

# An improved method for detecting anthropogenic CO<sub>2</sub> in the oceans

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**Abstract.** An improved method has been developed for the separation of the anthropogenic CO<sub>2</sub> from the large natural background variability of dissolved inorganic carbon ( $C$ ) in the ocean. This technique employs a new quasi-conservative carbon tracer  $\Delta C^*$ , which reflects the uptake of anthropogenic CO<sub>2</sub> and the air-sea disequilibrium when a water parcel loses contact with the atmosphere. The air-sea disequilibrium component can be discriminated from the anthropogenic signal using either information about the water age or the distribution of  $\Delta C^*$  in regions not affected by the anthropogenic transient. This technique has been applied to data from the North Atlantic sampled during the Transient Tracers in the Ocean North Atlantic (TTO NAS) and Tropical Atlantic study (TTO TAS) cruises in 1981-1983. The highest anthropogenic CO<sub>2</sub> concentrations and specific inventories (inventory per square meter) are found in the subtropical convergence zone. In the North Atlantic, anthropogenic CO<sub>2</sub> has already invaded deeply into the interior of the ocean, north of 50°N it has even reached the bottom. Only waters below 3000 m and south of 30°N are not yet affected. We estimate an anthropogenic CO<sub>2</sub> inventory of  $20 \pm 4$  Gt C in the North Atlantic between 10°N and 80°N. The 2.5-dimensional ocean circulation model of *Stocker et al.* [1994] and the three-dimensional ocean general circulation biogeochemistry model of *Sarmiento et al.* [1995] predict anthropogenic CO<sub>2</sub> inventories of 18.7 Gt C and 18.4 Gt C, respectively, in good agreement with the observed inventory. Important differences exist on a more regional scale, associated with known deficiencies of the models.

## Introduction

It is estimated that the ocean has taken up about 30% ( $2.0 \pm 0.8$  Gt C yr<sup>-1</sup>; 1 Gt = 10<sup>15</sup> g) of the  $7.1 \pm 1.1$  Gt yr<sup>-1</sup> released to the atmosphere by human activities in the decade from 1980 to 1989, second in importance only to the accumulation in the atmosphere itself [*Schniel et al.*, 1994]. This estimate is based entirely on indirect methods including observational constraints [*Keeling et al.*, 1989; *Quay et al.*, 1992; *Keeling and Shertz*, 1992; *Enting et al.*, 1995] and ocean models validated mainly with observations of the bomb radio-

carbon distribution. Although we firmly support the magnitude of these model estimates [*Sarmiento et al.*, 1992; *Sarmiento and Sundquist*, 1992; *Siegenthaler and Sarmiento*, 1993; *Siegenthaler and Joos*, 1992; *Stocker et al.*, 1994], it must be acknowledged that neither bomb radiocarbon nor the more recently introduced halogenated carbon tracers are ideal tracers of the CO<sub>2</sub> invasion into the oceans. The characteristic air-sea equilibration time of radiocarbon is about an order of magnitude greater than that of CO<sub>2</sub>, whereas the equilibration time for freons is about 10 times smaller [*Broecker and Peng*, 1982]. Hence the oceanic inventory of bomb radiocarbon is primarily determined by the air-sea exchange rate, whereas the inventory of anthropogenic CO<sub>2</sub> is controlled by the vertical water transport [*Sarmiento et al.*, 1992; *Siegenthaler and Joos*,

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1992; Siegenthaler and Sarmiento, 1993]. Moreover, the temporal evolution of the bomb radiocarbon and freon input into the ocean are very different from that of anthropogenic CO<sub>2</sub>. Bomb radiocarbon has been injected in a pulse like manner into the stratosphere in the 1960s with subsequent redistribution into the other carbon reservoirs. The freons, although slowly being stabilized because of their banning, show an increase over time similar to CO<sub>2</sub> but with a much smaller characteristic timescale of about 10 years compared with about 30 to 40 years for anthropogenic CO<sub>2</sub>. Until such a time as we are able to pin down the anthropogenic invasion by direct observation, there will always be room for challenges to our estimates of the ocean sink, such as the study of Tans *et al.* [1990] claiming that the oceanic sink for 1980 to 1989 was only 0.3 to 0.8 Gt C yr<sup>-1</sup>.

