How accurate is the estimation of anthropogenic carbon in the ocean? An evaluation of the ΔC^* method

Katsumi Matsumoto[1]

Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan

Lamont-Doherty Earth Observatory, Columbia University, Palisades, New York, USA

Nicolas Gruber

Institute of Geophysics and Planetary Physics (IGPP) and Department of Atmospheric and Oceanic Sciences, University of California, Los Angeles, California, USA

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[1] The ΔC^* method of Gruber et al. (1996) is widely used to estimate the distribution of anthropogenic carbon in the ocean; however, as yet, no thorough assessment of its accuracy has been made. Here we provide a critical re-assessment of the method and determine its accuracy by applying it to synthetic data from a global ocean biogeochemistry model, for which we know the "true" anthropogenic CO_2 distribution. Our results indicate that the ΔC^* method tends to overestimate anthropogenic carbon in relatively young waters but underestimate it in older waters. Main sources of these biases are (1) the time evolution of the air-sea CO_2 disequilibrium, which is not properly accounted for in the ΔC^* method, (2) a *p*CFC ventilation age bias that arises from mixing, and (3) errors in identifying the different end-member water types. We largely support the findings of Hall et al. (2004), who have also identified the first two bias sources. An extrapolation of the errors that we quantified on a number of representative isopycnals to the global ocean suggests a positive bias of about 7% in the ΔC^*-derived global anthropogenic CO_2 inventory. The magnitude of this bias is within the previously estimated 20% uncertainty of the method, but regional biases can be larger. Finally, we propose two improvements to the ΔC^* method in order to account for the evolution of air-sea CO_2 disequilibrium and the ventilation age mixing bias.

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1. Introduction

[2] Understanding the fate of anthropogenic CO_2 is one of the most important goals in global carbon cycle research. Two developments during the last decades have made relatively reliable, data-based estimations of anthropogenic carbon in the ocean possible. One is the generation of a large number of high quality inorganic carbon data from the World Ocean Circulation Experiment (WOCE) and the Joint Global Ocean Flux Study (JGOFS) [*Key et al.*, 2004]. The other is the formulation of the ΔC^* method, which is an empirical procedure to separate the small anthropogenic signal from the much larger, inorganic CO_2 background in the ocean [*Gruber et al.*, 1996]. The ΔC^* method has been applied to all three major oceanic basins [*Gruber*, 1998; *Lee et al.*, 2003; *Sabine et al.*, 2002, 1999]. In a summary of the WOCE/JGOFS data analyses, *Sabine et al.* [2004b] estimate a global oceanic inventory of anthropogenic carbon for a nominal year of 1994 of 118 ± 19 Pg-C (Pg = 10^{15} grams), which represents about 50% of the fossil fuel CO_2 emitted between 1800 and 1994. They inferred from this, together with the well-known accumulation of CO_2 in the atmosphere and total emissions from fossil fuel burning and cement production, that the terrestrial biosphere was a net source of CO_2 to the atmosphere by 39 ± 28 Pg-C over this period.

[3] The validity of this important conclusion hinges critically on the reliability of the ΔC^*-derived anthropogenic CO_2 estimates. The uncertainty reported by *Sabine et al.* [2004b] accounts for random and mapping errors (i.e., errors in extrapolating sparsely covered data to a regular grid) but not systematic biases in the method. Like the earlier methods proposed by *Brewer* [1978] and *Chen and Millero* [1979], the ΔC^* method starts from the measurement of dissolved inorganic carbon (DIC) and separates from it the relatively small anthropogenic signal by removing the much larger biological and CO_2 solubility components. The separation requires DIC data as well as measurements of temperature, salinity, and various nutrients

[1]Now at Department of Geology and Geophysics, University of Minnesota, Minneapolis, Minnesota, USA.

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and gases including chlorofluorocarbons (CFC). The method involves a number of steps and assumptions, some of which are difficult to verify or only approximations. For example, a central assumption is that the air-sea CO_2 disequilibrium (i.e., the difference between in situ DIC and surface water DIC that would be in equilibrium with atmospheric pCO_2) has remained constant since preindustrial times. This assumption is not strictly correct, because it is the change over time of the CO_2 disequilibrium that drives the uptake of anthropogenic CO_2 by the ocean.

[4] The ΔC^* method has been a subject of much scrutiny. For example, *Hall et al.* [2004] examined the reliability of chlorofluorocarbon (CFC) concentrations as means to determine the water parcel ventilation age, which is needed by the method to estimate the air-sea CO_2 disequilibrium. They conclude that because the CFC-derived ventilation ages tend to be biased young, the amount of anthropogenic CO_2 in the ocean is overestimated. Other studies have compared the anthropogenic CO_2 reconstructions from the ΔC^* method with those from other methods as they were applied to the same sets of hydrographic and carbon data [*Coatanoan et al.*, 2001; *Sabine and Feely*, 2001; *Wanninkhof et al.*, 1999]. They found substantial differences in the anthropogenic CO_2 estimates but were unable to explain the discrepancies and determine with confidence which methods were superior. More recently, *Matsumoto et al.* [2004] showed that the same ocean carbon cycle models that can adequately simulate the distribution of natural radiocarbon and CFC inventories are unable to reproduce the inventory of anthropogenic carbon as estimated by the ΔC^* method. Since CFCs and natural radiocarbon are either directly measured or derived from measurements with little ambiguity, this suggests that either the models are making fundamental errors simulating these transient tracers or that the estimated anthropogenic CO_2 is biased.

[5] In this work, we critically re-evaluate the ΔC^* method (section 2) and quantify its systematic errors by applying the method to model-derived synthetic ocean data, for which we know the "true" anthropogenic carbon distribution (sections 3–5). Our analysis will show that uncertainty in the estimation of air-sea CO_2 disequilibrium is the largest source of error in the method and that its whole ocean anthropogenic carbon inventory is biased by approximately +7%.

2. ΔC^* Method

[6] For a parcel of seawater collected at time $t = t_{obs}$, the ΔC^* method aims to isolate the relatively small anthropogenic CO_2 component $C_{ant}(t_{obs})$ from the measured DIC concentration, $DIC_m(t_{obs})$, by removing: (1) the addition of DIC from the remineralization of organic carbon and the dissolution of $CaCO_3$, ΔDIC_{bio}, and (2) the preformed, preindustrial DIC concentration. The latter is estimated in parts by separating it into a preindustrial equilibrium component, $DIC_{eq}(t_0)$ and a preindustrial disequilibrium component, $\Delta C_{diseq}(t_0)$. We can thus write

$$C_{ant}(t_{obs}) = DIC_m(t_{obs}) - \Delta DIC_{bio} - DIC_{eq}(t_0) - \Delta C_{diseq}(t_0), \\ = \Delta C* - \Delta C_{diseq}(t_0), \quad (1)$$

where ΔC^* represents the sum of three first terms, all of which can be estimated from data. Figure 1 illustrates the basic concept of the method following a water parcel's history from the time it was last in contact with the atmosphere to the time that it is sampled in the interior.

[7] As explained in detail in the auxiliary material[1] and by *Gruber et al.* [1996], the crux of the ΔC^* method is to accurately estimate $\Delta C_{diseq}(t_0)$, for which there are two mutually exclusive ways. The first is applicable to relatively deep isopycnal surfaces, parts of which can be assumed to contain no anthropogenic CO_2. Equation (1) indicates that the average ΔC^* in those parts represents $\Delta C_{diseq}(t_0)$. The second way is applicable to shallower isopycnal surfaces that likely contain anthropogenic CO_2 everywhere. If we can reliably estimate the age of the water parcel $\tau = t_{obs}$-t (i.e., the time elapsed since leaving the surface), we would be able to estimate the preformed DIC concentration (point C, Figure 1). Since we can also determine the surface ocean DIC concentration in equilibrium with atmospheric pCO_2 at times in the past ($DIC_{eq}(t)$, dash-dotted curve in Figure 1), we can define a new quantity ΔC^*_t as the difference between the estimated preformed DIC concentration, $DIC_0(t)$, and $DIC_{eq}(t)$. This new quantity represents the air-sea disequilibrium for time t and is identical to ΔC^*, except that the equilibrium DIC is now referenced to some postindustrial $pCO_2(t)$ instead of the preindustrial $pCO_2(t_0)$. If we make the assumption that air-sea disequilibrium does not change with time, then $\Delta C^*_t = \Delta C_{diseq}(t_0)$. This estimation of $\Delta C_{diseq}(t_0)$ is done on isopycnal surfaces, because ocean transport and mixing of tracers, including the disequilibrium signal, occurs primarily along isopycnal surfaces.

[8] Table 1 summarizes most of the assumptions of the ΔC^* method that may introduce systematic errors in the anthropogenic CO_2 estimates. We review these possible systematic errors in the next sections and refer the readers to *Gruber et al.* [1996] for a discussion on random errors.

2.1. Errors Associated With the Steady State Assumption

[9] The ΔC^* method assumes that the natural carbon cycle of the ocean was in equilibrium with the atmosphere in preindustrial times and largely remained in steady state ever since. If true, the only process that would increase the total oceanic inorganic carbon content is the uptake of anthropogenic carbon from the atmosphere. However, there are observations that suggest the present ocean is not in steady state. For example, the heat content of the world ocean increased substantially over the last few decades [*Levitus et al.*, 2000]. In addition, changes in ocean circulation [*McPhaden and Zhang*, 2002] and a wide-spread decrease in the oxygen content of thermocline waters in several ocean basins [*Andreev and Watanabe*, 2002; *Emerson et al.*, 2001; *Keller et al.*, 2002; *Matear et al.*, 2000; *Pahlow and Riebesell*, 2000] have been reported.

[10] By design, the ΔC^* method can only estimate the DIC changes that are directly driven by the anthropogenic

[1] Auxiliary material is available at ftp://ftp.agu.org/apend/gb/2004GB002397.

