Comparison of recent Indian Ocean anthropogenic CO_2 estimates with a historical approach

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Abstract. This work compares the classic *Chen and Millero* [1979] approach for estimating anthropogenic CO_2 from ocean carbon measurements with the more recent ΔC^* technique used by *Sabine et al.* [1999] to estimate anthropogenic CO_2 concentrations in the Indian Ocean. Application of the Chen technique to the WOCE/JGOFS Indian Ocean data set gives a total anthropogenic CO_2 inventory that is essentially the same as the ΔC^* inventory, but there are substantial differences in the distributions within the water column. Some of these differences result from details of the application of the techniques such as the choice of which equation to use for the preformed alkalinity concentration or the choice of stoichiometric ratio to use for the biological correction. More significant differences, however, result from two fundamental differences in the techniques. One fundamental difference between the two techniques is that changes in the properties of the subsurface waters are referenced to a single deep water value in the Chen approach instead of the multiple reference points from the isopycnal analysis used in the ΔC^* approach. The second fundamental difference is in the estimation of the preindustrial TCO_2 distribution. Many of the differences examined have counteracting effects that may result in a total anthropogenic CO_2 inventory that is similar for the two techniques. However, this similarity does not imply that both approaches are right. Comparison with global carbon models and other measurement-based techniques do not clearly demonstrate that one technique is better than another. However, given the additional constraints of the transient tracers and the isopycnal analysis, we believe that the ΔC^* technique provides a more robust estimate.

1. Introduction

Many new research ideas and scientific papers have resulted from analysis of the data collected during the Geochemical Ocean Sections Study (GEOSECS) of the 1970s. One area of research that made major advances during the GEOSECS era was the estimation of anthropogenic CO_2 from carbon measurements. *Brewer* [1978] first proposed a technique for estimating anthropogenic CO_2 using deep South Atlantic GEOSECS data. TCO_2 measurements, corrected for the oxidation of organic matter and the dissolution of carbonates, were used to derive initial pCO_2 values for Antarctic Intermediate Water. The change in initial pCO_2 with latitude

was related back to the change in atmospheric CO_2 from fossil fuel burning. At about the same time, *Chen and Millero* [1979] published a similar approach for estimating anthropogenic CO_2 by examining changes in TCO_2 inventory in the water column. Chen and colleagues have since published anthropogenic CO_2 estimates for many regions of the world oceans based, in large part, on the GEOSECS global data set [e.g., *Chen,* 1982a, b; *Chen et al.,* 1986; *Chen,* 1987; *Poisson and Chen,* 1987; *Chen and Chen,* 1989; *Krumgalz et al.,* 1990; *Chen,* 1994; *Chen et al.,* 1990, 1995]. The validity of this approach (hereafter referred to as the Chen technique) has been discussed by *Shiller* [1981], *Chen et al.* [1982], *Shiller* [1982], *Broecker et al.* [1985], and *Chen and Drake* [1986]. Chen points out in several of his papers [e.g., *Chen,* 1993] that the accuracy of the estimates is not well known because the method is subject to relatively large uncertainties. As a result, the

Chen technique has not been widely accepted in the scientific community as a technique for quantitatively determining anthropogenic CO$_2$.

Recently, *Gruber et al.* [1996] proposed an approach for estimating anthropogenic CO$_2$ based on many of the principles outlined in the Chen technique but also addressing several of the criticisms of the original approach. This approach (hereafter referred to as the ΔC* technique) has been applied to the Geochemical Ocean Sections Study (GEOSECS), Transient Tracers in the Ocean (TTO), and South Atlantic Ventilation Experiment (SAVE) data in the Atlantic Ocean [*Gruber et al.,* 1996; *Gruber,* 1998]. With the recent completion of the World Ocean Circulation Experiment (WOCE)/Joint Global Ocean Flux Study (JGOFS) CO$_2$ survey, a global data set with well over an order of magnitude more samples and much better precision and accuracy than GEOSECS is available for evaluation of the anthropogenic CO$_2$ signal in the oceans. *Sabine et al.* [1999] used the ΔC* technique, with slight modifications, to estimate the anthropogenic CO$_2$ concentrations in the Indian Ocean based on the global survey data. These results have been compared with model estimates [*Sabine and Key,* 1998; *Sabine et al.,* 1999; *Caldeira and Duffy,* 2000; *Orr et al.,* 2000] and with the anthropogenic estimates of *Goyet et al.* [1999] based on an optimum multiparameter mixing analysis [*Coatanoan et al.,* 2000]. This study examines the similarities and differences between the ΔC* and Chen techniques. A direct compar-

ison of the two techniques is accomplished by applying the Chen approach to the WOCE/JGOFS Indian Ocean data set.

2. WOCE/JGOFS Data Set

Figure 1 shows the locations of the 1352 stations occupied by the U. S. WOCE program as part of the Indian Ocean survey between December 1994 and July 1996. As part of a cooperative JGOFS program, over 20,000 water samples were analyzed for both TCO$_2$ and total alkalinity (TA) using standard coulometric and potentiometric techniques, respectively. For reference, the 46 GEOSECS Indian Ocean stations have also been plotted on Figure 1. Details of WOCE/JGOFS measurement and quality assurance/quality control protocols have been described by *Johnson et al.* [1998] for TCO$_2$ and *Millero et al.* [1998] for TA. Certified Reference Material (CRM) samples with known concentrations of TCO$_2$ and TA [*Dickson,* 1990; A. G. Dickson, Oceanic carbon dioxide quality control available as http://www-mpl.ucsd.edu/people/ adickson/ CO2_QC, 2000] were analyzed every 12 hours to confirm calibration of the shipboard systems. The accuracy of the TCO$_2$ and TA measurements was estimated to be ± 2 and ± 4 μmol kg^{-1}, respectively [*Johnson et al.,* 1998; *Millero et al.,* 1998]. Primary hydrographic data from the CTD/Rosette were collected and analyzed following standard procedures [*Millard,* 1982]. Salinity, oxygen,
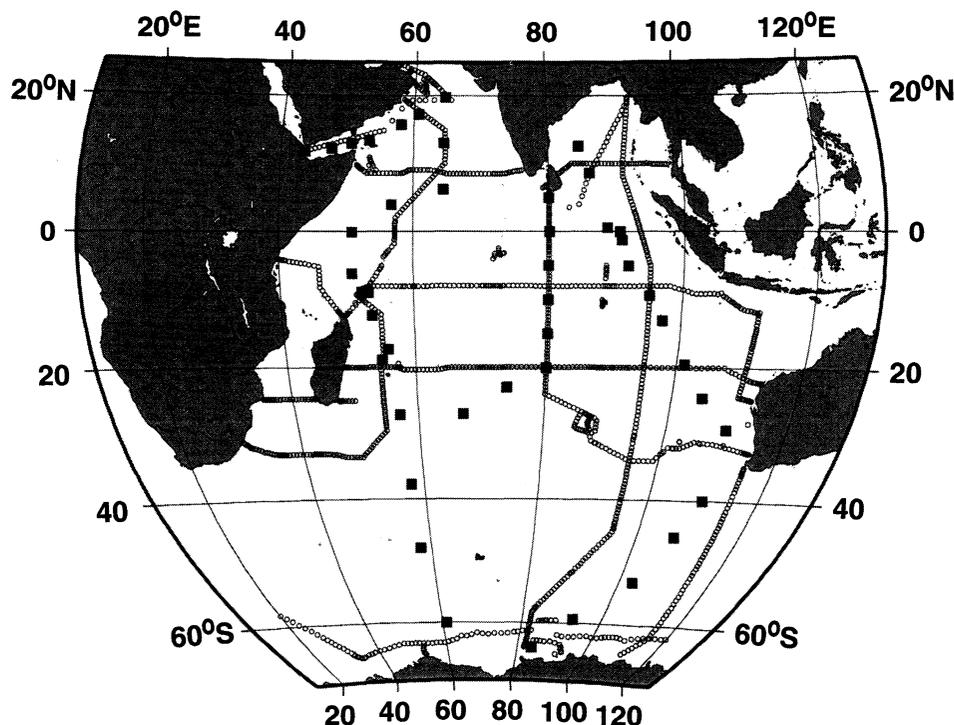