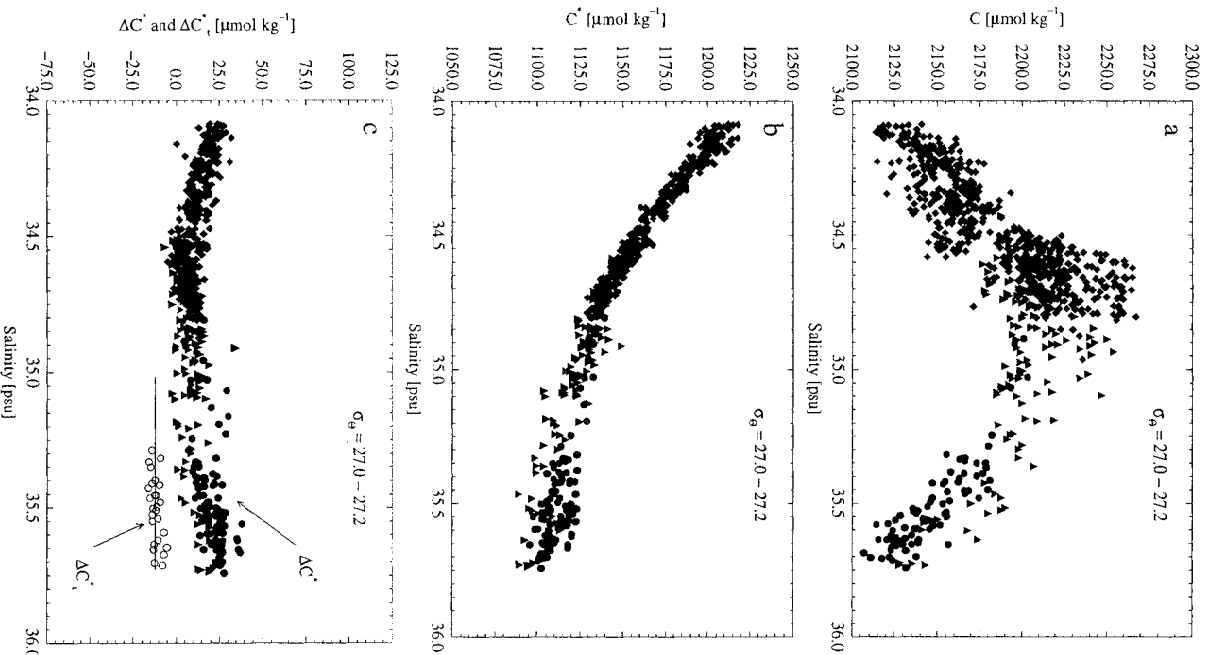
Direct determination of the uptake of anthropogenic CO<sub>2</sub> by the oceans can be done following two different strategies (see Wallace [1995] for review). One way is by repeated surveys of the carbon system in the ocean that would reveal the increase in concentration over time. However, large variability of the carbon occurs on all timescales because of ocean circulation and seasonal changes in biology and temperature. This variability is comparable in magnitude to the amount of anthropogenic CO<sub>2</sub> and thus obscures the temporal trend of that signal. Furthermore, the high-frequency resampling that is required to get around this problem is difficult to achieve on a large scale. These problems would be largely overcome following the second strategy where a direct estimate of the anthropogenic invasion is attempted. Brewer [1978] and Chen and Millero [1979] were the first to point out that the anthropogenic CO<sub>2</sub> in the ocean interior can be estimated by correcting the measured *C* in a water sample for the changes incurred due to the remineralization of organic matter and the dissolution of carbonates since it lost contact with the surface and by subtracting the preformed preindustrial *C*. Variations of this approach have been pursued by several investigators over the years with varying details [Chen and Pytkowicz, 1979; Chen, 1982; Chen, 1993; Poisson and Chen, 1987; Chen *et al.*, 1990; Chen *et al.*, 1995; Goyet and Brewer, 1993; Tsunogai *et al.*, 1993]. However, the Brewer and Chen/Millero approach has not found general acceptance, since the uncertainties associated with the estimates were regarded as too large [Shiller, 1981; Shiller, 1982; Broecker *et al.*, 1985a]. The main points under discussion are the role of mixing of different water types with poorly known initial concentrations, which can lead to nonlinear effects, the difficulty of choosing appropriate preindustrial end-member water types [Shiller, 1981], and the large uncertainties in the assumptions relating to the constant stoichiometric ratios and the use of the apparent oxygen utilization (AOU) [Broecker *et al.*, 1985a] for determining the contribution of the remineralization of organic matter.

In this paper, we describe a new technique that eliminates the nonlinear effects due to mixing and which determines the preindustrial *C* of end-member water types by extrapolation from the distribution of properties in the interior of the ocean. We use water age estimates obtained by tracers to correct the end-member *C* distribution back to preindustrial times in areas where all interior waters are already contaminated by anthropogenic CO<sub>2</sub>. We demonstrate that the contribution of other problems to the final estimates of anthropogenic CO<sub>2</sub> are relatively small (within twice the error of the measurements). The technique is applied to the North Atlantic, where Transient Tracers in the Ocean (TTO) observations of good quality are available. The greatly improved observations presently being obtained by the Joint Global Ocean Flux study (JGOFS) program on World Ocean Circulation Experiment (WOCE) hydrographic sections will soon provide an outstanding opportunity to extend this analysis to the world ocean.

The paper is organized as follows: In the first section we present the new technique employed to separate the anthropogenic CO<sub>2</sub> from the natural background variability. We then describe briefly the data employed in our study and provide an analysis of the error in our estimate of anthropogenic CO<sub>2</sub>. Afterward, the results are presented and compared with predictions of two ocean models of different complexity.

## Methods

The dissolved inorganic carbon (*C*) distribution in the ocean is controlled by air-sea gas exchange including the uptake of anthropogenic CO<sub>2</sub> (solubility pump), the biological processes of photosynthesis, respiration, and remineralization (soft-tissue pump), and the formation and dissolution of carbonate particles (carbonate pump) [Volk and Hoffert, 1985]. In order to directly quantify the anthropogenic CO<sub>2</sub> from ocean carbon data, a careful technique that accounts for each of these processes must be established. We begin this section with a qualitative description of the approach we follow, using as an example the *C* data on the sigma theta ( $\sigma_\theta$ ) 27.0–27.2 surface in the Antarctic Intermediate Water of the Atlantic Ocean. Figure 1a shows the *C* distribution on this surface plotted versus salinity. The low salinity waters on the left of the diagram originate in the southern hemisphere, whereas the high salinity waters on the right originate in the northern hemisphere. The dominant feature of the data in Figure 1a is the large increase in *C* concentration in the interior regions due to the influence of the soft-tissue pump and the carbonate pump. We can eliminate the soft tissue contribution by using as an indicator the oxygen concentration; since for each carbon atom added to the deep water because of the remineralization of organic matter, a proportional amount of oxygen is used. The carbonate pump contri-



**Figure 1.** (a) Plot of dissolved inorganic carbon ( $C$ ) versus salinity in the  $\sigma_\theta$  interval 27.0–27.2 in the Atlantic Ocean (Antarctic Intermediate Water). Diamonds denote samples from the South Atlantic Ventilation Experiment (SAVF) cruises, triangles denote samples from the Transient Tracer in the Oceans (TTO) Tropical Atlantic Study (TAS) cruises and circles denote samples from the TTO North Atlantic Study (NAS) cruises. Remineralization of  $C$  in the interior of the ocean causes the upward bow. (b) Plot of the conservative tracer  $C^*$  versus salinity in the same  $\sigma_\theta$  interval. The observations should fall on a straight line, since the internal sources and sinks have been removed. Invasion of anthropogenic CO<sub>2</sub>, however, has caused increasing  $C^*$  values near the outcrops. (c) Plot of  $\Delta C^*$  and  $\Delta C_t^*$  versus salinity in the same  $\sigma_\theta$  interval. The amount of anthropogenic CO<sub>2</sub> can be determined by the difference between  $\Delta C^*$  and  $\Delta C_t^*$ .

bution is eliminated, using as an indicator the alkalinity distribution corrected for nitrate cycling. These corrections yield the new tracer  $C^*$  which is a composite of the preformed oxygen, alkalinity, and preindustrial  $C$  concentrations, plus the anthropogenic CO<sub>2</sub> invasion (Figure 1b).