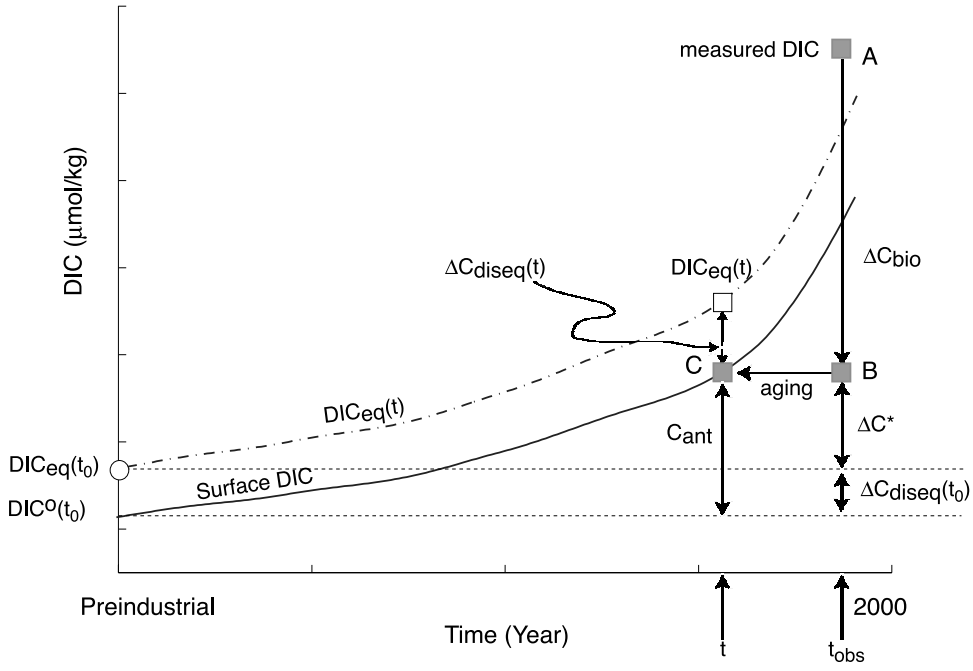

Figure 1. A schematic diagram of the ΔC^* method. The upper dash-dotted $DIC_{eq}(t)$ curve indicates the surface water DIC that would be in equilibrium with the rising atmospheric pCO_2 for a parcel of seawater (i.e., fixed temperature, salinity, and alkalinity). The lower solid curve is the theoretical surface DIC, offset by a fixed distance from the upper curve. The shaded boxes and arrows indicate the movement of a parcel of seawater from the time t that it was last at the surface (C) to a subsequent time t_{obs} that it was sampled in the interior (A). The method retraces the water parcel DIC history from A to B by biological corrections and from B to C by age determination. The difference in DIC between B and DIC_{eq}^{0} defines ΔC^*. The air-sea CO_2 disequilibrium for time t is given by $\Delta C_{diseq}(t)$, which is the difference in surface water DIC between the actual (C) and the equilibrium $DIC_{eq}(t)$. See auxiliary material for detailed description.

perturbation of atmospheric CO_2. The method is not designed to detect DIC changes caused by alterations in the natural carbon cycle, even if they are driven by anthropogenic climate change. This latter change would include, for example, a loss of DIC as a result of ocean warming. The reason why the ΔC^* method is relatively insensitive to changes in the natural carbon cycle is that most such changes are accounted for by the biological correction ΔDIC_{bio}. For example, if a slowdown in circulation causes waters to spend, on average, more time away from the surface, the resulting anomalous accumulation of DIC from respiration will be reflected in a larger ΔDIC_{bio}. Similarly, changes in particulate matter remineralization rates that are driven, for example, by changes in export production would be reflected in ΔDIC_{bio} as well.

[11] A way climate change can affect the estimation of anthropogenic CO_2 is if the air-sea CO_2 disequilibrium were to change beyond that induced by the rise of atmospheric CO_2 or if the preformed oxygen concentrations were to change. Ocean warming will likely cause a change in the air-sea CO_2 disequilibrium, because warming reduces the CO_2 solubility in seawater. An estimated temperature dependence of the CO_2 system in the ocean [*Sarmiento and Gruber*, 2005] indicates a loss of DIC of about 2×10^{-9} mol C per Joule of heat increase. The observed heat content increase of 2×10^{23} J between the mid 1950s and mid 1990s [*Levitus et al.*, 2000] therefore would imply a loss of about 4×10^{14} mol C or 5 Pg-C over this period. If this loss occurred at a constant rate over this 40-year period, the air-sea CO_2 disequilibrium would have had to change by less than 1 μmol kg^{-1} in order to generate this flux. The actual change may be smaller than this, because the ocean carbon cycle can in part compensate the warming-induced outgassing of natural CO_2 with an increased uptake due to a more efficient biological pump [*Sarmiento et al.*, 1998].

[12] Model simulations that include the effect of global warming on the net exchange of CO_2 between the atmosphere and ocean support the notion that the observed climate change in the twentieth century has a moderate impact on the uptake of anthropogenic CO_2 by the ocean. *Plattner et al.* [2001] found a reduction of less than 0.1 Pg-C yr^{-1} in the uptake of anthropogenic CO_2 for the 1980s between simulations with and without global warming. While we emphasize that the observed warming in the twentieth century likely had limited influence on the ΔC^*-based estimates of anthropogenic CO_2, global warming likely did influence the natural ocean carbon cycle. *Plattner et al.* [2001] estimate, for example, that the change in climate between 1765 and 2000 led to a loss of about 9

Table 1. Sources and Impact of Biases in the ΔC^*-Derived Anthropogenic CO_2 Inventory[a]

Source	Assumption	Discussion (Accounted by the ΔC^* Method?)	Impact	Bias
Steady state	natural carbon and oxygen cycles have remained in steady state	changes in ocean heat content, circulation, and biology may have changed the natural carbon cycle (no)	moderate	±
Stoichiometry	elemental ratios in organic matter remineralization are constant and constrained	ratios offset from standard ratios cause inversely proportional changes in the inventory; variability is unknown (no)	?	±
O_2-saturation	surface ocean is saturated with respect to oxygen	high-latitudes surface is often undersaturated but ΔDIC_{bio} in the method accounts for undersaturation (yes)	small	(±)
Preformed alkalinity	surface alkalinity has not changed over time, and preformed concentration is predictable	little evidence for change in surface alkalinity; prediction is based on regression models, which can perform poorly in low oxygen waters (yes)	small	(±)
Denitrification	N*-based, biological correction accounts correctly for denitrification	Correction appears to work well (yes)	small	(±)
Air-sea CO_2 disequilibrium	disequilibrium has remained constant through time	assumption is not correct and introduces a bias in the upper ocean, where ΔC^*_t is used to estimate ΔC_{diseq} (no)	moderate	+
Ventilation age	CFCs give correct ventilation age estimates	no, where mixing involves "old" waters that would bias the CFC ages young; impact is limited to the upper ocean, where ΔC^*_t is used to quantify ΔC_{diseq}	moderate	+
"Old" waters	waters without anthropogenic CO_2 can be correctly identified	assumption affects the deep ocean, where ΔC^* is used to quantify ΔC_{dis} equation Identification is problematic in the Atlantic.	small	-
Water mass mixing	OMP analysis correctly attributes the fractional contribution of identified source water types	OMP analysis tends to be underconstrained, but bias appears to be limited when the analysis is judiciously applied	moderate	(±)

[a]DIC, dissolved inorganic carbon; MLR, multiple linear regression; PO, quasi-conservative tracer ($PO = O_2 + 170{*}PO_4$).

Pg-C of carbon from the ocean. Such a loss would not be accounted for by the ΔC^* method.

[13] With regard to changes in the preformed oxygen concentrations, model simulations suggest that the observed ocean warming [*Levitus et al.*, 2000] led to a net loss of oceanic oxygen into the atmosphere ($F(O_2)$) of 2.4×10^{15} moles [*Plattner et al.*, 2001]. If we assume that most of this warming occurred over the last 20 years, the required change in the oxygen disequilibrium to drive this flux is negligibly small: about 0.2 μmol kg^{-1} (i.e., $\Delta O_2 = F(O_2)/(A \times k_w \times \Delta t)$), with $A = 360 \times 10^{12}$ m^2 being the ice-free surface area of the surface ocean, k_w representing the gas exchange velocity for oxygen (about 0.2 m h^{-1}) and Δt = 20 years).

2.2. Errors Associated With the Biological Correction

[14] The biological correction ΔDIC_{bio} may be a possible source of errors as it relies on a number of assumptions: (1) Stoichiometric ratios of remineralization of organic matter are constant and known; (2) the preformed concentration of oxygen is correctly estimated by its saturation concentration; and (3) preformed alkalinity concentration Alk^0 has not changed over time and can be reliably estimated. See auxiliary material for more details of this section.

[15] *Gruber* [1998] and *Sabine et al.* [1999] examined the first assumption and showed that a constant offset in stoichiometry leads to changes in the estimated anthropogenic CO_2 that are approximately inversely proportional to changes in the apparent oxygen utilization. For example, a carbon to oxygen ratio that is ∼13% lower than their standard ratio of $r_{C:O2} = 0.688$ (i.e., 117:−170 [*Anderson and Sarmiento*, 1994] would increase the anthropogenic carbon inventory by about 20% in the Atlantic and about 18% in the Indian. A ratio that is ∼13% higher than their standard ratio (i.e., approaching the classical "Redfield" ratio of 106:−138) would roughly decrease the inventory by 15% in the Indian but only 8% in the Atlantic. As discussed by *Gruber* [1998], these inventory changes are smaller than expected simply by propagating the initial ratio errors.

[16] With regard to the second assumption, it is well known that wintertime oxygen concentrations in high latitudes are often not at saturation. Since preformed concentrations are primarily set during the winter in the outcrop regions, any deviation of the preformed oxygen concentration from the saturation concentration is transported into the interior and leads to an error in ΔDIC_{bio}. *Ito et al.* [2004] recently suggested that the deviation can be more than 50 μmol kg^{-1} and thus can cause errors in ΔDIC_{bio} as large