Figure 1. Map of Indian Ocean. Circles show location of WOCE/JGOFS stations. Filled squares show location of GEOSECS stations.

and nutrient samples were collected and analyzed for every Niskin using WOCE standard techniques [*United Nations Educational, Scientific, and Cultural Organization (UNESCO)*, 1981; *Culberson et al.*, 1991; *Gordon et al.*, 1992]. Chlorofluorocarbon samples were analyzed on a gas chromatograph using the techniques of *Bullister and Weiss* [1988]. Complete details of the analytical protocols and personnel can be obtained from the individual cruise reports available through the WOCE Office.

3. Principles of the Two Approaches

Both the ΔC^* and Chen techniques are based on the premise that the anthropogenic CO_2 concentration (TCO_2^{ant}) can be isolated from measured TCO_2 values (TCO_2^m) by subtracting the contribution of the biological pumps (ΔTCO_2^{bio}) and the physical processes involving the preindustrial end-members and the effects of the solubility pump (TCO_2^{phys}):

$$TCO_2^{ant} = TCO_2^m - \Delta TCO_2^{bio} - TCO_2^{phys}. \quad (1)$$

This general approach is based on the assumption that ocean circulation and the biological pump have operated in steady state since preindustrial times. Although both approaches are grounded in this same fundamental principle, the details of how the individual terms in (1) are derived are different. This paper examines

the different approaches and assumptions necessary for evaluating TCO_2^{ant} in the Indian Ocean.

3.1. TCO_2^m

One significant difference between the anthropogenic CO_2 estimates of *Sabine et al.* [1999] and those of *Chen* [i.e., *Chen and Chen*, 1989; *Chen*, 1993] is the fact that different data sets were used for the calculations. Chen's published calculations for the Indian Ocean are based primarily on the GEOSECS data. Substantial changes in the anthropogenic CO_2 inventory have occurred in the 18 years between GEOSECS and the WOCE/JGOFS survey [*Sabine et al.*, 1999]. Furthermore, the precision, accuracy, and spatial coverage of the measurements have improved by an order of magnitude. These differences complicate a direct comparison of published results. Potential biases in one of the data sets could introduce or mask differences that are not directly related to the technique. For this study we have applied the Chen technique to the WOCE/JGOFS data set. Using this approach, the TCO_2^m term in (1) is identical for the two methods. Sections 3.2 and 3.3 will examine how the last two terms in (1) differ between the two approaches.

3.2. ΔTCO_2^{bio}

The biological pump correction must account for the decomposition of organic matter and the dissolution of
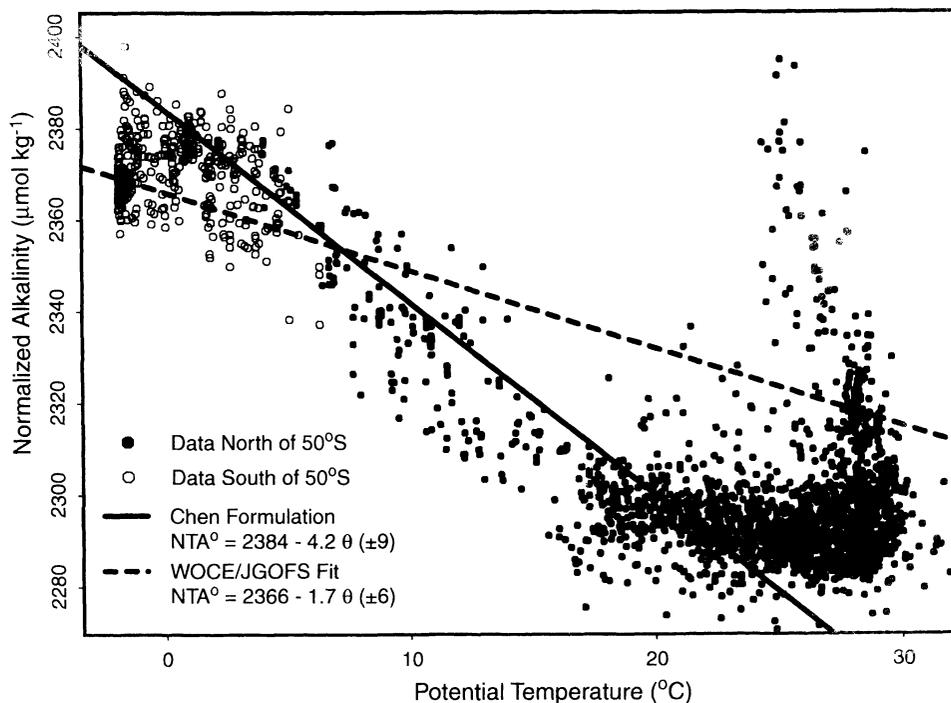

Figure 2. Plot of WOCE/JGOFS salinity normalized surface alkalinity (pressure <60 dbar) versus potential temperature. Open circles are data south of 50°S. The solid line is the *Chen et al.* [1986] preformed relationship. The dashed line is a linear fit of the data south of 50°S.

calcium carbonate. Both approaches assume that these terms can be estimated from changes in dissolved oxygen and total alkalinity (TA) using constant stoichiometric ratios (i.e., Redfield ratios). *Brewer* [1978] proposed the function:

$$\Delta TCO_2^{bio} = R_{C:O2}\Delta O_2 + 0.5(\Delta TA + R_{N:O2}\Delta O_2), \quad (2)$$

where $R_{C:O2}$ is a stoichiometric carbon to oxygen ratio, $R_{N:O2}$ is a stoichiometric nitrogen to oxygen ratio, ΔO_2 is the difference between the measured dissolved oxygen and the oxygen content that water would have if it were adiabatically raised to the surface and allowed to equilibrate with the atmosphere, and ΔTA is the difference between the measured total alkalinity and a reference total alkalinity (TA^0).