The dominant feature of the  $C^*$  distribution is a higher  $C^*$  concentration in the southern hemisphere than in the northern hemisphere. The north-south difference of over 100  $\mu\text{mol kg}^{-1}$  is due mainly to the effect of variations in surface salinity and temperature on the solubility of oxygen, with the colder and less salty waters of the southern hemisphere having a greater solubility. We can eliminate most of this trend by correcting  $C^*$  for the preformed concentrations using oxygen saturation concentration, surface alkalinity observations, and the preindustrial equilibrium  $C$  concentration as a first estimate of preindustrial preformed  $C$ . This defines a new tracer  $\Delta C^*$  (Figure 1c) that reflects the uptake of anthropogenic CO<sub>2</sub> and the air-sea disequilibrium at the time the water last contact with the atmosphere plus any residual effects due to our choice of oxygen and alkalinity end-members, as well as data and parameter uncertainties. If there were no anthropogenic CO<sub>2</sub> invasion, these data would all fall on a straight line between the southern hemisphere end-member disequilibrium and the northern end-member disequilibrium. One can see an indication of the anthropogenic invasion in the upward trend of  $\Delta C^*$  as one moves from the interior to the boundaries at either end.

The final task we must achieve in order to identify the anthropogenic CO<sub>2</sub> is to eliminate the air-sea disequilibrium and other residual effects. We make here the assumption that the ocean operates in a steady state and that the CO<sub>2</sub> air-sea disequilibrium has not changed over time. On deeper density surfaces one can use the interior  $\Delta C^*$  distribution extrapolated to the surface in order to estimate the disequilibrium and residual effects. However, the  $\sigma_\theta$  27.0–27.2 surface has anthropogenic CO<sub>2</sub> at all depths. We therefore use tritium helium-3 ages (available only for the northern hemisphere) to estimate a new tracer  $\Delta C_t^*$ , calculated relative to the actual atmospheric CO<sub>2</sub> at the time the water parcel left the surface. This gives the lower set of data points at higher salinities in Figure 1c, which show an effective disequilibrium of about  $-12 \mu\text{mol kg}^{-1}$ . The difference between  $\Delta C_t^*$  and  $\Delta C^*$  is the portion of the original  $C$  tracer that can be attributed to the anthropogenic invasion of CO<sub>2</sub>. We now describe in more detail the procedures we follow and the assumptions we make in each step of the process that lead to the final analysis in Figure 1. We will also provide an estimate of uncertainty.

### Definition of $C^*$

In the interior of the ocean, away from the surface euphotic layer, the cycling of  $C$  is controlled by the remineralization of organic matter and the dissolution of solid calcium carbonates. The latter represents also the main controlling process for alkalinity ( $Alk$ ).  $Alk$  is also affected by the soft-tissue pump due to a proton flux associated with the redox reactions between reduced organic nitrogen and nitrate [Brewer *et al.*, 1975]. The magnitude of this proton flux has been called into question by *Shiller and Gieskes* [1980] and *Shiller* [1981] but seems to be well established today [Broecker and Peng, 1982; *Goyet and Brewer*, 1993]. By contrast, the biogeochemical cycling of oxygen is entirely governed by the soft-tissue pump. The tracer continuity equation for  $C$ ,  $Alk$ , and  $O_2$  in the interior of the ocean can therefore be written as

$$\Gamma(C) = J_{\text{soft}}(C) + J_{\text{carb}}(C), \quad (1)$$

$$\Gamma(Alk) = J_{\text{soft}}(Alk) + J_{\text{carb}}(Alk), \quad (2)$$

$$\Gamma(O_2) = J_{\text{soft}}(O_2), \quad (3)$$

where  $J_{\text{soft}}$  denotes the source minus sink term due to the remineralization of organic matter and  $J_{\text{carb}}$  denotes the source minus sink term due to the dissolution of solid calcium carbonates. The operator  $\Gamma$  represents the transport and time rate of change:

$$\Gamma(T) = \frac{\partial T}{\partial t} + \vec{n} \cdot \nabla T - \nabla \cdot (D \cdot \nabla T), \quad (4)$$

where  $T$  represents any tracer concentration,  $\nabla$  represents the gradient operator in three – dimensions,  $\vec{n}$  represents the velocity field, and  $D$  represents the eddy diffusivity tensor.

We assume that the soft-tissue pump influences  $C$  and  $O_2$  with a constant stoichiometric ratio ( $r_{C:O_2}$ ) and that the carbonate pump changes alkalinity twice as much as it changes  $C$ . The proton flux during the processes of photosynthesis, respiration, and remineralization is assumed to be proportional to the change in the nitrate concentration, which in turn is proportional to the change in  $O_2$  through the constant stoichiometric ratio  $r_{N:O_2}$  thus

$$J_{\text{soft}}(C) = r_{C:O_2} J_{\text{soft}}(O_2), \quad (5)$$

$$J_{\text{carb}}(C) = \frac{1}{2} J_{\text{carb}}(Alk), \quad (6)$$

$$J_{\text{soft}}(Alk) = -J_{\text{soft}}(NO_3) = -r_{N:O_2} J_{\text{soft}}(O_2). \quad (7)$$

Substituting these relationships (equations (5) – (7)) into (1) and (2) gives

$$\Gamma(C) = r_{C:O_2} J_{\text{soft}}(O_2) + \frac{1}{2} J_{\text{carb}}(Alk), \quad (8)$$

$$\Gamma(Alk) = -r_{N:O_2} J_{\text{soft}}(O_2) + J_{\text{carb}}(Alk). \quad (9)$$