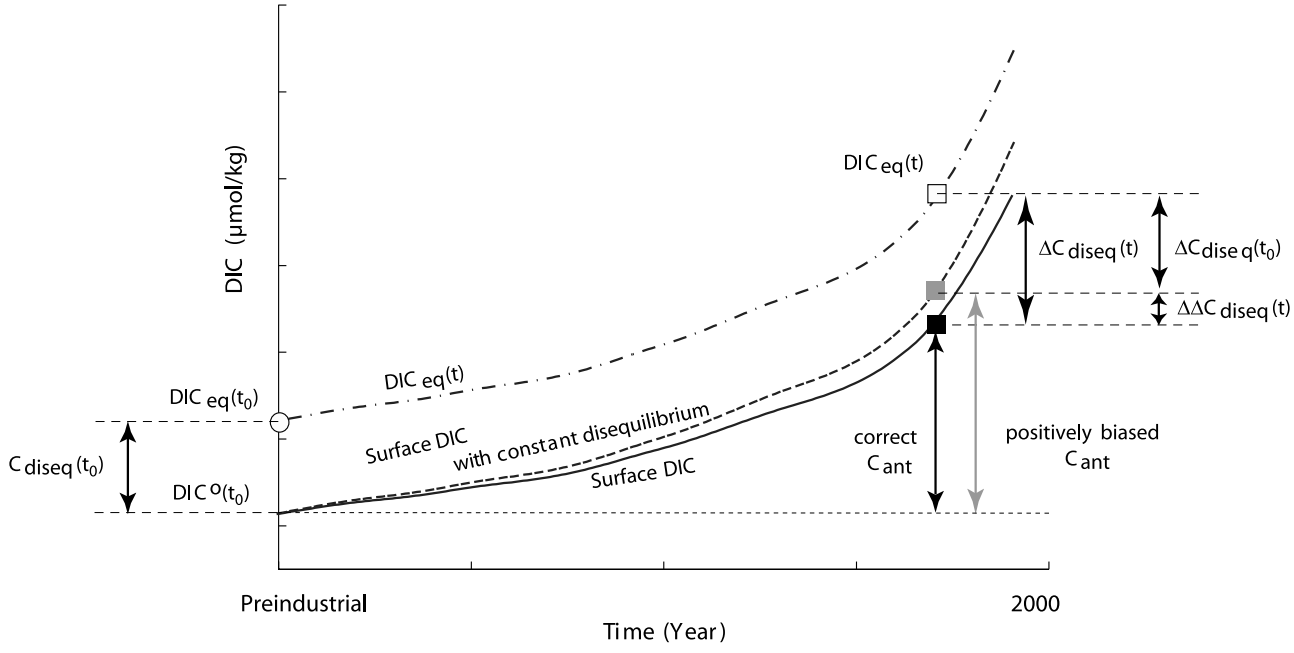

Figure 2. Effect on the ΔC^* method of the temporal change in air-sea CO_2 disequilibrium. The upper dash-dotted curve represents the equilibrium $DIC_{eq}(t)$. The middle dashed curve is the actual surface DIC offset by a fixed distance from the upper curve, as in Figure 1. The lower solid curve is the "actual" surface DIC that does not keep up with the rising atmospheric pCO_2 (i.e., the disequilibrium increases with time). The distance between the open and solid squares is the actual disequilibrium $\Delta C_{diseq}(t)$ at time t. The distance between the open and shaded squares is the time-constant disequilibrium $\Delta C_{diseq}(t_0)$ that the ΔC^* method assumes. The difference between the shaded and solid squares is the $\Delta\Delta C_{diseq}(t)$.

as of 30 μmol kg^{-1}. Fortunately, as long as this error does not change with time for particular water mass, it cancels out when anthropogenic CO_2 is determined.

[17] Last, there is little evidence that would suggest that the third assumption regarding Alk^0 is wrong. The saturation horizon for aragonite has been affected by the invasion of anthropogenic CO_2 [*Feely et al.*, 2004], but the reported changes are small. The only error of concern is the validity of the linear regression model used to estimate Alk^0. One possibility that we will later discuss is that most studies used "PO" [*Broecker and Peng*, 1982] as a conservative tracer in their regression models. However, in regions influenced by denitrification, PO is not conservative.

2.3. Errors Associated With the Estimation of the Air-Sea CO_2 Disequilibrium

[18] The estimation of $\Delta C_{diseq}(t_0)$ requires the following assumptions: (1) ΔC_{diseq} has remained constant through time; (2) CFCs or other age tracers provide accurate ventilation age; (3) regions that do not contain anthropogenic CO_2 can be identified without error; and (4) water type end-members and their mixing ratios making up a particular water parcel can be determined without systematic errors.

[19] A justification for the first assumption is that global mean disequilibrium of about 5 μmol kg^{-1}, which is needed to account for the oceanic uptake of 2 Pg-C yr^{-1} of anthropogenic CO_2 in the recent decades, is too small for the ΔC^* method to detect [*Gruber et al.*, 1996]. Recently, *Hall et al.* [2004] showed that neglecting a change in air-sea CO_2 disequilibrium would cause the ΔC^* method to overestimate the anthropogenic CO_2 uptake. However, this bias is introduced only when ΔC_{diseq} is determined by ΔC_t^* in shallower isopycnal. This bias can be illustrated with a "shortcut" method [*Gruber et al.*, 1996], where the definition of ΔC_t^* is combined with equation (1), to give anthropogenic CO_2 directly,

$$C_{ant}(t_{obs}) = DIC_{eq}(t) - DIC_{eq}(t_0) \; + \; \Delta C_{diseq}(t) - \Delta C_{diseq}(t_0). \tag{2}$$

[20] Equation (2) states that the anthropogenic CO_2 can be estimated entirely by the knowledge of the age distribution and of how the disequilibrium has changed over time. This forms the basis of the age spectrum method of *Hall et al.* [2002, 2004] and was used by *McNeil et al.* [2003] to infer decadal changes in oceanic anthropogenic CO_2. The uptake of anthropogenic CO_2 by the ocean requires that ΔC_{diseq} has become more negative over time, that is, $\Delta C_{diseq}(t) < \Delta C_{diseq}(t_0)$, making the last two terms in equation (2), $\Delta C_{diseq}(t)$-$\Delta C_{diseq}(t_0)$, negative. This leads to an overestimation of anthropogenic CO_2 (Figure 2).

[21] As we will demonstrate in sections 4 and 5, the change of the air-sea disequilibrium over time constitutes probably the single most important contribution to the overall bias in the ΔC^*-based anthropogenic CO_2 distribution. However, the global-scale impact of this bias is

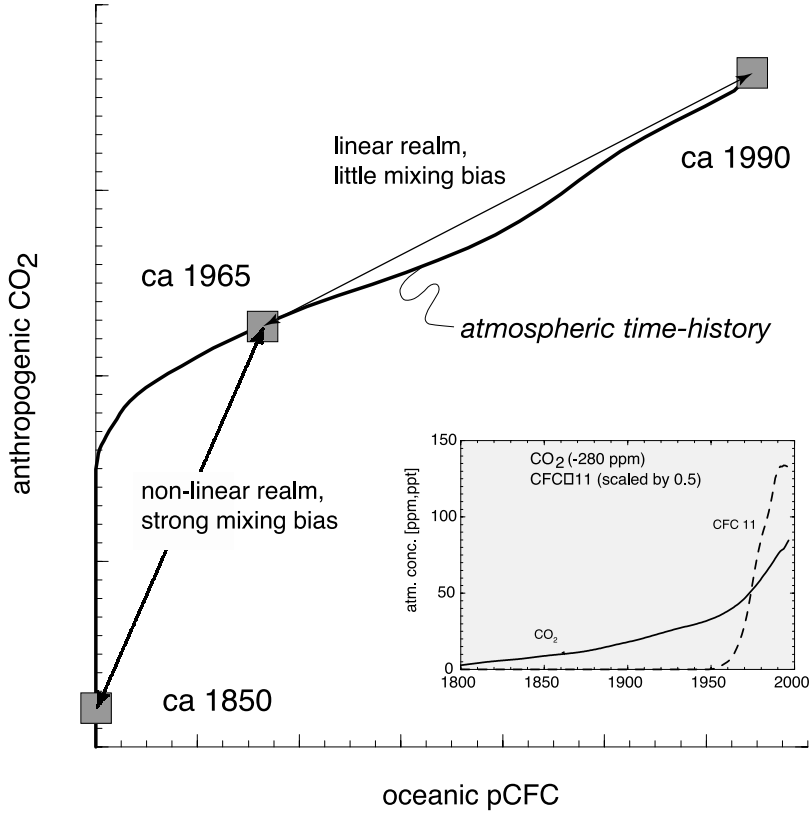

Figure 3. Theoretical time histories of fully equilibrated concentrations of anthropogenic CO_2 and *p*CFC for the mean surface ocean. The inset shows their atmospheric time histories.

limited, since ΔC_t^* is only applied to the upper ocean to estimate the air-sea CO_2 disequilibrium.

[22] With regard to the second assumption, CFCs have been the preferred "age" tracers in recent applications of the ΔC^* method; the exception is the very first application by *Gruber et al.* [1996], who used ^{3}H-^{3}He ages. In the upper ocean, where CFCs are used in conjunction with equation (2), the ΔC^* method is essentially equivalent to a simpler method based almost entirely on CFCs [*McNeil et al.*, 2003]. However, this equivalence is not true elsewhere, where air-sea CO_2 disequilibrium is not estimated directly and solely by CFCs.

[23] The accuracy of the CFC-derived ages depends on the extent to which the following conditions are met: (1) that preformed CFC concentration was the saturation concentration, and (2) that preformed concentration is relatively well conserved as the signal is transported into the interior of the ocean. Except in very high latitudes, observations show that CFCs at their outcrops are generally very close to saturation. However, mixing can be a problem. There were very little CFCs prior to about 1960 (Figure 3), and so any mixing involving waters from the pre-1960s waters with younger waters will yield a mixture, whose inferred *p*CFC ventilation age will be biased young [*Haine and Hall*, 2002]. More fundamentally, the concept of a single ventilation age is strictly only valid in the limiting case of zero mixing [*Hall et al.*, 2002]. Since mixing along isopycnal surfaces is quite strong in the ocean, a better concept is perhaps an age spectrum [*Beining and Roether*, 1996; *Hall et al.*, 2002].

[24] The consequence of using a single ventilation age in the ΔC^* method is an overestimation of anthropogenic carbon in the ocean, whose magnitude depends sensitively on the time period under consideration. As illustrated in Figure 3, mixing of waters that were at the surface between about 1960 and 1990 is expected to have a limited impact on the estimated anthropogenic CO_2, since both tracers increased roughly linearly. However, *Waugh et al.* [2003] show that even waters in this range is not free of older waters. By contrast, mixing of waters that were last at the surface before 1960 will cause the estimated age to be biased young and hence C_{ant} to be biased high. In most applications of the ΔC^* method, only pCFC ages of 30 years or less are used (i.e., within the linear realm), so this positive bias is limited.

[25] The third assumption is relevant for deeper waters, where the air-sea CO_2 disequilibrium is estimated using the quantity ΔC^*. This assumption is more of an issue in the Atlantic, where anthropogenic carbon has penetrated the deep waters. The challenge associated with this assumption is illustrated in a study of the deep South Atlantic that found CCl_4 but no CFC-11 or CFC-12 [*Wallace*, 2001]. The absence of CFCs could erroneously lead one to decide that this region is free of anthropogenic CO_2. However, the presence of CCl_4, which was introduced into the atmosphere in substantial amounts after 1860, clearly indicates

that the region is not free of anthropogenic CO_2. If a region that has anthropogenic carbon is mistakenly identified as having none, then the bias on C_{ant} is obviously negative.

[26] Finally, the validity of the fourth assumption (i.e., accurate identification of the important water mass end-members and their mixing ratios) depends strongly on ocean basin. For example, in the deep Atlantic, the two end-members from the northern and southern sources can be easily identified, whereas identifying more than three water masses in the thermocline of the North Pacific is difficult. To address this difficulty, *Sabine et al.* [2002] introduced the optimal multiparameter (OMP) analysis [*Tomczak*, 1981] which can determine the mixing ratios of multiple water masses. Although the analysis provides some objectivity, it still involves judgment calls in selecting the water mass end-members and hence is not free of errors.