3.2.1. Carbonate correction. The second term on the right-hand side of (2) corrects for the dissolution of calcium carbonate in the water column. Since TA is not believed to have been influenced by the rise in atmospheric CO$_2$, carbonate dissolution can be determined from the change in TA since the water was last at the surface. Both approaches estimate TA^0 from a fit of surface alkalinity to hydrographic parameters. Chen used surface GEOSECS data from latitudes south of 50°S to derive an equation for preformed alkalinity, normalized to a constant salinity of 35, as a function of potential temperature (θ) [*Chen and Chen*, 1989; *Chen et al.*, 1986]:

$$NTA^0 = 2384 - 4.2\ \theta. \quad (3)$$

Figure 2 shows the relation of the Chen formulation to the WOCE/JGOFS measurements shallower than 60 dbar. This equation does a fair job of representing the general trend with temperatures up to ~25°C. The warmer data from the northern Indian Ocean, however, clearly have a different trend that is not adequately represented with this equation. The Chen equation also overestimates the normalized alkalinity of waters south of 50°S (shown as open circles in Figure 2). An attempt to reevaluate the Chen equation by fitting data south of 50°S gives a very different slope from Chen and does not fit the warmer data as well as (3) (Figure 2). In a description of how the preformed values were derived, *Chen et al.* [1986] note that "adding some stations north of the Antarctic Convergence increases the sample size, covers a wider range of temperature, and yields a more reliable regression line." Adding in data from farther north does improve the fit at warmer temperatures, but the normalized alkalinity values at temperatures less than ~1°C are ~20–30 μmol kg^{-1} lower than the trend defined by (3) (Figure 2). This difference could result from the fact that most of the WOCE/JGOFS data at those latitudes were collected in the austral winter, while all of the high-latitude GEOSECS data were collected in the austral summer. *Chen* [1982a] estimated that high-latitude summer bias in the GEOSECS data
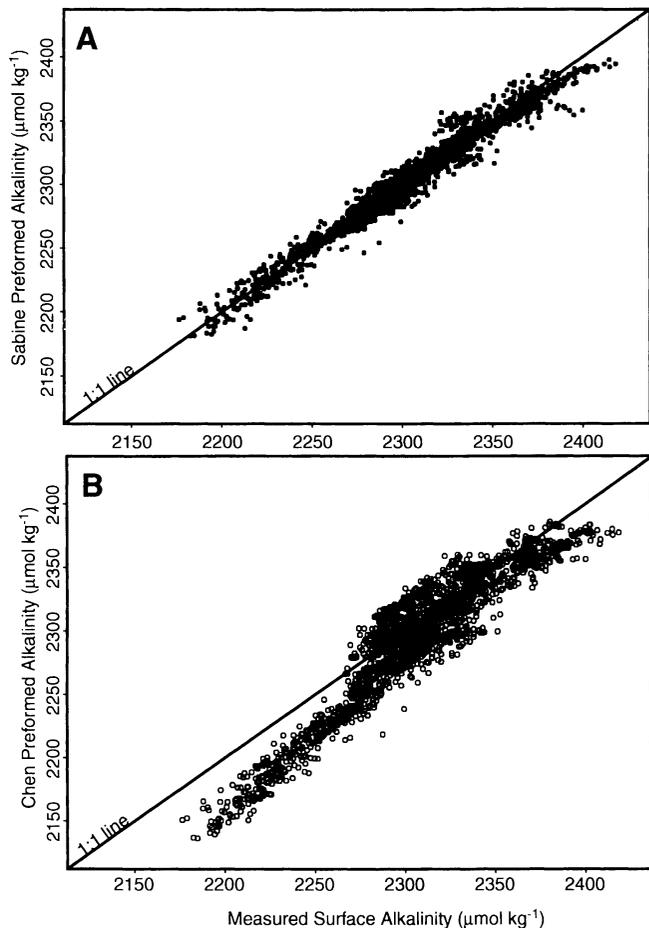

Figure 3. Plots of preformed alkalinity estimated from (a) *Sabine et al.* [1999] and (b) *Chen et al.* [1986] versus the measured surface alkalinity (pressure <60 dbar). The solid line in both plots shows 1:1 trend.

could contribute to a systematic error of up to 15 μmol kg^{-1} in the Chen based anthropogenic estimates.

Sabine et al. [1999] used the WOCE/JGOFS surface data from all latitudes in the Indian Ocean to derive a function for TA^0. Sabine et al. did not normalize the surface alkalinity values. Instead, they used a multiparameter least squares fit of alkalinity to salinity, potential temperature, and *Broecker*'s [1974] PO tracer (PO = O$_2$ + 170 P):

$$TA^0 = 378.1 + 55.22\ S + 0.0716\ PO - 1.236\ \theta. \quad (4)$$

Figure 3 is a plot of the Indian Ocean surface alkalinity values estimated from (4) and using Chen's formulation (denormalized using the WOCE/JGOFS salinity values) versus the WOCE/JGOFS measured values. The Sabine et al. model provides a better fit to the data, particularly at lower alkalinities where the Chen formulation estimates values that are up to 50 μmol kg^{-1} low.
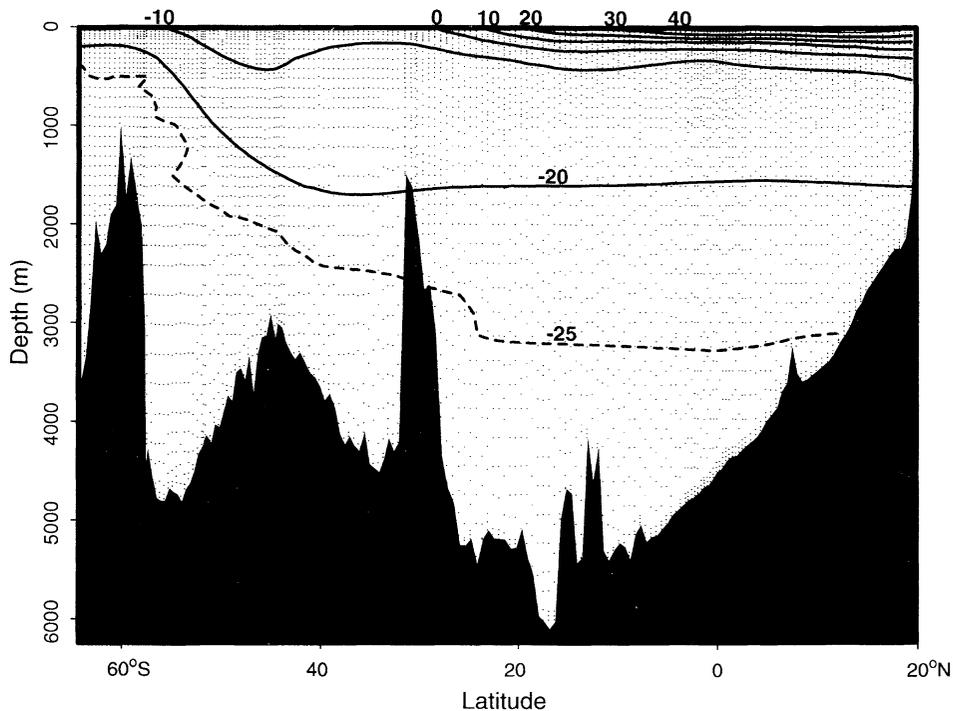
Figure 4. Section of ΔNTA^0 (μmol kg^{-1}; Sabine TA^0 normalized to a constant salinity minus the Chen formulation) in the eastern Indian Ocean at $\sim$93°E. Dots indicate sample locations used to make the section.