We can eliminate the  $J_{\text{soft}}$  and  $J_{\text{carb}}$  terms from the  $C$

equation (8) by subtracting  $r_{C:O_2} \Gamma(O_2)$  and  $\frac{1}{2} \Gamma(Alk) + r_{N:O_2} \Gamma(O_2)$  from it:

$$\Gamma(C) - r_{C:O_2} \Gamma(O_2) - \frac{1}{2} (\Gamma(Alk) + r_{N:O_2} \Gamma(O_2)) = 0. \quad (10)$$

Since we assumed constant stoichiometric ratios ( $r_{C:O_2}$  and  $r_{N:O_2}$ , respectively), the  $C$ ,  $Alk$ , and  $O_2$  equations are linear, and therefore the transport and time rate of change operators  $\Gamma$  can be combined to  $\Gamma(C - r_{C:O_2} O_2 - \frac{1}{2} (Alk + r_{N:O_2} O_2))$ . This permits us to define a new tracer  $C^*$ ,

$$C^* = C - r_{C:O_2} O_2 - \frac{1}{2} (Alk + r_{N:O_2} O_2), \quad (11)$$

with conservative properties

$$\Gamma(C^*) = 0. \quad (12)$$

The distribution of  $C^*$  is strongly influenced by the preformed concentrations of  $C$ ,  $Alk$ , and  $O_2$  and reflects therefore, similar to Broecker's conservative water mass tracer  $PO$  [Broecker, 1974], mostly differences in the origin of the different water masses (see Figure 1).

### Definition of $\Delta C^*$

We can eliminate most of the influence of the origins of the different water masses by only considering deviations of  $C^*$  from its preindustrial preformed value  $C^{*0}$  and denoting this new quantity by  $\Delta C^*$ :

$$\Delta C^* = C^* - C^{*0}, \quad (13)$$

$$C^{*0} = C^0 - r_{C:O_2} O_2^0 - \frac{1}{2} (Alk^0 + r_{N:O_2} O_2^0), \quad (14)$$

where the superscript zero denotes preformed concentrations. We estimate the preindustrial preformed concentration of  $C$  ( $C^0$ ) by the equilibrium  $C$  concentration ( $C_{\text{eq}}$ ) for a preindustrial atmospheric  $CO_2$  fugacity of 280  $\mu\text{atm}$  [Neftel *et al.*, 1994] thereby neglecting for the moment the fact that surface  $C$  is seldom in equilibrium with the atmospheric  $CO_2$  fugacity. Preformed  $O_2$  ( $O_2^0$ ) is estimated by its saturation concentration  $O_2^{\text{sat}}$  and preformed  $Alk$  ( $Alk^0$ ) by a multiple linear regression (see appendix A). We wish to maintain the conservative properties of  $\Delta C^*$ . This requires linearizing the  $C_{\text{eq}}$  and  $O_2^{\text{sat}}$  equations. Appendix A shows how we linearize  $C_{\text{eq}}$ . For  $O_2^{\text{sat}}$  we assume that the nonlinear effects on a given density surface are negligible compared to other uncertainties. We thus have

$$\begin{aligned} \Delta C^* = C - C_{\text{eq}}(S, T, Alk^0) \Big|_{r_{CO_2} = 280 \mu\text{atm}} \\ - r_{C:O_2} (O_2 - O_2^{\text{sat}}) \\ - \frac{1}{2} (Alk - Alk^0 + r_{N:O_2} (O_2 - O_2^{\text{sat}})), \end{aligned} \quad (15)$$

$$\Gamma(\Delta C^*) \approx 0. \quad (16)$$

The variability of  $\Delta C^*$  reflects then only the ocean uptake of anthropogenic CO<sub>2</sub> and the CO<sub>2</sub> air-sea disequilibrium at the time the water lost contact with the atmosphere plus any residual effects due to our choice of end-members and data uncertainties. The determination of the preformed values in (15) and its uncertainties are described in detail in appendix A.

We use the stoichiometric ratios determined by *Anderson and Sarmiento* [1994] throughout our study. By using a nonlinear inverse method on neutral surfaces, they found that these ratios are  $P : N : C_{org} : O_2 = 1 : 16 \pm 1 : 117 \pm 14 : -170 \pm 10$  and approximately independent of depth and ocean basin. These stoichiometric ratios have been the subject of an intense scientific debate over recent years, and several modifications have been proposed to the “traditional”  $P : N : C_{org} : O_2$  stoichiometric ratios of *Redfield et al.* [1963] (1 : 16 : 103 : -138). *Takubashi et al.* [1985a], *Broecker et al.* [1985b], and *Peng and Broecker* [1987] concluded in their studies that the  $O_2 : P$  ratio is significantly higher at -172 and -175, respectively, and that this ratio is nearly constant at all depths throughout the entire ocean. In conflict with this, *Minster and Boudahdid* [1987] and *Boudahdid and Minster* [1989] suggested that the  $O_2 : P$  ratio, while near -172 in the thermocline, decreases in depth to approximately -115 in all oceans. The study of *Anderson and Sarmiento* [1994], which encompasses all previous ones with regard to data coverage and treatment of the mixing problem, generally confirms the results of *Takubashi et al.* [1985a] and *Broecker et al.* [1985b]. We therefore consider the proposed ratios of *Anderson and Sarmiento* [1994] to be the best ones currently available.

### Calculating the Anthropogenic CO<sub>2</sub>

Since the variability of  $\Delta C^*$  is due to the uptake of anthropogenic CO<sub>2</sub> and the air-sea disequilibrium of CO<sub>2</sub> when a water parcel was last in contact with the atmosphere plus any residual effects of our choice of oxygen and alkalinity end-members, we must eliminate the total “effective” disequilibrium effect from  $\Delta C^*$ , to obtain a purely anthropogenic signal. The assumptions are made that the ocean has been operating in a steady state, that the effective disequilibrium has stayed more or less constant within the outcrop region of a particular isopycnal surface, and that the water transport is predominantly along isopycnal surfaces. If these assumptions are correct, the concentration of  $\Delta C^*$  on a isopycnal surface should reveal the history of the CO<sub>2</sub> uptake (see Figure 1). We will determine the effective air-sea equilibrium for the outcrops of 28 isopycnal surfaces in the North Atlantic and then use a smoothing spline to represent this disequilibrium as a function of the density of the seawater,  $\Delta C_{dis}^{eq}(\rho)$ .