3. Method to Quantify the Biases

[27] The synthetic data, to which we applied the ΔC^* method, were generated by the PRINCE model as submitted by the Princeton University modeling group to the second phase of the Ocean Carbon Cycle Model Intercomparison Project (OCMIP-2). Details of the ocean general circulation model (OGCM) and simulations are given in the auxiliary material. The results are available at the OCMIP-2 website (http://http://www.ipsl.jussieu.fr/OCMIP) and described in OCMIP-2 publications [e.g., *Dutay et al.*, 2002; *Matsumoto et al.*, 2004]. We use simulation results for the year 1994 to match the canonical year of the WOCE/JGOFS surveys.

[28] We require some adaptations to the ΔC^* method that are specific for our application to the model synthetic data. These include new formulations of preformed alkalinity and a biological correction based on preformed phosphate (instead of N*) in low oxygen waters (see auxiliary material).

[29] Since the application of the ΔC^* method is very labor intensive, we apply the method to only a number of representative isopycnal surfaces, which are grouped into three on the basis of how the air-sea CO_2 disequilibrium is estimated. The first category is the "shallow" surfaces that only contain waters with *p*CFC ages of 30 years and younger, and we use ΔC^*_t in the shortcut method (equation (2)) to estimate anthropogenic carbon. Data coverage must be complete in this case, because the shortcut method requires the difference between ΔC^* and ΔC^*_t at each data point. We are not concerned with water mixing, as we are in the linear realm of Figure 3. For these "shallow" isopycnals, any mismatch between the simulated and method-derived anthropogenic carbon can be attributed to any combination of: (1) uncertainties in the age estimate that would lead to erroneous $DIC_{eq}(t)$, (2) the degree to which the constant disequilibrium assumption is false, and (3) uncertainties in the linearized models of equilibrium DIC (i.e., estimation of $DIC_{eq}(t_0)$ and $DIC_{eq}(t)$).

[30] The second category consists of "deep" isopycnals that for the most part contain very little or no CFCs. The disequilibrium signal in such "deep" isopycnals is assumed to be captured by the ΔC^* values far from the outcrop regions. A possible source of error that is unique to this category is the assumption that anthropogenic carbon does not exist at all in waters far away from the outcrop regions and these regions can be identified (i.e., fourth assumption in section 2.2).

[31] The final category is the "mid-depth" isopycnals, which contain significant amounts of waters with *p*CFC ages both younger and older than 30 years. The quantification of the air-sea CO_2 disequilibrium component is most difficult for waters older than 30 years, because the presence of measurable CFC concentrations indicate the existence of anthropogenic carbon, yet the concentrations are too low to provide a reliable ventilation age. We cannot use the shortcut method of equation (2) and instead use a combination of ΔC^*_t and solutions of the OMP analysis to estimate the disequilibrium component for each water parcel. Uncertainties for this isopycnal category include those from the OMP analysis and most sources of error mentioned for the other two categories. The ΔC^*-derived anthropogenic CO_2 concentration is thus likely to be most uncertain for this category.

4. Results

4.1. A "Mid-Depth" Isopycnal: $\sigma_\theta = 26.8$ in the Pacific

[32] We demonstrate the application of the ΔC^* method to "mid-depth" model data from the Pacific on the isopycnal surface $\sigma_\theta = 26.8$, which represents intermediate waters. This surface is deepest in the western parts of the northern and southern subtropical gyres reaching depths as deep as 700 m. The isopycnal outcrops along about 50°S in the Southern Hemisphere and in the Sea of Okhotsk and Bering Sea in the Northern Hemisphere. The "true" or model-simulated anthropogenic carbon concentrations on this isopycnal are highest in the southern outcrop region, where concentrations exceed 40 μmol kg^{-1} (Figure 4a). In the northwest outcrop region, a tongue of elevated concentrations above 30 μmol kg^{-1} extends southeastward. The most poorly ventilated waters of the eastern tropics have concentrations less than 10 μmol kg^{-1}.

[33] An examination of the T-S properties on this isopycnal surface suggests four distinct water types or end-members on this surface, and we determined their fractional contributions to every water parcel on this surface using the OMP method (auxiliary material). The air-sea disequilibria of three of these end-members were then estimated using their ΔC^*_t values, because the pCFC ages near their outcrop regions were younger than 30 years. Mixing will have a limited effect for these water types, because they are within the linear realm of Figure 3. However, the same is not true for the forth water type, which is found in the eastern equatorial region and formed most likely by mixing in the ocean interior instead of ventilation. At its core, the fourth water type has *p*CFC ages that are much older than 30 years, consistent with its low concentrations of the "true" anthropogenic carbon (Figure 4a). Lacking an unequivocal way to estimate the air-sea disequilibrium of this water type, we assign source disequilibrium values representing extreme cases and discuss the sensitivity of the resulting anthropogenic carbon to the different assignments.

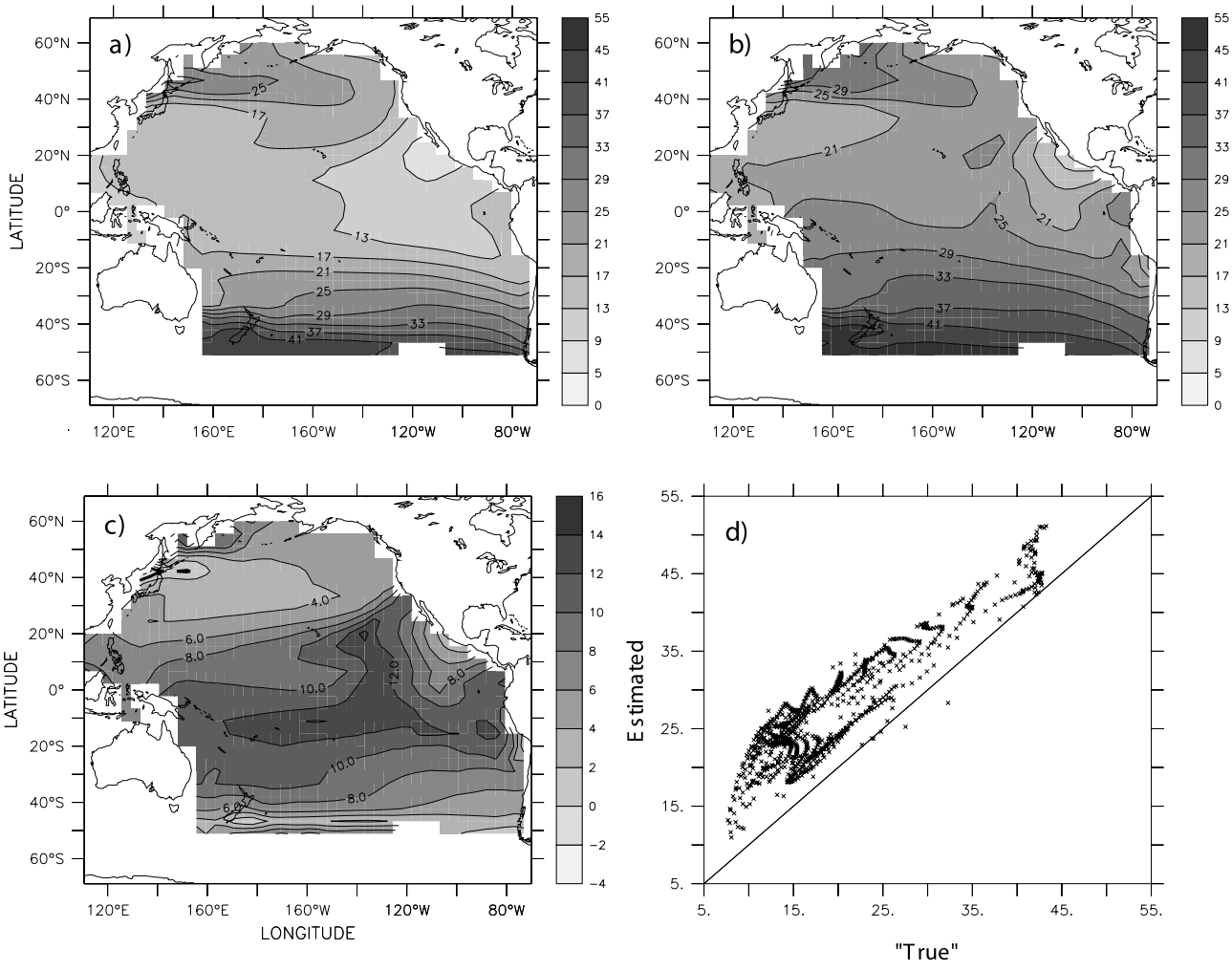

Figure 4. Comparison of the "true" and ΔC^*-derived C_{ant} on the $\sigma_\theta = 26.8$ Pacific isopycnal. (a) The "true" distribution as simulated by the forward model. (b) The ΔC^*-derived distribution. (c) The deviation of the estimated from the "true." (c) The "true" (x axis) versus the ΔC^*-derived (y axis). Unit is μmole-C kg^{-1}.

[34] In a case that is arguably the most reasonable, we assume that the fourth water type was formed by a strong vertical mixing with the overlying surface water, whose disequilibrium value can be determined by ΔC_t^*. The C_{ant} distribution using the overlying ΔC_t^* as the fourth water type disequilibrium (Figure 4b) is qualitatively very similar to the "true" (Figure 4a). C_{ant} is highest along the southern boundary and then decreases monotonically away from the outcrop region. This feature is evident in the "true" and consistent with the penetration of the southern ventilated waters into the interior. The ΔC^* method also captures the entry of anthropogenic carbon in the far northwest. Furthermore, the method correctly yields the least amount of anthropogenic carbon in the eastern portion of the low latitudes, farthest away from the outcrop regions.

[35] Despite the close resemblance in the spatial pattern, it is clear that the derived quantity is larger everywhere than the directly simulated (Figures 4c and 4d). The deviation of the scatter from the 1-to-1 line is mostly parallel. The derived anthropogenic carbon overestimates the "true" by as much as 15 μmol kg^{-1}. The areally weighted mean bias is 8 ± 3 μmol kg^{-1} (±1 standard deviation) (Table 2).

[36] The bias of the C_{ant} is relatively insensitive to different assumptions about the disequilibrium of the fourth water type. If it is assumed to be derived entirely from the ventilated waters from the northwest, the positive mean bias is 6 ± 4 μmol kg^{-1}. If the origin of the fourth water type is instead assumed to be the ventilated waters from the southern boundary, the mean bias is 10 ± 4μmol kg^{-1}. Finally, if it is assumed to represent a 50–50 mixture of waters from the north and the south, the mean bias is 8 ± 3 μmol kg^{-1}. The positive bias is therefore robust within a few μmol kg^{-1} to the choice of different disequilibrium values for the fourth water type.