The potential impact of the choice of TA^0 equations on the anthropogenic estimates can be evaluated from a section of the difference in TA^0 (Sabine minus Chen) at 93°E in the eastern Indian Ocean (Figure 4). Combining (1) and (2) suggests that half of the TA^0 error would get translated into TCO_2^{ant} for both the ΔC^* and Chen techniques. However, both methods normalize the predicted change in carbon to one or more reference values. For the Chen technique the change in carbon is subtracted from the deep carbon excess where the waters are presumed to be free of anthropogenic CO_2. The TA^0 error therefore would be relative to any error in the deep waters. For the differences shown in Figure 4, the effect on TCO_2^{ant} would be half of the difference between the deep water value of -25 and the value at the point of interest. Thus the TCO_2^{ant} differences resulting from the use of the Sabine alkalinity formulation instead of the original Chen formulation would increase from zero in the deep waters to 32.5 μmol kg^{-1} [(40 + 25)/2] in the surface waters of the northern Bay of Bengal. The largest differences occur in the upper 500 m north of 20°S. For most of the deeper portions of the water column with anthropogenic CO_2, the different formulas for estimating TA^0 translates into a difference of $\sim$10 μmol kg^{-1} in the TCO_2^{ant} using the Chen technique. The ΔC^* technique is evaluated over relatively small isopycnal intervals and uses a different reference value for each isopycnal surface. Potential errors in the ΔC^* es-

timates of TCO_2^{ant} therefore are related to the difference between the in situ TA and the TA at the outcrop for that isopycnal surface rather than the difference relative to the bottom waters. Since the differences between the TA^0 formulations shown in Figure 4 roughly follow the isopycnals, the ΔC^* anthropogenic CO_2 estimates are much less sensitive to this potential bias.

3.2.2. Organic matter correction. The first term on the right-hand side of (2) corrects for the decomposition of organic matter in the water column. There is also a small organic adjustment on the carbonate correction term to account for the effect of the proton flux on TA. The ΔO_2 term is estimated in the same manner by both techniques, by taking the difference between the measured dissolved oxygen concentration and the oxygen saturation value calculated from the salinity and potential temperature at one atmosphere total pressure [*Weiss*, 1970]. This difference is also known as the Apparent Oxygen Utilization (AOU). The ΔC^* technique solves for (2) based on stoichiometric values for $R_{C:O2}$ and $R_{N:O2}$ given in the literature. The Chen technique does not explicitly include the carbonate correction term but evaluates a net stoichiometric ratio for the biological correction from the slope of a linear fit of $\Delta NTCO_2$–0.5 ΔNTA versus AOU in the deep waters. Here ΔNTA is the difference between the measured, salinity normalized TA and the NTA^0 discussed above. Here $\Delta NTCO_2$ is the difference between the
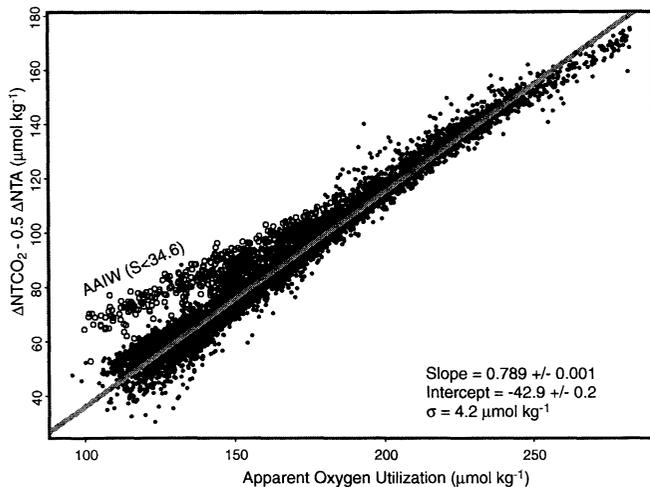
Figure 5. Plot of $\Delta NTCO_2 - 0.5\ \Delta NTA$ versus AOU for samples from pressures greater than 1100 dbar. Open circles are Antarctic Intermediate Waters (AAIW), identified as samples with a salinity less than 34.6. These data are presumed to be contaminated with anthropogenic CO$_2$ and were not included in the linear regression. The text gives the coefficients and standard deviation for the fit shown with the gray line.

measured, salinity normalized TCO$_2$ and a preformed value (NTCO$_2^0$), which will be discussed later.

The validity of the organic matter correction has been extensively debated in the literature [*Shiller,* 1981; *Chen et al.,* 1982; *Shiller,* 1982; *Broecker et al.,* 1985; *Gruber et al.,* 1996; *Brewer et al.,* 1997; *Sabine et al.,* 1999; *Coatanoan et al.,* 2000]. The two primary potential sources of error in this calculation are (1) that the dissolved oxygen of the waters may not have been in equilibrium with the atmosphere when they were formed and (2) that the decomposition of organic matter may not follow a constant stoichiometric ratio. Initial estimates of the oxygen equilibrium issue [e.g., *Broecker et al.,* 1985] may have been overestimated because the relatively large surface water oxygen supersaturations noted by Broecker et al. were all based on summertime measurements [*Gruber et al.,* 1996]. Measurements during the winter months, when deep and bottom waters are more likely to form, suggest that oxygen concentrations are within 1–2% of saturation. The problems associated with the assumption of a constant stoichiometric ratio are potentially more significant.