The amount of anthropogenic CO<sub>2</sub> in the ocean

( $\Delta C_{ant}$ ) can finally be calculated by

$$\Delta C_{ant} = \Delta C^* - \Delta C_{dis}^{eq}(\rho). \quad (17)$$

In the next section we describe in detail how the CO<sub>2</sub> air-sea disequilibrium can be estimated from  $\Delta C^*$  and information about the apparent age of a water parcel.

### Determining the Effective Air-Sea Disequilibrium

We determine the effective disequilibrium as a function of the potential density of a water parcel using two different methods.

**$\Delta C^*$  method.** In the first method we look at the variability of  $\Delta C^*$  on deep ocean density surfaces in regions far away from the outcrop, where one can safely assume that there is no anthropogenic CO<sub>2</sub> contamination.  $\Delta C^*$  in these uncontaminated regions reflects therefore a mixture of the effective air-sea disequilibria of the different end-member water masses. It turns out, in all the cases we consider in the deep North Atlantic and tropical Atlantic, that  $\Delta C^*$  in the uncontaminated regions does not show a significant trend with amount of southern and northern end-member water mass (determined from  $PO_4$  [*Broecker et al.*, 1991]). We therefore neglect this potential complication and calculate the effective air-sea disequilibrium as if all water has a single end-member water mass,

$$\Delta C_{dis}^{eq} = \overline{\Delta C^*} \Big|_{\sigma=\text{const}}, \quad (18)$$

where  $\overline{\Delta C^*} \Big|_{\sigma=\text{const}}$  represents the mean  $\Delta C^*$  of the isopycnal surface interval in the region without anthropogenic influence.

The  $\Delta C^*$  method does not work, however, for shallow isopycnal surfaces since anthropogenic CO<sub>2</sub> has already affected the entire surface, and therefore no region without anthropogenic CO<sub>2</sub> can be found. It also fails for surfaces in the Greenland and Norwegian Seas (density surfaces greater than  $\sigma_\theta = 27.90$ ) because here anthropogenic CO<sub>2</sub> has also penetrated into the whole water column, as is evident from the presence of bomb tritium [*Schlosser et al.*, 1995]. We therefore use the first method only for all surfaces denser than  $\sigma_2 = 36.95$  (average depth 2000 m) with the exception of the water masses in the Greenland and Norwegian Seas.

**$\Delta C_t^*$  method.** For shallower surfaces and the waters in the Greenland and Norwegian Seas we employ a second method to determine  $\Delta C_{dis}^{eq}$ . If the age of a water parcel is known, the  $C$  concentration in equilibrium with the atmospheric CO<sub>2</sub> for the time when the water parcel left the surface ( $C_{eq}(t)$ ) can be calculated. Subtracting  $C_{eq}(t)$  instead of  $C_{eq}$  in (15) gives  $\Delta C_t^*$ :

$$\begin{aligned} \Delta C_t^* = & C - C_{eq}(S, T, Alk^0, fCO_2(t_{\text{sample}} - \tau)) \\ & - \tau C_{:O_2} (O_2 - O_2^{\text{sat}}) \\ & - \frac{1}{2} (Alk - Alk^0 + \tau N_{:O_2} (O_2 - O_2^{\text{sat}})), \end{aligned} \quad (19)$$

where  $fCO_2(t_{\text{sample}} - \tau)$  denotes the atmospheric CO<sub>2</sub> fugacity at the moment when the water parcel was last in contact with the atmosphere. This date is calculated by subtracting the water age  $\tau$  from the sampling date,  $t_{\text{sample}}$ . This substitution removes the anthropogenic CO<sub>2</sub> signal from  $\Delta C^*$  but does not correct for residual effects due to our choice of oxygen and alkalinity end-members. However, we argue in appendix A that these residual effects should be relatively small. As on deeper surfaces, we find that  $\Delta C_t^*$  is constant within the uncertainty, implying that the different source regions for this water mass have very nearly the same air-sea disequilibrium. The effective air-sea disequilibrium  $\Delta C_{\text{dis}}^*$  eq is thus determined by

$$\Delta C_{\text{dis}}^* \text{ eq} = \overline{\Delta C_t^*} \Big|_{\sigma=\text{const}} \text{ ,} \quad (20)$$

where  $\overline{\Delta C_t^*} \Big|_{\sigma=\text{const}}$  is the mean  $\Delta C_t^*$  on the density surface under consideration.

It should be possible to use any tracer or tracer combination that contains water age information (CFC 11/CFC 12, <sup>228</sup>Ra/<sup>226</sup>Ra and tritium helium-3) to determine  $C_{\text{eq}}(t)$ . We use concurrent tritium (<sup>3</sup>H) and helium-3 (<sup>3</sup>He) measurements to calculate the tritium helium-3 age ( $\tau_{\text{T/He}}$ ) following the method of *Jenkins* [1987]:

$$\tau_{\text{T/He}} = \lambda^{-1} \cdot \ln \left( 1 + \frac{[{}^3\text{He}]}{[{}^3\text{H}]} \right) \text{ ,} \quad (21)$$

where the brackets denote the concentrations in appropriate units (tritium units) and  $\lambda$  is the tritium decay constant ( $1.77 \cdot 10^{-9} \text{ s}^{-1}$ ).

We are able to determine the <sup>3</sup>H-<sup>3</sup>He age and  $\Delta C_t^*$  for the North Atlantic north of 15°N only, since we have tritium and helium observations available only from the transient tracer in the ocean North Atlantic Study (TTO NAS, 1980). These data were obtained by the Woods Hole Oceanographic Institution Helium Isotope Laboratory headed by W. J. Jenkins. The atmospheric CO<sub>2</sub> fugacity at the time the water left the surface ( $t_{\text{sample}} - \tau_{\text{T/He}}$ ) was estimated from a smoothing spline fit through atmospheric CO<sub>2</sub> data obtained from direct observations after 1958 [*Keeling and Whorf*, 1994] and ice-core data before 1958 [*Neftel et al.*, 1994].