[37] The positive bias of C_{ant} is not unique to the Pacific $\sigma_\theta = 26.8$ isopycnal. Application of the same "mid-depth" analysis to the Indian ($\sigma_\theta = 25.6$) and Atlantic ($\sigma_\theta = 27.3$) isopycnals also consistently yields too high anthropogenic carbon concentrations: The bias is +3 μmol kg^{-1} on the Indian isopycnal and +2 μmol kg^{-1} on the Atlantic iso-

Table 2. Bias of the ΔC^* Method as Applied to a Set of 1994 Synthetic Data[a]

	Atlantic		Indian		Pacific		Global	
Isopycnals	Anth-C Bias, μmole/kg	Volume, 10^{15} m^3	Anth-C Bias, μmole/kg	Volume, 10^{15} m^3	Anth-C bias, μmole/kg	Volume, 10^{15} m^3	Inventory bias, Pg-C	"True" inv., Pg-C
Shallow	(σ_θ = 25.6) +7 ± 4	30.1	(σ_θ = 24.6) +5 ± 4	2.2	(σ_θ = 25.6) +4 ± 3	40.9	5 ± 3	34.7
Mid-depth	(σ_θ = 27.3) +2 ± 7	24.7	(σ_θ = 25.6) +3 ± 8	9.2	(σ_θ = 26.8) +8 ± 3	55.2	7 ± 6	32.9
Deep	(σ_θ = 37.02) −2 ± 5	284.2	(σ_2 = 36.6) +1 ± 3	67.6	(σ_2 = 36.9) 0 ± 2	603.9	−5 ± 7	32.3
Total							7 ± 10	99.9

[a]The ΔC^* method was applied to OCMIP-2 PRINCE model "data" from simulation year 1994. The specific isopycnal surfaces that we analyzed are indicated by parentheses. Inventory bias is the product of the biased concentration, "Anth-C bias," on each isopycnal surface and the volume that the biased concentration represent. The "true" inventory as directly simulated for this simulation year is 99.9 Pg-C for the globe, 36.3 Pg-C for the Atlantic, 20.1 Pg-C for the Indian, and 43.6 Pg-C for the Pacific. The Arctic is excluded.

pycnal (Table 2). These results are obtained assuming that the source disequilibrium signals of any water type older than 30 CFC years, like the Pacific fourth water type, are derived from the overlying surface waters. The magnitude of these biases are similarly insensitive to different choices of source disequilibrium values as was the case on the Pacific σ_θ = 26.8 isopycnal.

[38] Any reason that contributes to the positive, systematic bias of C_{ant} on these "mid-depth" isopycnals must account for the fact that the method was applied independently on the three surfaces. It is therefore unlikely, for example, that some particular choice of weighting in the OMP analysis is the reason. Similarly, the denitrification correction using performed PO_4 is probably not the reason, because the correction was applied to restricted, low O_2 waters, whereas the bias is basin-wide. As noted in section 2, likely causes of the bias is the temporal change of the air-sea CO_2 disequilibrium and the uncertainty in the *p*CFC age due to water mass mixing (Table 1).

4.2. A "Shallow" Isopycnal: σ_θ = 24.6 in the Indian

[39] We demonstrate the application of the ΔC^* method in Indian Ocean to the "shallow" isopycnal surface of σ_θ = 24.6 (Figure 5). This surface is everywhere shallower than 200 m and outcrops in the Arabian Sea near the mouth of the Persian Gulf as well as along the southern boundary. The *p*CFC age is near zero at these outcrop regions but reaches a maximum of about 25 years in the Bay of Bengal in the northeast. These are consistent with the "true" distribution of anthropogenic carbon, which is highest in the outcrop regions and lowest in the Bay of Bengal (Figure 5a). Somewhat elevated concentrations are also found in the Arabian Sea, where the isopycnal surface comes very close to the surface. Evidently, the entire isopycnal surface has been exposed to the postindustrial atmosphere, because even the Bay of Bengal waters have more than 20 μmol kg^{-1} of anthropogenic carbon. As shown in Figure 5b, the large-scale features of the C_{ant} estimated by the $\Delta C^* - \Delta C_t^*$ difference at each data point (equation (2)) are consistent with the "true" distribution. However, as on the "mid-depth" isopycnals, the reconstructed C_{ant} on this "shallow" isopycnal is everywhere higher than the "true" concentrations (Figures 5c and 5d). The areally weighted, mean positive bias on this Indian isopycnal is 5 ± 4 μmol kg^{-1} (Table 2). On the "shallow" Pacific and Atlantic isopycnals, the bias is likewise consistently positive. It is 4 ± 3μmol kg^{-1} on the Pacific σ_θ = 25.6 surface and 7 ± 4 μmol kg^{-1} on the Atlantic σ_θ = 25.6 surface (Table 2). In Figure 5c, the overestimate is most prominent in the northern parts of the isopycnal, where the positive bias is as large as 16 μmol kg^{-1}. This large localized systematic error may be related to an error in the estimation of ALK^0, which is partly based on PO and is not likely to be accurate in low oxygen waters where denitrification occurs (see auxiliary material). Aside from this regional error, the changing air-sea CO_2 disequilibrium and the *p*CFC age bias due to mixing are again the likely reasons for the consistently positive bias.

4.3. A "Deep" Isopycnal: σ_2 = 37.02 in the Atlantic

[40] We illustrate our analysis of a "deep" isopycnal on σ_2 = 37.02 in the Atlantic Ocean (Figures 6 and 7). This surface is located for the most part in water depths between 2000 and 2500 m and slopes upward in the Southern Ocean, outcropping in the Weddell Sea. In the north, the surface deepens near the Labrador Sea but outcrops in the Greenland-Iceland-Norwegian seas (GIN Sea). There is very little CFC on this surface except in these outcrop regions, where simulated anthropogenic carbon is abundant (Figure 6a). In the Northern Hemisphere, anthropogenic carbon is somewhat elevated along the western boundary, indicating the influence of the North Atlantic Deep Water (NADW). The σ_2 = 37.02 surface in the model is, however, a few hundred meters deeper than the core of NADW, which is characterized by a mid-depth maximum in anthropogenic CO_2.

[41] As expected for a "deep" isopycnal, ΔC^* becomes smaller in older waters (Figure 7a) and with greater distance from the high-latitude outcrop regions (Figure 7b). This indicates the decreasing presence of anthropogenic carbon, which presumably becomes negligible where ΔC^* become "flat." The mean value of ΔC^* in the flat part, which extends from about 40°S to 20°N, is 24 ± 1 μmol kg^{-1}. We assume that this value represents ΔC_{diseq} on this surface.

[42] We derived C_{ant} on this σ_2 = 37.02 isopycnal (Figure 6b), by subtracting this ΔC_{diseq} value from the ΔC^* field. When compared to the "true" distribution (Figure 6a), the overall spatial pattern of the derived anthropogenic carbon is quite similar but lower in most parts of the isopycnal surface except in the far south (Figures 6c and 6d). The areally weighted bias of the reconstructed C_{ant} is −2 ± 5 μmol kg^{-1} (Table 2). This indicates the predominance of the negative bias in older waters over the positive bias of younger waters on this particular "deep" Atlantic isopycnal. The balance of the

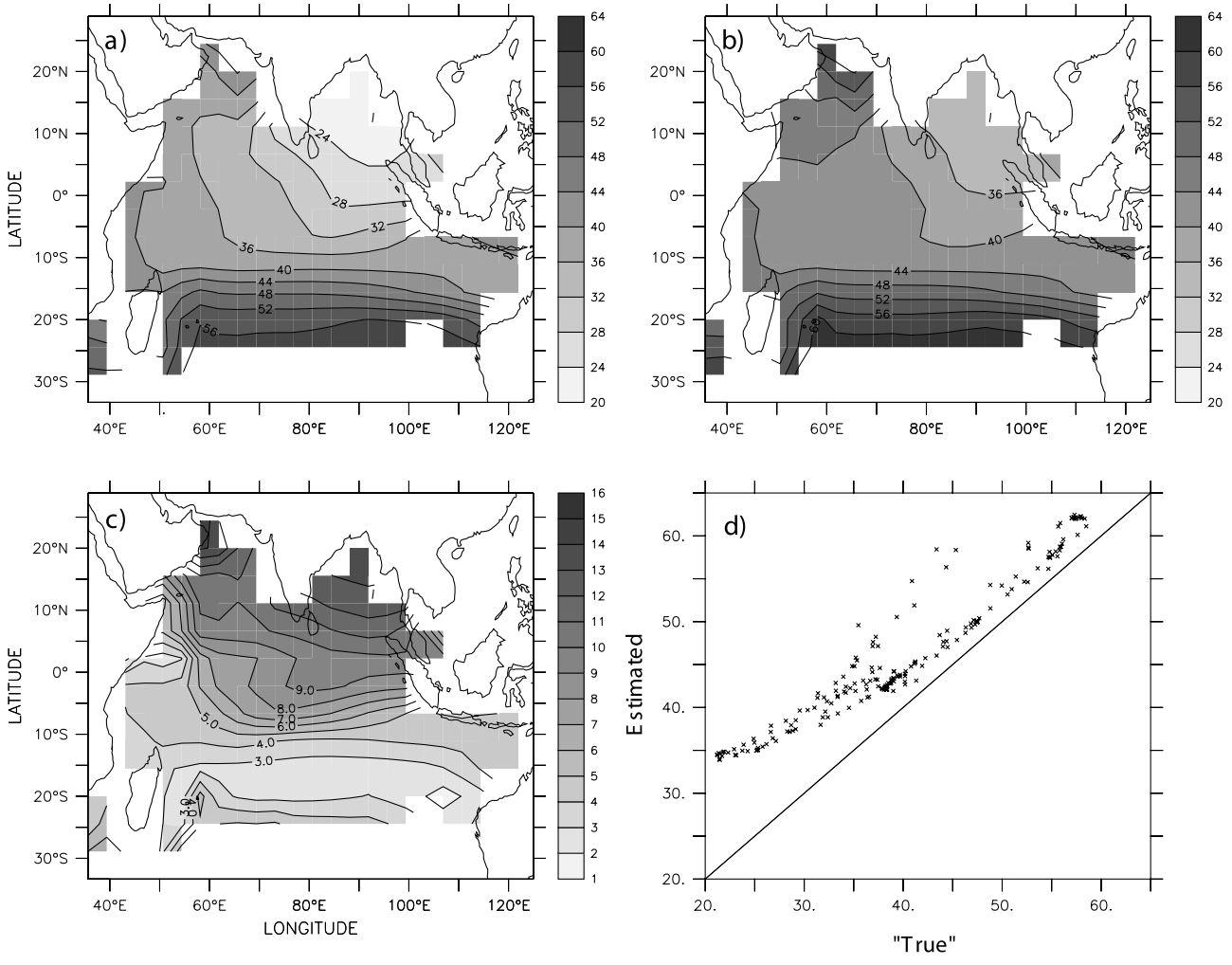

Figure 5. Comparison of the "true" and ΔC^*-derived on the $\sigma_\theta = 24.6$ Indian isopycnal. See Figure 4 for part descriptions.

negative and positive biases is however not the same on other "deep" isopycnals. On the Pacific $\sigma_2 = 36.9$ isopycnal for example, there is no significant bias in old waters (i.e., *p*CFC ages greater than 30 years; bias is 0 ± 1 μmol kg^{-1}), while the positive bias in younger waters is 3 ± 2 μmol kg^{-1}. Overall there is negligible bias on this "deep" Pacific isopycnal (Table 2). On the Indian $\sigma_2 = 36.6$ isopycnal, the negative bias where pCFC age is greater than 30 years is again insignificant (0 ± 1 μmol kg^{-1}), while the positive bias in younger waters is 3 ± 3 μmol kg^{-1}. The mean bias on this Indian surface is $+1 \pm 3$ μmol kg^{-1} (Table 2).