The Indian Ocean ΔC^* calculations of *Sabine et al.* [1999] were based on a carbon to oxygen ratio of 0.688 and a nitrogen to oxygen ratio of 0.094 as determined by *Anderson and Sarmiento* [1994]. *Sabine et al.* [1999] also included an additional correction for denitrification based on the N* tracer and a carbon to nitrogen ratio of 106:104 [*Gruber and Sarmiento,* 1997]. Because the carbon term in the Chen approach does not explicitly

include the proton correction to the ΔTA, the slope will reflect both stoichiometric ratios in (2) (i.e., $R_{C:O2}$ + 0.5 $R_{N:O2}$). *Chen and Chen* [1989] determined that the ratio of the combined terms was 0.778 from the GEOSECS Indian Ocean data below the AOU maximum ($\sim$750 dbar). The same approach was used to evaluate the slope for the WOCE/JGOFS data set. Figure 5 is a plot of $\Delta NTCO_2$–0.5 ΔNTA versus AOU based on the *Chen and Chen* [1989] preformed equations and the WOCE/JGOFS data. Given that anthropogenic CO$_2$ has penetrated deeper today than during GEOSECS, the upper limit of the data used for the fit was changed to 1100 dbar. Values in the Antarctic Intermediate Water (AAIW; open circles in Figure 5; salinity <34.6) appeared to have a different trend from the rest of the data. Since both *Chen and Chen* [1989] and *Sabine et al.* [1999] showed that the deepest penetration of anthropogenic CO$_2$ was associated with the AAIW, these waters were eliminated from the fit. Both the published Indian Ocean ratio of *Chen and Chen* [1989] (0.778) and the ratio determined by applying the Chen approach to the WOCE/JGOFS data (0.789 ± 0.001) are higher than the corresponding value of 0.735 (0.688 + 0.5(0.094)) used by *Sabine et al.* [1999] but are within the standard error of ±0.092 estimated by propagating the uncertainties given by *Anderson and Sarmiento* [1994].

The potential impact of the different ratios on TCO$_2^{ant}$ can be seen in Figure 6. The published anthropogenic CO$_2$ estimates of *Sabine et al.* [1999] indicate a shallower penetration in the southern latitudes and a deeper penetration in the northern Indian Ocean than the estimates based on the original Chen preformed equations (Figure 6). The vertical gradients in TCO$_2^{ant}$ are also stronger with the Chen approach. Replacing Chen's NTA^0 with the formulation in (4) gave a slope of 0.820 ± 0.001, very similar to the upper range (0.688 + 0.092 + 0.5(0.094) = 0.827) tested by *Sabine et al.* [1999]. As demonstrated previously, the choice of equations for NTA^0 has a strong effect on the slope and intercept of the $\Delta NTCO_2$–0.5 ΔNTA versus AOU plot. To keep from violating the basic assumptions of the Chen approach, the compatible slope and intercept terms must be used when calculating TCO$_2^{ant}$ values using a different TA^0 equation. Using the Sabine TA^0 equation and a ratio of 0.82 generally resulted in a deepening of the Chen TCO$_2^{ant}$ contours that increased toward the north. For the ΔC^* TCO$_2^{ant}$ estimates, the higher ratio resulted in a deepening of the contours in the south and a shoaling of the contours in the north (Figure 6). The different response of the two methods to the larger slope is related to the fact that the Chen technique is referenced to the mean deep water values, and the ΔC^* approach is referenced to the outcrop region for each isopycnal surface. The changes in the ΔC^* estimate are more dramatic than the Chen
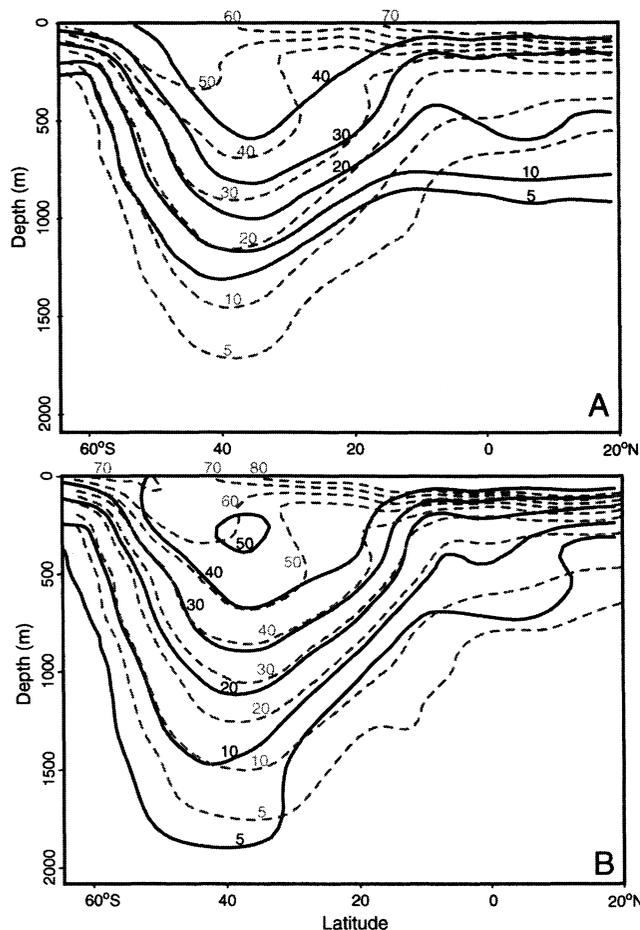
Figure 6. Sections of anthropogenic CO_2 (μmol kg^{-1}) in the eastern Indian Ocean at ~93°E. (a) Solid lines and numbers are results from *Sabine et al.* [1999] (ΔC^* technique with a combined stoichiometric ratio of 0.735). Gray dashed lines and numbers in Figure 6a are contours from the Chen technique based on the *Chen et al.* [1986] preformed values (ratio of 0.789). (b) Solid lines and numbers are results from ΔC^* technique with a combined ratio of 0.827. Gray dashed lines and numbers in Figure 6b are contours from the Chen technique based on the *Sabine et al.* [1999] TA^0 and *Chen et al.* [1986] $NTCO_2^0$ values (ratio of 0.820).

values because the change in stoichiometric ratios was much larger. Changing the ratios to match for the two approaches did make the penetration depths more similar, but the vertical gradient is still greater with the Chen approach (Figure 6).

At this point, there is no clear evidence regarding the "correct" ratio for the remineralization of organic matter. For the Indian Ocean (north of 35°S), changing the combined ratio from 0.735 to 0.827 resulted in a relatively small 7% decrease in the total ΔC^* anthropogenic CO_2 inventory (from 13.6 to 12.7 Pg C). A much smaller change in ratio from 0.789 to 0.820 for the Chen technique resulted in a 31% total inventory

increase (from 13.5 to 19.6 Pg C). Again, the different response of the two techniques is related to the different reference layers used. However, it should be pointed out that an evaluation of errors associated with the validity of the stoichiometric ratio used in these calculations is very difficult. Both techniques have diagnostic checks to evaluate the most appropriate ratio. *Sabine et al.* [1999] showed that a $C:O_2$ ratio of 0.78 (resulting in a combined ratio of 0.827) did not give results consistent with that technique unless carbon was accumulating in the ocean faster than in the atmosphere. Likewise, the *Anderson and Sarmiento* [1994] ratio is not consistent with the Chen approach shown in Figure 5. However, it should be noted that the slope determination also includes any errors in the preformed equations. As noted above, using (4) for the preformed TA instead of (3) resulted in a change in slope from 0.789 to 0.820. *Brewer et al.* [1997] showed that the *Anderson and Sarmiento* ratios were more consistent with a reanalysis of the original *Brewer* [1978] approach in the North Pacific than the classic Redfield values.