The  $\Delta C_t^*$  method to determine the air-sea disequilibrium would also permit a shortcut for determining the anthropogenic CO<sub>2</sub> directly. Replacing the mean  $\Delta C_t^*$  along an isopycnal surface in (20) by the individual  $\Delta C_t^*$  values and inserting the resulting expression for  $\Delta C_{\text{dis}}^*$  eq into (17) for  $\Delta C_{\text{ant}}^*$  yields

$$\Delta C_{\text{ant}} = C_{\text{eq}}(S, T, Alk^0, fCO_2(t_{\text{sample}} - \tau)) - C_{\text{eq}}(S, T, Alk^0) \Big|_{fCO_2 = 280 \mu\text{atm}} \text{ .} \quad (22)$$

Thus all that is necessary to determine anthropogenic CO<sub>2</sub> in the ocean is an exact knowledge of the water

age and measurements of the standard hydrographic parameters, for example, temperature, salinity, phosphate, and oxygen. However, we did not make use of this shortcut for two reasons. First, there are almost an order of magnitude fewer observations available for tritium and helium-3 in comparison to carbon thereby reducing the number of estimates for anthropogenic CO<sub>2</sub> by that amount. Second, the uncertainties with regard to the water age would enter directly into the estimate of anthropogenic CO<sub>2</sub>, without control over whether the assumptions behind this shortcut are reasonable or not.

**Caveats.** Although many of the assumptions we make to determine  $\Delta C_{\text{dis}}^*$  eq are problematic and have large uncertainties (e.g., constant air-sea disequilibrium, etc.), the feasibility of them can be tested with the observational results, and it turns out this test generally confirms the assumptions. However, there are two caveats that need further discussion. The first caveat concerns the assumption of a constant air-sea disequilibrium over time, and the second is related to the estimate of the water age.

Regarding the first major caveat, we must take into consideration that the global mean CO<sub>2</sub> air-sea disequilibrium has not stayed constant, since the ocean is lagging behind the atmospheric anthropogenic CO<sub>2</sub> increase. The global mean anthropogenic air-sea disequilibrium required to sustain the present global anthropogenic CO<sub>2</sub> uptake of about 2 Gt C yr<sup>-1</sup> is of the order of 8  $\mu\text{atm}$  [*Siegenthaler and Sarmiento*, 1993]. Such a  $\Delta fCO_2$  of about 8  $\mu\text{atm}$  corresponds to an air-sea disequilibrium of about 5  $\mu\text{mol kg}^{-1}$  in  $C$ . It should be possible, in principle, to detect this trend in the data and to correct for it. However, the uncertainties in the data and parameters we use give a  $\Delta C^*$  uncertainty of 9  $\mu\text{mol kg}^{-1}$ , which is too large to see this trend.

For the determination of  $\Delta C_t^*$  we must consider that the <sup>3</sup>H-<sup>3</sup>He age is not equal to the true water age. Mixing affects the <sup>3</sup>H-<sup>3</sup>He age in a nonlinear way by making it younger compared to the “true” water age [*Jenkins*, 1987]. *Thiele and Sarmiento* [1990] investigated the difference between the true and the <sup>3</sup>H-<sup>3</sup>He age along isopycnals and found that the difference is strongly influenced by the the water age and by the relative importance of advection and diffusion. For waters younger than a decade the difference is only important if diffusion is the dominant transport process along these isopycnal surfaces. However, for most areas of the ocean, advection is thought to be controlling the transport, and we therefore neglect the difference between the true and the <sup>3</sup>H-<sup>3</sup>He age.

**Isopycnal Surfaces.** We determined  $\Delta C_{\text{dis}}^*$  eq on a total of 28 isopycnal surfaces in the North Atlantic. For the thermocline and the middepth waters we chose more or less the same surfaces as *Kawase and Sarmiento* [1985] and *Kawase and Sarmiento* [1986] and augmented them with additional isopycnal layers near the surface,

Table 1. Potential Density Surfaces Used in This Study

Potential Density Midvalue	Potential Density Interval	Depth, m <sup>a</sup>	Description	Water Masses <sup>b</sup>
<i>σ<sub>θ</sub> Surfaces</i>				
25.30	25.00 - 25.45	50-100	salinity maximum	Subtropical Underwater
25.60	25.45 - 25.75	50-150	oxygen maximum	
25.90	25.75 - 26.05	100-200		
26.20	26.05 - 26.35	150-400		18° Water
26.50	26.35 - 26.65	200-700		Subpolar Mode Water
26.80	26.65 - 26.95	450-900		Antarctic Intermediate
27.10	26.95 - 27.25		salinity minimum	Antarctic Intermediate
27.30	27.25 - 27.35		salinity minimum	
27.40	27.35 - 27.45	700-1050		
<i>σ<sub>2</sub> Surfaces</i>				
36.45	36.40 - 36.50	800 - 1100	salinity minimum	Antarctic Intermediate
36.55	36.50 - 36.60	1100 - 1150	salinity maximum	Mediterranean Outflow
36.65	36.60 - 36.70	1150 - 1200	salinity maximum	Mediterranean Outflow
36.75	36.70 - 36.80	1200 - 1500	salinity maximum (eastern basin)	Mediterranean Outflow
36.85	36.80 - 36.90	1500 - 1600	silica maximum salinity maximum	Labrador Sea, Upper NADW
36.95	36.90 - 36.98	1950 - 2350	oxygen maximum (western basin)	middle NADW, DSOw, ISOW
37.00	36.98 - 37.03	2300 - 2800	oxygen maximum	middle NADW, DSOw, ISOW
37.05	37.03 - 37.08	2950 - 3300		DSOW, ISOW
<i>σ<sub>4</sub> Surfaces</i>				
45.825	45.813 - 45.838	3200 - 3400	oxygen minimum nutrient maximum	
45.850	45.838 - 45.863	3500 - 3800	oxygen maximum	lower NADW
45.875	45.863 - 45.888	3800 - 3900	oxygen maximum nutrient minimum	lower NADW (ISOW, DSOw) (western basin only)
45.900	45.888 - 45.913	4500 - 4700	low salinity	Antarctic Bottom
45.925	45.913 - 45.938	5000 - 5500	low oxygen	(western basin only)
45.950	45.938 - 45.963	5500 - 6000		(western basin only)
<i>σ<sub>θ</sub> Surfaces in the Greenland and Norwegian Seas</i>				
27.92	27.90 - 27.94			
27.96	27.94 - 27.98			
28.00	27.98 - 28.02			
28.04	28.02 - 28.06			
28.08	28.06 - 28.10			

<sup>a</sup>Depth range of the surface south of the steeply sloping region leading to the outcrop.