5. Discussion

5.1. Causes of Systematic Errors

[43] There is a clear distinction in our results between the "shallow" and "mid-depth" versus the "deep" isopycnal analyses. For the first group, whose air-sea CO_2 disequilibrium was determined using ΔC_t^*, the ΔC^* method consistently overestimates C_{ant}. For the latter, the disequilibrium was determined using ΔC^* far from the outcrop regions. On these "deep" isopycnal surfaces, the ΔC^* method tends to underestimate C_{ant} in older waters (greater than 30 CFC years) but tends to overestimate C_{ant} in younger waters.

[44] The positive bias in the "shallow" and "mid-depth" surfaces is consistent with the conclusions of *Hall et al.* [2002, 2004] and our expectations based on our assessment of the temporal evolution of the air-sea CO_2 disequilibrium (Figure 2) and the *p*CFC ventilation age bias due to mixing (Figure 3).

[45] Our forward model simulation shows that the global mean air-sea CO_2 disequilibrium increased from -7 μmol kg^{-1} in preindustrial times to about -12 μmol kg^{-1} in 1990 (Figure 8a). This change in disequilibrium $\Delta\Delta C_{diseq}(t)$ ($\Delta\Delta C_{diseq}(t) = \Delta C_{diseq}(t) - \Delta C_{diseq}(t_0)$) has relatively little uncertainty, because it depends primarily on the global uptake flux of anthropogenic CO_2, which is well constrained (e.g., see summaries by *Le Quéré et al.* [2003] and *Sabine et al.* [2004a]). Indeed, Figure 8a shows that $\Delta\Delta C_{diseq}(t)$ scales nearly linearly with the globally integrated anthropogenic CO_2 uptake flux. However, $\Delta\Delta C_{diseq}(t)$

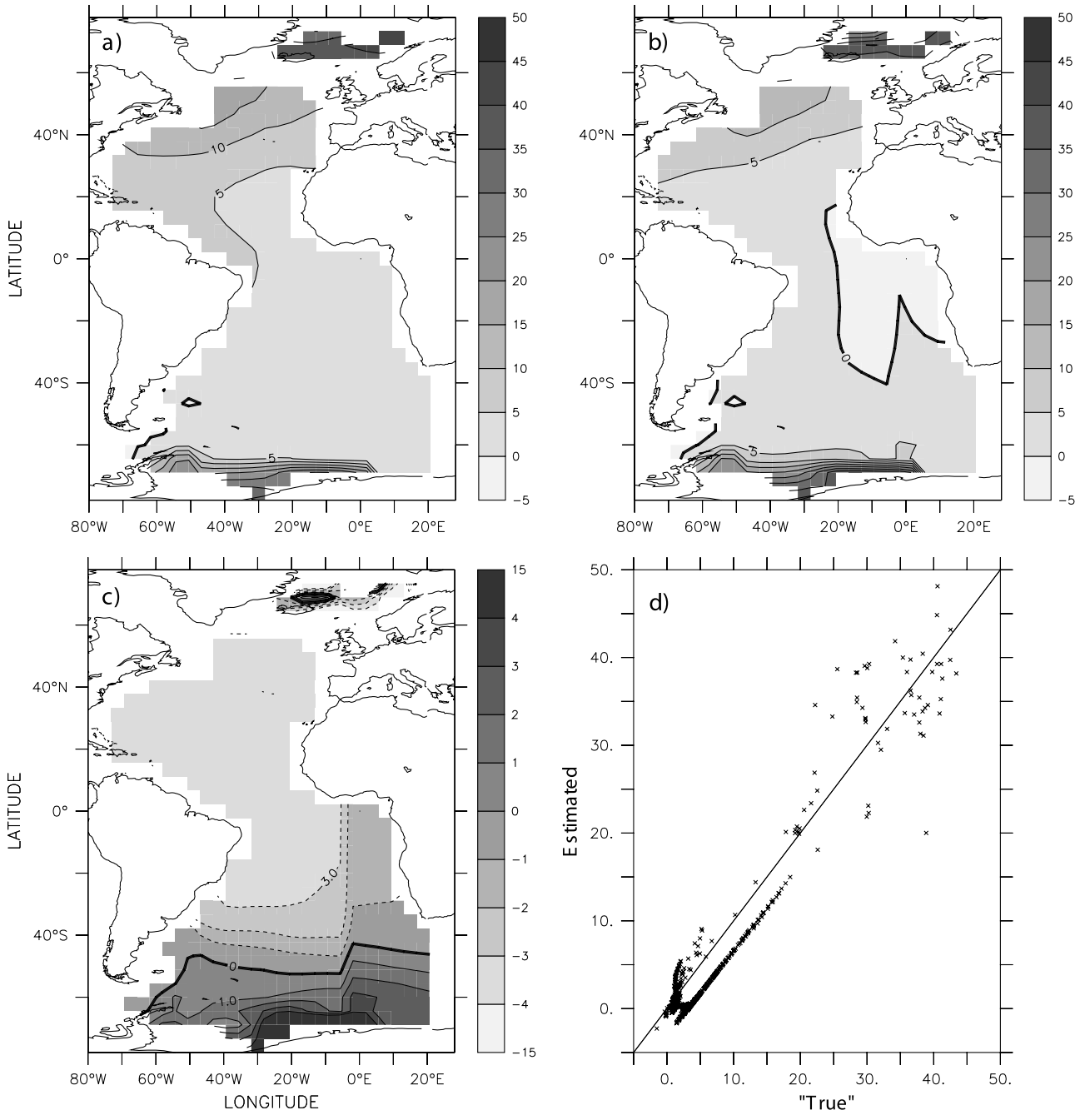

Figure 6. Comparison of the "true" and ΔC^*-derived on the $\sigma 2 = 37.02$ Atlantic isopycnal. See Figure 4 for part descriptions.

exhibits large regional differences (Figure 8b), with the subtropics showing the smallest changes (less than -3 μmol kg^{-1}), the high latitudes moderate changes, and the equatorial upwelling regions the largest changes (up to -20 μmol kg^{-1}). These regional variations are surprising at first since the flux of anthropogenic CO_2 is relatively uniform (Figure 8c).

[46] However, we can understand the spatial distribution of $\Delta\Delta C_{diseq}(t)$ and its relation to the flux of anthropogenic CO_2 by restating the bulk formula for the exchange of CO_2 across the air-sea interface in terms of the anthropogenic perturbations to oceanic and atmospheric pCO_2:

$$F_{ant}(t) = k_{ex}\left(pCO_{2atm}^{ant}(t) - pCO_{2oc}^{ant}(t)\right), \tag{3}$$

where k_{ex} is the gas exchange coefficient, $pCO_{2atm}^{ant}(t)$ is the anthropogenic perturbation in atmospheric pCO_2 (i.e., $pCO_{2,\ atm}(t)$-$pCO_{2,atm}(t_0)$), and $pCO_{2oc}^{ant}(t)$ is the equivalent change in oceanic pCO_2. Since changes in oceanic pCO_2 are related to changes in surface ocean DIC by the buffer factor,

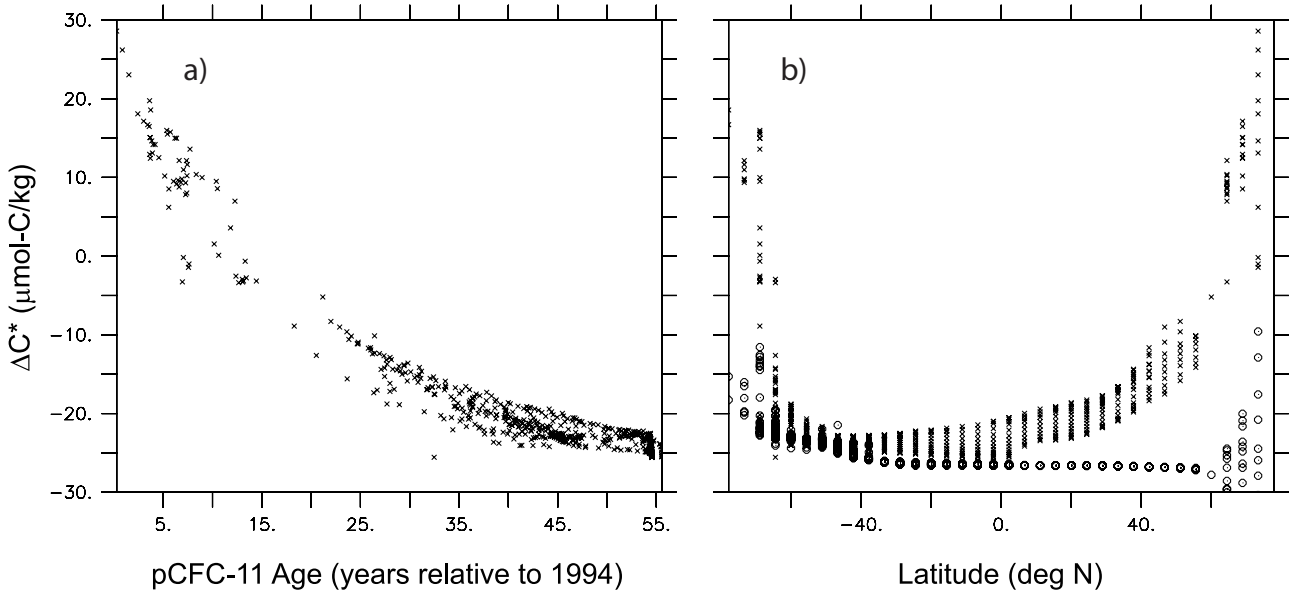

Figure 7. Comparison of ΔC^* versus (a) *p*CFC ventilation age and (b) latitude on the $\sigma 2 = 37.02$ Atlantic isopycnal. In both panels, the crosses indicate the 1994 ΔC^*. In Figure 7b, open circles indicate the preindustrial ΔC^*. Unit is μmole-C kg^{-1}.