3.3. TCO_2^{phys}

Most of the differences described in section 3.2 (i.e., differing equations for the preformed alkalinity or the choice of stoichiometric ratios) involve how the technique is applied rather than a fundamental difference in the two approaches. The first fundamental difference between the two techniques is that changes in the properties of the subsurface waters are referenced to the mean deep water values in the Chen approach, whereas the ΔC^* approach divides the water column into isopycnal intervals and references the changes back to the outcrop region for each interval. The effect of the single deep reference versus multiple isopycnal references can be seen in the magnitude of the effects of the application differences described above for the two different techniques. In the upper water column, where most of the anthropogenic CO_2 exists, the changes relative to deep water are typically larger than changes relative to the isopycnal outcrop. This makes the Chen approach much more sensitive to the choice of preformed alkalinity and the correct stoichiometric ratio than the ΔC^* approach.

The second fundamental difference between the Chen and ΔC^* techniques for estimating anthropogenic CO_2 lies in the assumptions associated with the solubility pump and the ability to estimate the preformed TCO_2 concentrations. The Chen approach determines the change in TCO_2 from a preformed end-member. The ΔC^* technique takes a different approach to estimating the effects of the solubility pump. Rather than attempting to determine a preformed TCO_2 concentration, the TCO_2^{phys} term is divided into the TCO_2 that the waters would have in equilibrium with a preindustrial atmosphere and a term that corrects for the fact that, be-
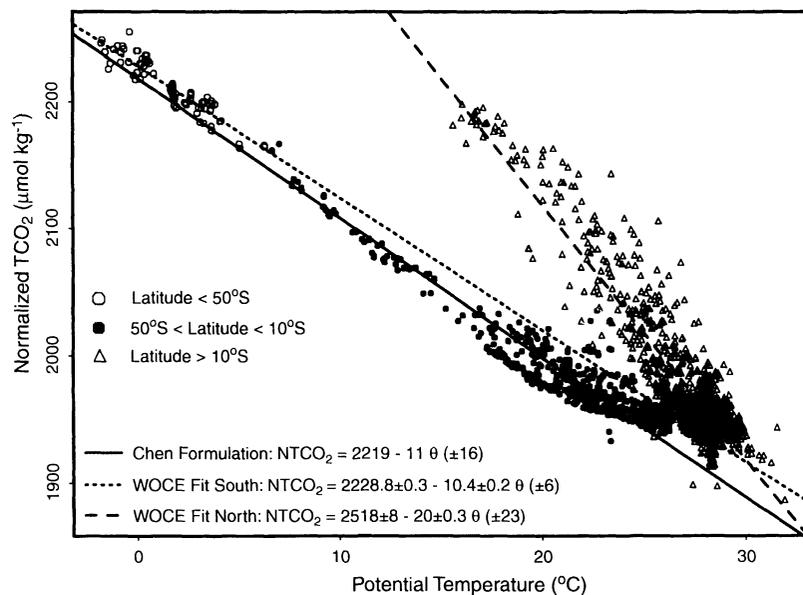
Figure 7. Plot of WOCE/JGOFS salinity normalized surface TCO_2 ($P < 60$ dbar) versus potential temperature. Open circles are data south of 50°S. Open triangles are data north of 10°S. The solid line is the *Chen et al.* [1986] preformed relationship. The dotted line is a linear fit of the data south of 50°S. The dashed line is a linear fit of the data north of 10°S.

cause CO_2 gas exchange is relatively slow [*Broecker and Peng*, 1974], surface waters are rarely in complete equilibrium with the atmosphere. The different approaches have different assumptions and limitations as discussed in section 3.3.1.

3.3.1. Preformed TCO₂. *Chen and Chen* [1989] used the preformed TCO_2 equation of *Chen et al.* [1986] which was determined by fitting the surface, salinity normalized TCO_2 values from GEOSECS stations south of 50°S as a function of potential temperature:

$$NTCO_2^0 = 2219 - 11\,\theta. \qquad (5)$$

Figure 7 shows the relation of the Chen formulation to the WOCE/JGOFS measurements shallower than 60 dbar. As with NTA, there are at least two distinct trends in the $NTCO_2$ plot. Chen's formulation does a reasonable job of fitting the data south of ~10°S but does not fit the data in the northern Indian Ocean (Figure 7). It is interesting that Chen's preformed $NTCO_2$ values fit the WOCE/JGOFS data as well as they do. This would imply that there has been no increase in the surface water TCO_2 concentrations in the southern Indian Ocean in the last 18 years despite a ~30% increase in atmospheric CO_2 concentrations. It is more likely that this agreement is coincidental. Recent papers have shown that the Indian Ocean GEOSECS TCO_2 values are 21–22 μmol kg^{-1} too high [*Peng et al.*, 1998; *Sabine et al.*, 1999]. This difference is nearly the same as the increase in TCO_2 expected if the surface ocean were keeping pace with the atmospheric increase. An attempt to fit the WOCE/JGOFS data south of 50°S resulted in

a trend that was not as consistent as the Chen formulation with the data at higher temperatures. As noted with the preformed alkalinity, adding in stations from farther north would improve the fit to the warmer data. This fit shows that there is some nonlinearity in the relationship between $NTCO_2$ and potential temperature even at lower temperatures.

The change in characteristics noted in Figure 7 for the northern Indian Ocean waters is roughly consistent with the latitude of the Chemical Front (10°–15°S) in the Indian Ocean [*Wyrtki*, 1973]. The Chemical Front is more easily observed in subsurface features than at the surface, but it marks the boundary between the low oxygen, high-nutrient waters of the northern Indian Ocean and the high oxygen, low-nutrient values of the subtropical gyre [*Wyrtki*, 1973]. A fit of all the surface data north of 10°S gives a slope that is almost twice the slope given in (5). Using this fit to evaluate the C:O₂ ratio, as described in section 3.2.2, resulted in a stoichiometric ratio of 1.22 and an inferred anthropogenic CO_2 concentration of 415 μmol kg^{-1} at the surface. These values are unreasonable, suggesting that the water mass properties of the surface waters in this region do not adequately represent the properties of the deeper waters.