<sup>b</sup>NADW, North Atlantic Deep Water; LSW, Labrador Sea Water; DSOw, Denmark Strait Overflow Water; ISOW, Iceland-Scotland Overflow Water.

in the deep ocean and in the Greenland and Norwegian Seas. A summary of the chosen surfaces and their characteristics is given in Table 1. For the analysis of  $\Delta C_{dis}^{eq}$  we excluded observations above 100 m depth, since our approach is limited to waters below the eu-

photic layer, which is on average about 50 to 100 m deep. We furthermore removed all stations lying poleward of the wintertime outcrops as determined from the National Oceanic and Atmospheric Administration (NOAA) Atlas [Levitus et al., 1994; Levitus and Boyer,

1994]. To obtain a continuous numerical representation of  $\Delta C_{\text{dis eq}}$  as a function of density,  $\Delta C_{\text{dis eq}}(\rho)$ , a smoothing spline function is applied to the results from the 28 density surfaces.

## Data Considerations

We use  $C$ ,  $Alk$ ,  $O_2$ , and nutrient data from the Geochemical Ocean Section Study (GEOSECS) program (1972–1978) [Bainbridge, 1981a; Broecker *et al.*, 1982; Weiss *et al.*, 1983], the Transient Tracers in the Ocean North Atlantic Study (TTO NAS) program (1981) [PCODF, 1986a; Brewer *et al.*, 1986], the Transient Tracers in the Ocean Tropical Atlantic Study (TTO TAS) program (1982–1983) [PCODF, 1986b] and the South Atlantic Ventilation Experiment (SAVE) program (1987–1989) [ODF, 1992a; ODF, 1992b, Takahashi, personal communication, 1995]. The station locations of the cruises in the Atlantic are shown in Figure 2. We use the revised version of the T<sup>1</sup>TTO NAS  $C$  data, recalculated from  $fCO_2$  and  $Alk$  by Takahashi and Brewer [1986], after a systematic discrepancy was discovered between the original  $C$  data and the measurements of the Carbon Dioxide Research Group (CDRG) at the Scripps Institution of Oceanography [Bradshaw

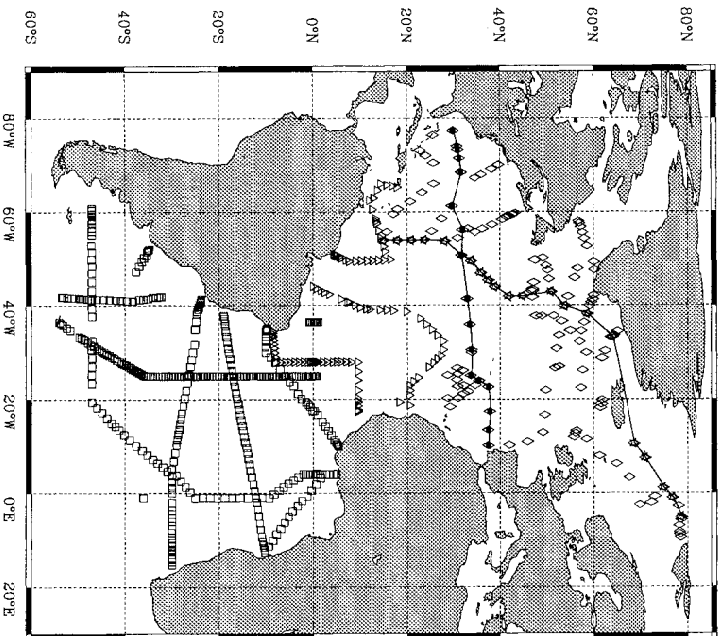
and Brewer, 1988]. The  $C$  and  $Alk$  data have been measured by many different methods and therefore have variable precision and accuracy as discussed in detail in appendix B.

For  $\Delta C^*$  to be a useful conservative tracer and for getting a high quality estimate of the amount of anthropogenic CO<sub>2</sub> in the ocean, it is necessary to insure the internal consistency of the  $C$  and  $Alk$  data sets. This consistency check has already been done for the GEOSECS data set (Broecker *et al.* [1985] and others), and we therefore applied the proposed corrections as summarized by Anderson and Sarmiento [1994] (see appendix B). We investigated the internal consistency of the more modern Atlantic data by looking at deep ocean (> 3500 m)  $C$  and  $Alk$  trends versus temperature in 10° latitude by 10° longitude areas which have been repeatedly sampled by different legs or cruises. Systematic offsets between the different legs and cruises have been found and corrected as described in detail in appendix B. Possible inaccuracies of the Atlantic carbon data were assessed by comparing them with the shore-based  $C$  and  $Alk$  measurements obtained by the Carbon Dioxide Research Group at the Scripps Institution of Oceanography (C.D. Keeling, personal communication, 1994). This comparison showed good agreement within the precision of the measurements (see appendix B).

The data in the Atlantic Ocean have been sampled over a period of 8 years. During this period, atmospheric CO<sub>2</sub> rose from approximately 340  $\mu\text{atm}$  in 1981 to 353  $\mu\text{atm}$  in 1989 [Keeling and Whorf, 1994]. Temporal variability has been assessed by comparing reoccupied and closely revisited stations between the TTO NAS, TTO TAS, and SAVE cruises. This analysis revealed mostly no significant changes in water mass characteristics, although such changes have been reported by Brewer *et al.* [1983], Broecker [1985], and Swift [1984b] for the preceding decade between 1972 and 1982 for the water masses south of Greenland. This variability seems to be restricted to the northern North Atlantic, where we only make use of the T<sup>1</sup>TTO NAS data set. In the overlapping regions of the different cruises, no such changes have been reported. We therefore neglect possible existing temporal variability in our data sets and combine all data as if they were synoptic.