γ_{DIC} [*Takahashi et al.*, 1981], we can rewrite air-sea pCO_2 differences in terms of air-sea DIC disequilibria (i.e., $\Delta C_{diseq} = \alpha/\gamma_{DIC}$ ($pCO_{2,atm} - pCO_{2,oc}$), where α is the ratio of surface ocean mean DIC to pCO_2. Thus we can reformulate equation (3) in terms of $\Delta\Delta C_{diseq}(t) = \Delta C_{diseq}(t)$-$\Delta C_{diseq}(t_0)$,

$$F_{ant}(t) = k_{ex}\frac{\gamma_{DIC}}{\alpha}\Delta\Delta C_{diseq}(t), \tag{4}$$

[47] For a given anthropogenic CO_2 flux, the air-sea disequilibrium is thus determined by the product of k_{ex} and γ_{DIC}, which are both generally low in the tropics and high in the Southern Ocean. Therefore, to maintain a relatively uniform $F_{ant}(t)$, $\Delta\Delta C_{diseq}(t)$ has to be high in the tropics and low in high-latitudes (Figure 8c). This distribution of $\Delta\Delta C_{diseq}(t)$ works to the advantage of the ΔC^* method, because most isopycnal surfaces are ventilated in the middle and high latitudes, where the $\Delta\Delta C_{diseq}(t)$ is close to the global average or smaller. Since the air-sea CO_2 disequilibrium becomes larger with time, the resulting positive bias in the estimated C_{ant} also grows with time (Figure 2).

[48] A comparison of the positive biases in Figures 4 and 5 indicates that the change in air-sea disequilibrium can explain a substantial part of the bias in very young waters but fails to explain the relatively large bias in intermediate-aged waters, where the *p*CFC-derived ventilation ages are problematic. This age bias manifests in the nonlinear realm of Figure 3 and the bias magnitude depends on how much old waters are involved in mixing. The OGCM that we employed has relatively low explicit isopycnal and diapycnal mixing, but its coarse resolution likely causes a significant amount of numerical diffusion, which would worsen the pCFC age bias problem. *Hall et al.* [2002] show with a box model that this age bias causes on average a 29% positive bias in the estimated C_{ant}. Their number is not applicable directly to our case, because they essentially used ΔC^*_t everywhere to estimate the air-sea CO_2 disequilibrium, while we use this quantity just for the upper isopycnal surfaces. However, on the "shallow" isopycnal surface $\sigma_\theta = 24.6$ in the Indian Ocean (Figure 5d), we do indeed see positive biases of this magnitude that increase strongly with decreasing C_{ant}.

[49] In summary, the superposition of the error structures of the disequilibrium (i.e., error increases with time) and the mixing (i.e., error decreases with time) tend to result in a relatively uniform positive bias in C_{ant} in relatively younger waters (Figure 4d). The magnitude of these biases is roughly between 10% and 30%. An inspection of the C_{ant} bias on the Pacific "mid-depth" isopycnal surface (Figure 4d) shows that these two sources of bias can explain a substantial amount of the total bias. The exception is in waters with intermediate values of C_{ant} that are located in the interior of the isopycnal surface, where we suspect that errors in the OMP analysis become large.

[50] The OMP analysis is often an underconstrained inverse problem. Also, the identification of end-member water types and their properties is somewhat subjective. We examine the effect of the OMP analysis on the ΔC^* method in two ways. The first is to compare the "true" and OMP-predicted ΔC^* for the preindustrial period, when there were no confounding factors such as anthropogenic carbon and the temporal change in air-sea CO_2 disequilibrium. Assuming that the biological correction ΔDIC_{bio} is accurate, the preindustrial ΔC^* is a truly conservative tracer. Therefore, if our OMP results are correct, we should be able to reconstruct the preindustrial ΔC^* distribution using the water type mixing ratios determined by the OMP analysis and their end-member values chosen in exactly the same manner

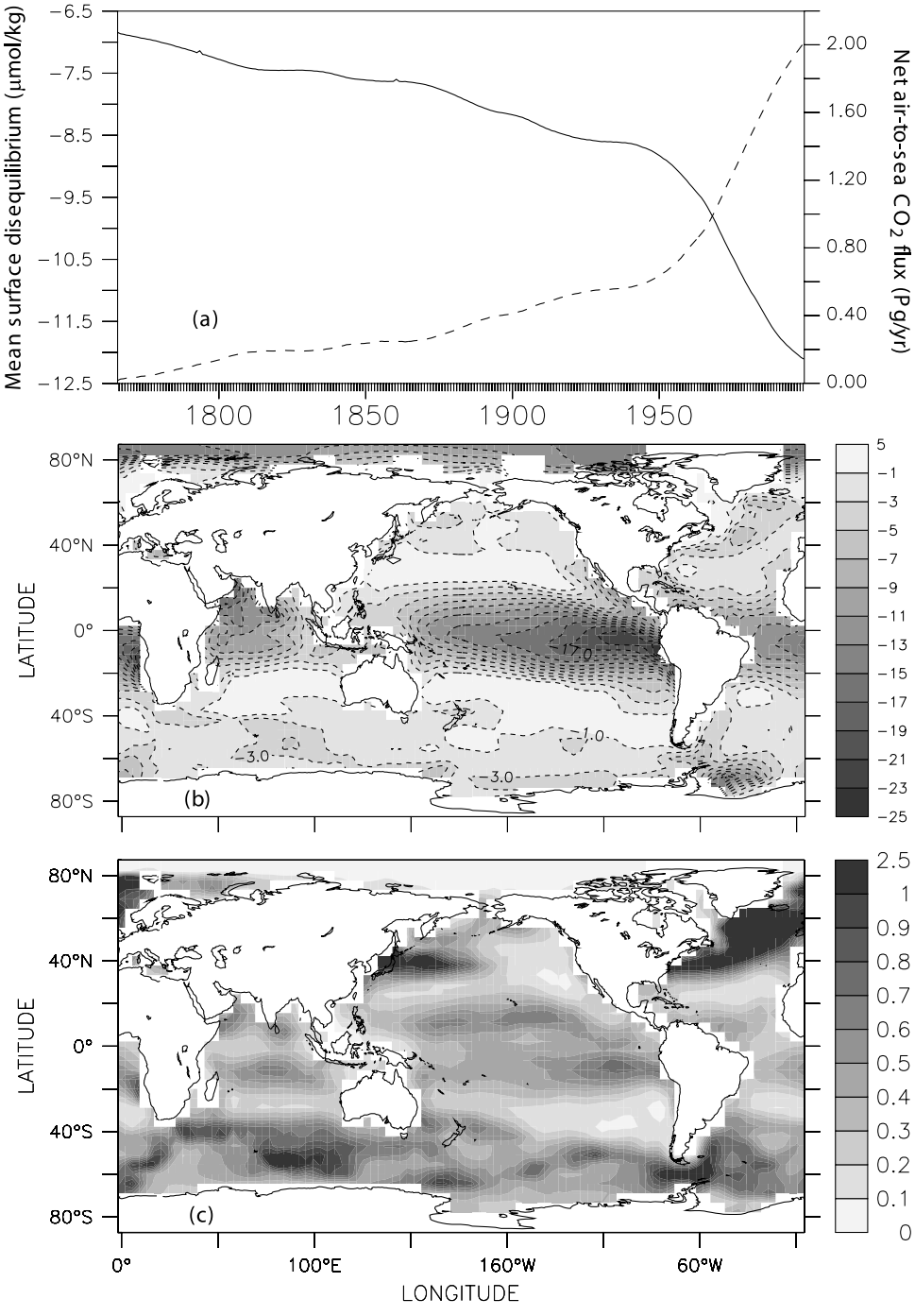

Figure 8. Time evolution of the air-sea CO_2 surface disequilibrium in the model. (a) Globally averaged surface disequilibrium (μmol-C kg^{-1}) and net air-to-sea CO_2 flux (Pg-C yr^{-1}). The disequilibrium represents the difference between model-simulated, surface DIC concentrations and theoretical equilibrium concentrations calculated using the observed atmospheric pCO_2 and simulated surface temperatures, salinities, and alkalinity. (b) Global map of the change in the air-sea CO_2 disequilibrium ($\Delta\Delta C_{diseq}$ in Figure 2, μmol-C kg^{-1}) between 1994 and 1765. (c) Global map of the air-sea flux of anthropogenic CO_2 in mol-C m^{-2} yr^{-1} for 1994.

as ΔC_t^* to quantify the air-sea CO_2 disequilibrium. Our analysis for the Pacific isopycnal $\sigma_\theta = 26.8$ shows that the OMP-derived preindustrial ΔC^* is generally within a few μmol-C kg^{-1} of the target distribution (auxiliary material). An exception is in the northwest Pacific, where there is a strong gradient in the fraction of the locally ventilated water type and the error there is as large as 10 μmol-C kg^{-1} (auxiliary material). The strong gradient appears to be an

artifact of the OMP analysis, because such as feature is not present in the true preindustrial ΔC^* distribution.

[51] The second way to assess the OMP method is to compare the C_{ant} obtained using the OMP solutions and that obtained using dye tracers. As described in the auxiliary material, the dye tracers are released from a number of predefined surface regions and allow exact determination of the fractional contributions of all source water regions to a given water parcel. The particular dye tracers that we use here are from the same circulation model that we employed in this study and were released from 36 surface regions (14 in the Atlantic; 7 in the Indian; and 15 in the Pacific) defined by *Gloor et al.* [2001]. A comparison of the C_{ant} from the Pacific "mid-depth" isopycnal $\sigma_\theta = 26.8$ estimated using the OMP and dye tracer results suggests that the OMP analysis, given the limitation in the number of water types that can be identified and solved, does a reasonable job of unmixing water types (see auxiliary material). We note also that the Pacific isopycnal examined here with four end-member water types is one of the more difficult isopycnal surfaces to deal with. In comparison, most isopycnal surfaces in the Atlantic and Indian oceans have fewer end-members.

[52] We can attribute yet another cause to the positive bias near southern outcrop region of the "deep" Atlantic isopycnal $\sigma_2 = 37.02$ (Figure 6c). The cause is that the ΔC_{diseq} estimated from data between 40°S and 20°N is not representative for the entire isopycnal but is more so for the northern end-member (i.e., NADW). This explains why we do not see the same positive bias in the northern outcrop region. Also, the meridional distribution of preindustrial ΔC^* on this surface indicates two sources of water, and the southern end-member ΔC_{diseq} is about 8 μmol kg^{-1} more positive than the northern end-member (Figure 7b). In addition, there are two other complications in the far south. One is that convective adjustment events occur frequently there in the model, even though the ΔC^* method assumes that mixing occurs primarily along isopycnal surface. The second complication is we used annual mean synthetic data, which presumably include data poleward of wintertime outcrop regions that actually contribute little to the isopycnal.

[53] We suggest that other possible sources of error in the ΔC^* method do not lead to a bias (i.e., a particular direction in the error) or are minor in magnitude. These include using PO_4^0 to account for denitrification and using *PO* to predict ALK^0 (Table 1, auxiliary material).