The waters south of the Chemical Front are primarily defined by the circumpolar waters moving north into the Indian Ocean. The waters north of the Chemical Front have mixed with waters from the Persian Gulf and the Red Sea. *Krumgalz et al.* [1990] estimated the anthropogenic CO_2 penetration in the northern Red Sea. The

preformed $NTCO_2^0$ derived for that study ($2297 - 8.8\,\theta$) intersects the northern data at $\sim 25°C$ but has a much shallower slope than the observations. *Chen and Wu* [1991] also discussed the anthropogenic CO_2 signal in the Red Sea and northwest Indian Ocean. The preformed values used in the Red Sea (1794 for $\theta < 27°C$ and $1432 + 13.4\,\theta$ for $\theta > 27°C$) are over 100 μmol kg^{-1} lower than any values observed in the WOCE/JGOFS data set. For the northern Indian Ocean estimates, *Chen and Wu* use the same preformed values given by *Chen and Chen* [1989] (i.e., (3) and (5)) that were based on high-latitude Southern Ocean data.

3.3.2. ΔC^* approach. The TCO_2^{phys} term in the ΔC^* approach is divided into the TCO_2 the waters would have in equilibrium with a preindustrial atmosphere ($TCO_2^{eq\,280}$) and a term that corrects for air-sea CO_2 disequilibrium in the surface waters (TCO_2^{diseq}). Substituting these terms into (1) gives

$$TCO_2^{ant} = TCO_2^m - \Delta TCO_2^{bio} - TCO_2^{eq\,280} - TCO_2^{diseq}$$
$$= \Delta C^* - \Delta TCO_2^{diseq} \qquad (6)$$

$TCO_2^{eq\,280}$ can be directly computed for each sample from potential temperature, salinity, TA^0, and a preindustrial pCO_2 of 280 μatm using known thermodynamic relationships. The three terms to the right of the first equal sign make up ΔC^*, which can be explicitly calculated for each sample [*Gruber et al.*, 1996]. The fact that ΔC^* is a quasi-conservative tracer helps remedy some of the mixing concerns over the Chen technique [e.g., *Shiller*, 1981; *Broecker et al.*, 1985]. The estimation of the disequilibrium term is more difficult and requires three important assumptions.

First, it is assumed that water masses move and mix predominantly along isopycnal surfaces. The ΔTCO_2^{diseq} is evaluated over small, discrete density intervals. There is no theoretical limit to the number of end-members considered, but in practice, a maximum of two end-members are generally considered for each density layer [*Gruber*, 1998; *Sabine et al.*, 1999]. In this case mixing of two potential outcrops along the isopycnal surface is considered, but cross-isopycnal mixing is not explicitly addressed. This problem is likely to be most important in the high-latitude Southern Ocean.

The second hypothesis is that ΔTCO_2^{diseq} has remained constant over time (i.e., surface water pCO_2 has increased at roughly the same rate as atmospheric pCO_2). We know that this assumption is not completely valid. *Gruber et al.* [1996] estimated that the global average disequilibrium has decreased by ~ 5 μmol kg^{-1} as a result of the anthropogenic CO_2 transient in the atmosphere. In theory, this trend should be detectable with this method, but thus far it still appears to be within the uncertainty of the calculation.

The third important assumption that can affect the ΔTCO_2^{diseq} estimates is that the ventilation age of the waters can be accurately estimated from transient tracers (i.e., CFCs or ^{3}H–^{3}He). For deep density surfaces the ΔTCO_2^{diseq} is evaluated from the mean ΔC^* values far away from the outcrop region. In these regions the waters are old enough to be free of anthropogenic CO_2 and the left-hand side of (6) is zero. Thus ΔC^* is equal to ΔTCO_2^{diseq}. On shallower density surfaces, where anthropogenic CO_2 is present over the entire isopycnal surface, transient tracers are necessary to evaluate the disequilibrium term. In these regions, ΔTCO_2^{diseq} is equal to the mean of ΔC^*_t:

$$\Delta C_t^* = TCO_2^m - \Delta TCO_2^{bio} - TCO_2^{eq\,t}, \qquad (7)$$

where $TCO_2^{eq\,t}$ is the TCO_2 in equilibrium with the atmospheric CO_2 partial pressure present at the time when the water parcel left the surface. This time is based on the ventilation age of the water determined from the distribution of transient tracers. If the ventilation age is incorrect, the atmospheric CO_2 concentration will be off, and ΔTCO_2^{diseq} will be incorrect. *Sabine et al.* [1999] estimated the ventilation ages from CFC concentrations measured by the WOCE CFC teams (J. Bullister, R. Fine, M. Warner, and R. Weiss) on the same Niskins. Modeling studies have shown that the difference between tracer age and the "true" age is usually less than 10% for ages less than 20 years [*Doney et al.*, 1997; *Karstensen and Tomczak*, 1998]. Errors in the ventilation age are predominantly associated with the assumption that there is no cross isopycnal mixing. Even if there is mixing, the resulting errors related to this assumption, and the effect on the ventilation age may be minimized if the mixing affects the transient tracers in the similar manner to the anthropogenic CO_2.

4. Discussion

It is difficult to quantify the significance of the two different approaches for estimating the TCO_2^{phys} component of the calculation. The issue comes down to a question of which is more reliable, the estimates of preformed TCO_2 or a thermodynamic equilibrium calculation corrected for an apparent air-sea disequilibrium. One comparison that can be made is to examine the similarities and differences in the final anthropogenic CO_2 estimates for the two techniques using the same data set.

