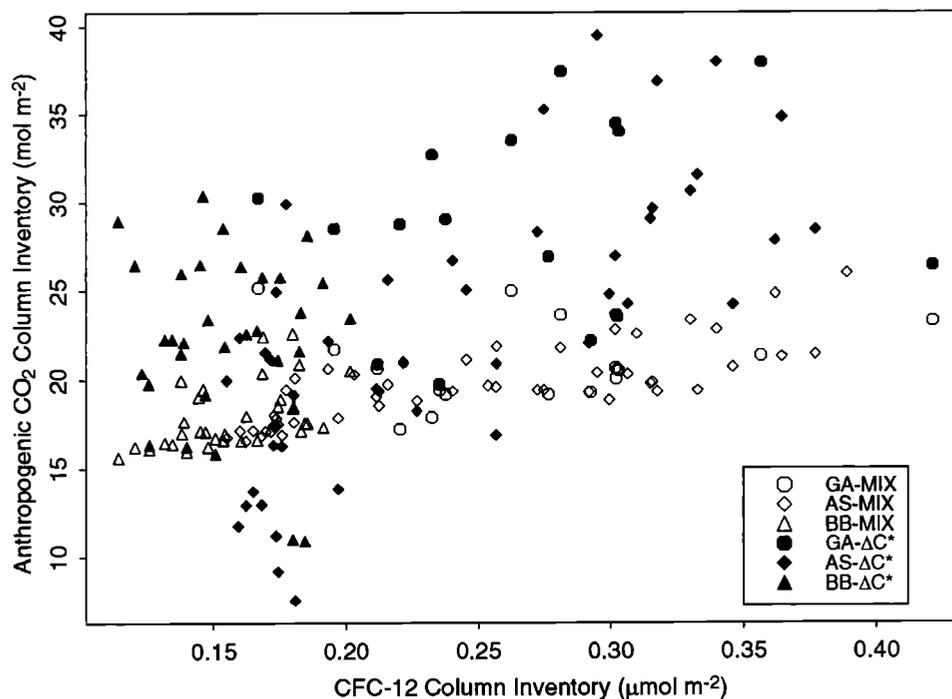


Figure 6. Plot of vertically integrated anthropogenic CO_2 (mol C m^{-2}) versus vertically integrated CFC-12 ($\mu\text{mol CFC m}^{-2}$). The circles, rhombs, and triangles represent the Gulf of Aden, the Arabian Sea, and the Bay of Bengal, respectively. The filled symbols are the estimates by the ΔC^* approach, and the open symbols are the estimates by the MIX approach. The lines represent the results of a linear regression using the method of least squares. The slope of the line through the ΔC^* data is $49 \pm 9 \text{ mol C } \mu\text{mol}^{-1} \text{ CFC}$ and the slope of the line through the MIX estimates is $22 \pm 2 \text{ mol C } \mu\text{mol}^{-1} \text{ CFC}$.

as large as that of the MIX approach, although masked by a much larger scatter. The larger slope of the ΔC^* approach is a result of a strong westward increase in the CFC and consequently in the ΔC^* anthropogenic CO_2 inventories in the Arabian Sea. The strong westward increase in the CFC inventories is mainly a consequence of the overflow of Red Sea Water which, as discussed previously, is relatively well ventilated and hence contains large amounts of CFCs.

In summary, the results of the ΔC^* approach suggest that as waters in the northern Indian Ocean accumulate CFC from the atmosphere, they also take up nearly corresponding amounts of anthropogenic CO_2 . The results from the MIX approach suggest that a $36.5 \pm 2.5\%$ variation in the anthropogenic CO_2 water column inventories occurs as the CFC inventories double. Given the fact that the ΔC^* approach depends heavily on the CFCs, it is impossible to conclude whether the steeper slope (Figure 6) is an independent result or a consequence of the assumptions.

5. Summary and Conclusion

The ΔC^* and MIX approaches represent two independent methods to quantify the concentration of anthropogenic CO_2 in the ocean based directly on inor-

ganic carbon measurements. In order to extract the anthropogenic signal from the large natural variability of TCO_2 , both methods have to make several assumptions. The ΔC^* and the MIX approaches employ very similar hypotheses in order to remove the contribution from the biological pumps. However, the contribution from the physical processes and the solubility pump are estimated on the basis of very different assumptions. As a result, substantial differences exist in the depth range between 200 and 600 m, where the ΔC^* method estimates anthropogenic CO_2 concentrations that are consistently higher by about $10\text{--}15 \mu\text{mol kg}^{-1}$. Below 800 m the MIX approach yields anthropogenic CO_2 estimates that are a few $\mu\text{mol kg}^{-1}$ higher. Vertically integrated anthropogenic CO_2 concentrations are significantly higher (20%) with the ΔC^* method.

Lacking any direct method to quantify the amount of anthropogenic CO_2 in the oceans, it is difficult to determine which estimate is closer to the "truth." We examined the most critical parameters and hypotheses in both methods and formulated a number of hypotheses that, with increasing data availability, can be used to discriminate the accuracy of both methods. If the lower anthropogenic CO_2 estimates of the MIX method are indeed correct and if all the other hypotheses of the ΔC^* method are correct, then the air-sea disequilibrium

in the surface waters of the Indian Ocean must be $\sim 15 \mu\text{mol kg}^{-1}$ more positive than estimated by Sabine *et al.* [1999]. This is equivalent to a $\Delta p\text{CO}_2$ difference of $\sim 20 \mu\text{atm}$ and should therefore be detectable with sufficient spatiotemporal sampling. The MIX anthropogenic CO_2 results may also imply that the $p\text{CFC}$ ages are biased in the direction of younger ages. Assuming the differences are only due to the $p\text{CFC}$ ages, the mean bias is of the order of 15–20 years for all $p\text{CFC}$ ages between ~ 0 and 30 years. More detailed analysis of the blurring effect of $p\text{CFC}$ ages could help in establishing whether such large mixing bias exist in the $p\text{CFC}$ ages. Alternatively, if the anthropogenic CO_2 concentrations estimated by the ΔC^* approach are correct, all the source water characteristics would have to be changed beyond the considered uncertainty. In addition, it is not possible to reproduce the sharp ΔC^* anthropogenic CO_2 decrease at ~ 800 m with the MIX method.

Comparison of the estimated anthropogenic CO_2 concentrations with CFC reveals that the two methods exhibit distinctly different relationships. The results of the ΔC^* method reflect the hypothesis that surface waters in the outcrop regions of the intermediate waters have tracked the atmospheric CO_2 increase relatively closely. The MIX results imply that these waters are taking up less anthropogenic CO_2 and are significantly lagging behind the atmospheric increase. Monitoring of the long-term evolution of inorganic carbon properties in the oceans will reveal which hypothesis is more appropriate.

To improve the accuracy of the quantification of anthropogenic CO_2 in the oceans, the different hypotheses that go into the two methods need further examination. Both experimental and modeling investigations are now necessary to examine these hypotheses and consequently to improve the accuracy of estimated anthropogenic CO_2 concentrations in the ocean. It is our hope that this study lays the groundwork for additional studies and that these ultimately lead to a better understanding and characterization of the oceanic uptake of anthropogenic CO_2 .

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