5.2. Improving the Accuracy of the ΔC^* Method

[54] Here we make two suggestions to improve the accuracy of the ΔC^* method by attempting to account for the temporal change of the air-sea CO_2 disequilibrium and the pCFC ventilation age bias due to mixing. Because the change in the disequilibrium with time, $\Delta\Delta C_{diseq}(t)$, scales with the uptake of anthropogenic CO_2 (Figure 8), it can be expressed as being proportional to the concentration of the estimated (i.e., uncorrected) C_{ant},

$$\Delta\Delta C_{diseq}(t) \approx \frac{\beta}{k_{ex}} C_{ant}^{uncorr}(t). \quad (5)$$

[55] The proportionality factor is given by the ratio of a constant β and the air-sea gas exchange coefficient, k_{ex}. Equation (5) is applicable in the upper ocean, where ΔC_t^* is used to estimate the air-sea CO_2 disequilibrium. A full derivation is given in the auxiliary material; our task here is basically to determine β. For this, we make use of a notion that the flux of anthropogenic CO_2, F_{ant}(t), scales approximately linearly with the atmospheric pCO_2 perturbation [*Gloor et al.*, 2003] (S. E. Mikaloff-Fletcher et al., Robust estimates of anthropogenic carbon uptake, transport, and storage by the ocean, submitted to *Global Biogeochemical Cycles*, 2005) (hereinafter referred to as Mikaloff-Fletcher et al., submitted manuscript, 2005),

$$F_{ant}(t) = \beta \cdot pCO_{2\,atm}^{ant}(t). \quad (6)$$

[56] The factor β can be estimated from the constraint that the global uptake flux of anthropogenic CO_2 integrated over the industrial period must equal the total inventory of anthropogenic CO_2 in the ocean. As shown in the auxiliary material, the integral constraint gives for β a value 0.0065 ± 0.0012 mol m^{-2} yr^{-1} μatm^{-1}. The globally averaged k_{ex} for CO_2 as determined by *Broecker et al.* [1985] is about 0.065 ± 0.015 mol m^{-2} yr^{-1} μatm^{-1}. Together they give for the ratio of β/k_{ex} a value of 0.10 ± 0.03. Our analysis thus suggests that we need to apply a roughly 10% downward correction to all C_{ant} estimates that have been made using C_t^* to quantify the air-sea disequilibrium. This correction should hold for much of the twentieth century, during which the flux of anthropogenic CO_2 is expected to have been proportional to the atmospheric CO_2 perturbation. Also, estimates of β/k_{ex} can be determined for different regions by applying the integral constraint to individual isopycnals in order to obtain regional β and by determining the corresponding regional k_{ex}. Accounting for regional differences should improve the global estimate of β/k_{ex} and thus provide a correction for the positive bias associated with a change in the air-sea CO_2 disequilibrium over time.

[57] The second improvement to the ΔC^* method aims to account for the bias in the ventilation age derived from *p*CFC. Following *Hall et al.* [2004], we suggest using an age spectrum or transit time distribution rather than a single age to estimate the equilibrium DIC concentration. In this case, $DIC_{eq}(t)$ would be computed as a weighted average of the equilibrium DIC concentration for all times, with the weights determined by the transit time distribution $G(\xi)$ of this water parcel,

$$DIC_{eq}(t) = \int_0^\infty DIC_{eq}(t_{obs} - \xi) \cdot G(\xi) d\xi, \quad (7)$$

where ξ is time. This method requires the estimation of $G(\xi)$, which is not straightforward [*Hall et al.*, 2002, 2004; *Waugh et al.*, 2003]. One difficulty is that a functional form of G needs to be assumed, and then this function is fit to the available tracer data to constrain its parameters. When only CFCs are used to constrain the function, only the most recent part of the overall transit time distribution can reliably be determined. Despite these drawbacks, as long as the first mode (the mean transit time) is estimated correctly,

this method will be more accurate than the use of a single transit time.

[58] Once G is estimated, one could presumably estimate anthropogenic CO_2 directly, following the method of *Hall et al.* [2002, 2004]. However, we do not necessarily endorse this, because while the uncertainties in G will have a limited influence the ΔC^* method through the estimation of the air-sea CO_2 disequilibrium in only the upper ocean, they will directly and proportionally affect C_{ant} in the method by *Hall et al.* [2002, 2004]. A combination of the age distribution method for estimating $DIC_{eq}(t)$ and the ΔC^* method would bring out the strengths of both methods.

5.3. Impact on Global Inventory

[59] We can quantify the bias of the ΔC^*-derived global C_{ant} inventory, if we assume that the biases we determined on the nine different isopycnal surfaces (three in the three major basins) are reasonably representative of each class of isopycnals in each basin (Table 2). We made a volume census of the model ocean to account for the three volumes corresponding to the three isopycnal classes in each basin (see auxiliary material). According to our calculations, the global biases for the ''shallow'', ''mid-depth'', and ''deep'' isopycnal layers are +5, +7, and −5 Pg-C respectively. The positive bias in the first two layers containing relatively young waters is almost 12 Pg-C but is offset by a negative bias of more than −5 Pg-C in the deep layer. For the whole ocean, the ΔC^* method overestimates anthropogenic carbon by about 7 Pg-C. Since the global inventory of the model simulated, ''true'' anthropogenic carbon in 1994 is just about 100 Pg-C, the whole ocean bias would be approximately +7%.

[60] This overall positive bias obtained in our application of the ΔC^* method to model ''data'' cannot be translated immediately to the real ocean applications however. First, we have not satisfactorily addressed the qualification that the nine isopycnal biases are representative of their respective volume categories. Second, the distributions of density and important biogeochemical species in the two oceans are not identical. Therefore that the ΔC^* method overestimates anthropogenic carbon by about 7% globally (Table 2) needs to be interpreted with some caution.

[61] How does this conclusion compare with that of *Hall et al.* [2004]? They found an Indian Ocean inventory between 13.1 and 18.8 Pg-C for the year 1995 using their transit time distribution method. These are 7% and 35% lower than the ΔC^*-based estimate of *Sabine et al.* [1999]. The two estimates of *Hall et al.* [2004] correspond to different assumptions about how strong mixing is in the ocean relative to advective transport. They suggest that the lower limit corresponding to the higher mixing regime is more realistic. In comparison, our estimated bias of the C_{ant} inventory in the Indian Ocean is +14%. Because our OGMC is relatively coarse and thus has an elevated numerical diffusion, the *p*CFC age mixing bias may be unrealistically large. Therefore, while we agree with *Hall et al.* [2004] that the *Sabine et al.* [1999] estimate needs to be revised downward, the revision is probably no more than 10% and very likely less than the 35% that *Hall et al.* [2004] prefer.

[62] We now return to two of the motivations for conducting this study. The first had to do with the conclusion of *Sabine et al.* [2004b] that the terrestrial biosphere was a net source of CO_2 to the atmosphere during the Anthropocene. Our result would suggest that their inventory of 118 ± 19 Pg-C be reduced by 7% to 110 ± 19 Pg-C. This would also reduce their inferred source strength of the terrestrial biosphere during the Anthropocene from 39 ± 28 Pg-C to 31 ± 28 Pg-C. The statistical significance of their inference is therefore diminished, but it is not contradicted.

[63] The second motivation was that those ocean biogeochemistry models that agreed with observational constraints given by natural ^{14}C and CFCs generally obtain higher C_{ant} inventories than those reconstructed by the ΔC^* method [*Matsumoto et al.*, 2004]. Our results do not provide an answer to the conundrum, as the suggested 7% positive bias in the reconstructed C_{ant} inventory actually accentuates the problem. If we apply a uniform 7% reduction to the C_{ant} inventory, the discrepancy becomes even larger. The resolution of the discrepancy more likely must be sought in the design of the models and their boundary conditions.

6. Conclusions

[64] Our review of the ΔC^* method and its application to synthetic ''data'' confirm that the quantification of the air-sea CO_2 disequilibrium is the most challenging step in the method. In relatively young waters whose disequilibrium is estimated with ΔC_t^*, the method consistently overestimates anthropogenic carbon, because the disequilibrium has increased with time and water mixing biases the *p*CFC age young [*Hall et al.*, 2004]. For older waters whose disequilibrium is estimated with ΔC^*, the method tends to underestimates anthropogenic carbon. The negative bias has to do with the difficulty in identifying appropriate isopycnals for using ΔC^* to estimate the disequilibrium. An additional source of error is the OMP analysis, whose impact on the final estimation of anthropogenic carbon varies strongly from case to case.

[65] Because the OMP analysis can be a source of error, it ought to be used only when necessary. A case in point is the treatment of surface waters in practice. As in our ''shallow'' isopycnals, *Sabine et al.* [2002, 1999] used the ''shortcut'' method, which does not involve the OMP analysis, while *Lee et al.* [2003] used the full ΔC^* method. Although we cannot quantify the extra error owing to the use of the OMP analysis by *Lee et al.* [2003], our results would suggest that the shortcut method is preferable in waters that have sufficient CFC data coverage and ventilation ages less than 30 years.

[66] Globally, we find a +7% bias for the whole ocean, which is within the previously estimated 20% error margin for the ΔC^* method that accounts for mostly random errors and some subjective consideration of systematic errors. We therefore conclude that the ΔC^* method is relatively robust. Also, the +7% bias weakens but does not alter the conclusions drawn from the ΔC^*-derived global inventory of anthropogenic CO_2 [*Sabine et al.*, 2004b]. Nevertheless, local errors in the estimated C_{ant} can be much larger than 7%, particularly in the central portions of the ''mid-depth''

isopycnal surfaces. Such a spatial distribution of error needs to be taken into account when reconstructed C_{ant} is used to derive air-sea fluxes of anthropogenic CO_2 (Mikaloff-Fletcher et al., submitted manuscript, 2005) or employed to evaluate model results [*Orr et al.*, 2001]. We have proposed two improvements to the ΔC^* method, which will help reduce the biases in the reconstructed C_{ant}.

[67] In the near future, strong constraints on the oceanic uptake of anthropogenic CO_2 will become available as the CO_2/Climate Variability (CLIVAR) repeat hydrography program will re-sample many sections that were occupied by the WOCE/JGOFS global CO_2 surveys. This will permit a direct evaluation of DIC changes over time, without resorting to the ΔC^* method to extract the small C_{ant} signal from the large natural DIC background. A challenge for the future would be to develop new methods to separate the observed DIC changes into a component directly driven by atmospheric CO_2 changes and a component driven by changes in the natural carbon cycle. The latter can be driven either by internal climate variability or anthropogenic climate change.

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N. Gruber, Institute of Geophysics and Planetary Physics (IGPP), University of California, Los Angeles, CA 90095, USA. (ngruber@igpp.ucla.edu)

K. Matsumoto, Department of Geology and Geophysics, University of Minnesota, 310 Pillsbury Drive SE, Minneapolis, MN 55455, USA. (katsumi@umn.edu)