The Chen technique estimates a total anthropogenic CO_2 inventory of 13.5 Pg C for the area north of 35°S. This value is essentially the same as the ΔC^* inventory for the same area (13.6 Pg C). However, there are significant differences in the spatial distribution of the anthropogenic CO_2 signal (Figure 8). Column inventories from the Chen technique are larger than the ΔC^* esti-
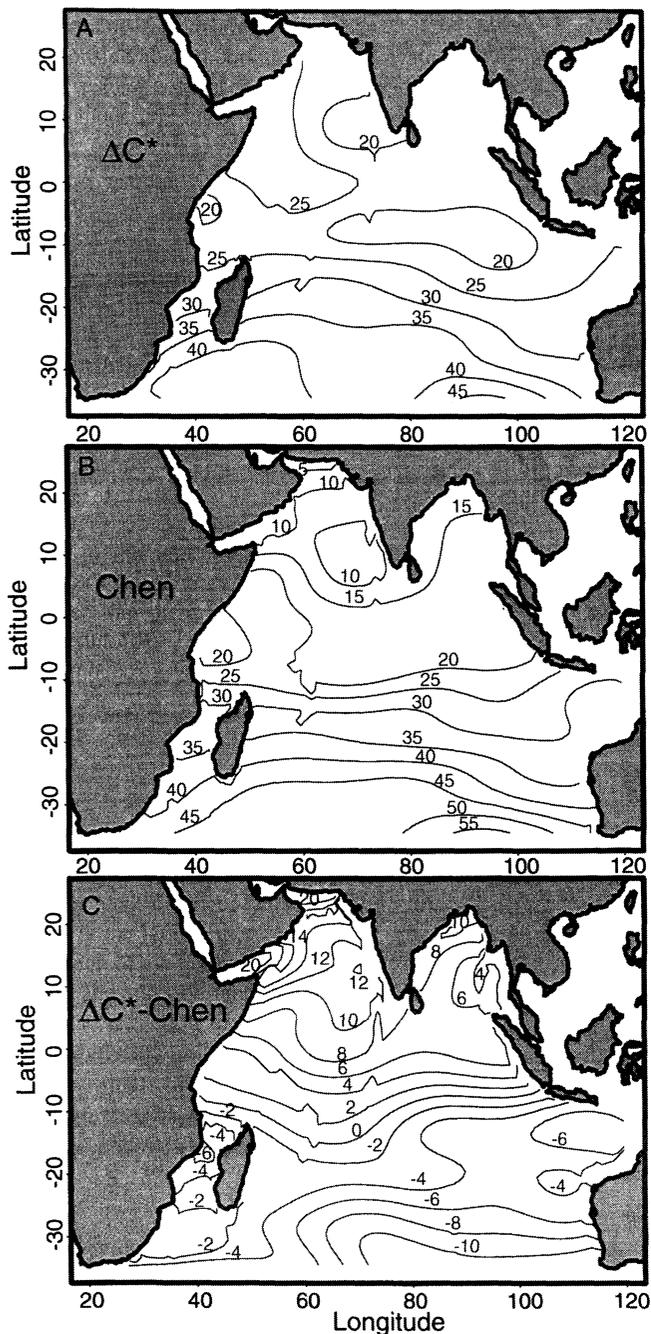
Figure 8. Column inventory $(mol\ m^{-2})$ maps of (a) anthropogenic CO_2 from *Sabine et al.* [1999], (b) anthropogenic CO_2 based on Chen technique using preformed values of *Chen et al.* [1986], and (c) the difference in anthropogenic CO_2 between the two methods.

mates south of ~10°S because of a deeper penetration and stronger vertical gradients in anthropogenic CO_2 (Figure 6). At 40°S the 5 μmol kg^{-1} contour from the Chen technique is 400 m deeper than with ΔC*. In the northern Indian Ocean the Chen technique has a shallower penetration. This results in column inventories

that are lower than the ΔC* estimates north of ~10°S. The largest difference between the two techniques is in the Arabian Sea (Figure 8). The larger ΔC* inventories result from a better characterization of inputs from the Red Sea. The fact that the total inventories are the same for both techniques is because the southern boundary of 35°S for the integration happens to correspond with the latitude at which the differences offset each other. This boundary was chosen because the U.S. WOCE survey did not adequately sample the southwestern Indian Ocean and we did not wish to complicate the comparison by including data from other time periods. If both techniques were integrated further south, the Chen estimate would be larger than the ΔC* inventory.

These results are consistent with the findings of *Gruber* [1998] and the recent comparison of the two techniques in the Atlantic Ocean by *Wanninkhof et al.* [1999]. Both studies found that the Chen technique resulted in inventories at high latitudes that were much higher than either the ΔC* estimates or the results of two different numerical models. The ΔC* results in the Atlantic were very similar to the National Center for Atmospheric Research (NCAR) and Princeton global carbon models. At low latitudes, the Chen inventories were lower than both the ΔC* and model results [*Gruber*, 1998; *Wanninkhof et al.*, 1999].

In the Indian Ocean, the Princeton model inventory (north of 35°S) is roughly 30% lower than estimates from either the ΔC* or the Chen technique. A recent comparison of the Indian Ocean ΔC* estimates with the Lawrence Livermore global carbon model gave mixed results [*Caldeira and Duffy*, 2000]. In the western Indian Ocean the model predicted similar distributions to the *Sabine et al.* [1999] estimates. In the eastern Indian Ocean, however, the Lawrence Livermore model predicted a deeper penetration at ~40°S and a shallower penetration of anthropogenic CO_2 in the north, more consistent with the results from the Chen technique. A comparison between the Indian Ocean ΔC* estimates and the anthropogenic estimates of *Goyet et al.* [1999] (referred to as the MIX technique) along WOCE line I1 also does not clearly favor one technique over another [*Coatanoan et al.*, 2000]. WOCE line I1 is a zonal section across the northern Indian Ocean at ~9°N. The MIX technique gives lower concentrations of anthropogenic CO_2 in the 200–600 m depth range than the ΔC* technique but gives very similar concentrations above and below this range [*Coatanoan et al.*, 2000]. The depth of the 5 μmol kg^{-1} contour at this latitude is ~900 m for both MIX and ΔC* but is closer to 500 m for the Chen technique. At a depth of ~400 m, Chen and MIX concentrations are ~10 μmol kg^{-1}, and the ΔC* concentrations are closer to 20 μmol kg^{-1}. Closer to the surface, the MIX and ΔC* values are similar and the Chen values become much larger.

5. Conclusions

The Chen and ΔC* techniques for estimating anthropogenic CO$_2$ are based on similar concepts but vary in the details of how these concepts are applied to the data. Application of the Chen technique to the WOCE/JGOFS data in the same manner it was applied to the older data sets gives a total anthropogenic CO$_2$ inventory that is essentially the same as the ΔC* inventory north of 35°S but there are substantial differences in the distributions within the water column. Some of these differences result from details of the application of the techniques. We have shown that the multiparameter regression of surface alkalinity does a better job of fitting the observed surface alkalinity. Using this revised equation and the associated stoichiometric ratio increases the Chen estimates of anthropogenic inventory by 31%. More significant differences, however, result from two fundamental differences in the techniques.

One fundamental difference between the two techniques is that changes in the properties of the subsurface waters are referenced to a single deep water value in the Chen approach instead of the multiple reference points from the isopycnal analysis used in the ΔC* approach. The second fundamental difference is in the estimation of the preindustrial TCO$_2$ distribution. The Chen approach estimates a preformed TCO$_2$ based on correlations of surface TCO$_2$ with potential temperature. Preindustrial values are estimated by referencing this trend to deep waters that are assumed to be free of anthropogenic CO$_2$. The ΔC* technique takes a different approach to estimating the preindustrial values. Rather than attempting to determine a preformed TCO$_2$ concentration, the TCO$_2$ term is divided into an equilibrium component and a term that corrects for the air-sea disequilibrium. The equilibrium component can be derived from known thermodynamic relationships. The disequilibrium component is subject to a number of the same assumptions and uncertainties as the preformed TCO$_2$ component in the Chen technique but is further constrained by other transient tracers (e.g., CFCs).

Many of the differences discussed above have counteracting effects that may result in a total anthropogenic CO$_2$ inventory that is similar for the two techniques. However, this similarity does not imply that both approaches are right. Comparison with global carbon models and other measurement-based techniques do not clearly demonstrate that one technique is better than another. However, given the additional constraints of the transient tracers and the isopycnal analysis, we believe that the ΔC* technique provides a more robust estimate.

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