## Error Assessment

Analysis of the variability of  $\Delta C^*$  requires assessment of the errors due to uncertainties in the stoichiometric ratios ( $\sigma_{\tau_{C:O_2}}$  and  $\sigma_{\tau_{N:O_2}}$ ), the determination of preformed  $Alk$  ( $\sigma_{Alk}$ ), the linearized  $C_{\text{eq}}$  ( $\sigma_{C_{\text{eq}}}$ ), the errors during tracer sampling and measurement ( $\sigma_C$ ,  $\sigma_{Alk}$ , and  $\sigma_{O_2}$ ), and the uncertainty due to a possible oxygen disequilibrium between the ocean and the atmosphere



**Figure 2.** Hydrographic station locations of the T<sup>1</sup>TTO North Atlantic Study (T<sup>1</sup>TTO NAS, 1981) (diamonds), TTO Tropical Atlantic Study (TTO TAS, 1982/1983) (triangles), and the South Atlantic Ventilation Experiment (SAVE, 1988/1989) (squares). The tracks of the sections used in later illustrations are shown as lines.



( $\sigma_{O_2^{\text{sat}}}$ ). We assume for the moment that systematic errors are relatively small and partially accounted for by our technique for finding  $\Delta C_{\text{ant}}$ . We neglect the very small errors in temperature and salinity sampling and analysis. We assume that the analytical determinations of the tracers and the stoichiometric ratios are unrelated and that therefore the associated errors are independent and uncorrelated. The error of  $\Delta C^*$  ( $\sigma_{\Delta C^*}$ ) is then given by

$$\begin{aligned} \sigma_{\Delta C^*}^2 = & \left\{ \frac{\partial \Delta C^*}{\partial C} \sigma_C \right\}^2 + \left\{ \frac{\partial \Delta C^*}{\partial C_{\text{eq}}} \sigma_{C_{\text{eq}}} \right\}^2 \\ & + \left\{ \frac{\partial \Delta C^*}{\partial r_{C:O_2}} \sigma_{r_{C:O_2}} \right\}^2 + \left\{ \frac{\partial \Delta C^*}{\partial O_2} \sigma_{O_2} \right\}^2 \\ & + \left\{ \frac{\partial \Delta C^*}{\partial O_2^{\text{sat}}} \sigma_{O_2^{\text{sat}}} \right\}^2 + \left\{ \frac{\partial \Delta C^*}{\partial Alk} \sigma_{Alk} \right\}^2 \\ & + \left\{ \frac{\partial \Delta C^*}{\partial Alk^0} \sigma_{Alk^0} \right\}^2 + \left\{ \frac{\partial \Delta C^*}{\partial r_{N:O_2}} \sigma_{r_{N:O_2}} \right\}^2 \end{aligned} \quad (23)$$

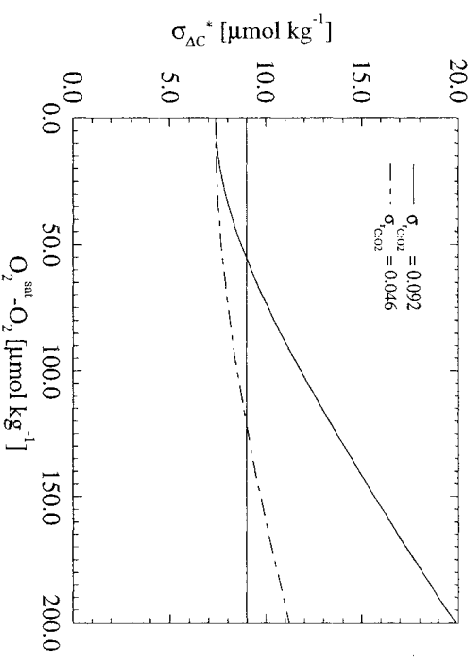
$$\begin{aligned} \sigma_{\Delta C^*}^2 = & \{ \sigma_C \}^2 + \{ -\sigma_{C_{\text{eq}}} \}^2 \\ & + \{ -(O_2 - O_2^{\text{sat}}) \sigma_{r_{C:O_2}} \}^2 \\ & + \{ (-r_{C:O_2} - \frac{1}{2} r_{N:O_2}) \sigma_{O_2} \}^2 \\ & + \left\{ (r_{C:O_2} + \frac{1}{2} r_{N:O_2}) \sigma_{O_2^{\text{sat}}} \right\}^2 \\ & + \left\{ -\frac{1}{2} \sigma_{Alk} \right\}^2 + \left\{ \left( -\frac{\partial C_{\text{eq}}}{\partial Alk} + \frac{1}{2} \right) \sigma_{Alk^0} \right\}^2 \\ & + \left\{ -\frac{1}{2} (O_2 - O_2^{\text{sat}}) \sigma_{r_{N:O_2}} \right\}^2. \end{aligned} \quad (24)$$

The error of  $\Delta C^*$  is therefore dependent on AOU ( $O_2^{\text{sat}} - O_2$ ). Figure 3 shows a plot of  $\sigma_{\Delta C^*}$  versus AOU based on the following error estimates:  $\sigma_C = 5 \mu\text{mol kg}^{-1}$ ;  $\sigma_{C_{\text{eq}}} = 4 \mu\text{mol kg}^{-1}$ ;  $\sigma_{r_{C:O_2}} = 0.092$ ;  $\sigma_{O_2} = 1 \mu\text{mol kg}^{-1}$ ;  $\sigma_{O_2^{\text{sat}}} = 4 \mu\text{mol kg}^{-1}$ ;  $\sigma_{Alk} = 5 \mu\text{eq kg}^{-1}$ ;  $\sigma_{Alk^0} = 11 \mu\text{eq kg}^{-1}$ ; and  $\sigma_{r_{N:O_2}} = 0.0081$ . The estimated uncertainties of the measurements and the performed values are discussed in detail in the appendices. The uncertainties of the stoichiometric ratios,  $\sigma_{r_{C:O_2}}$  and  $\sigma_{r_{N:O_2}}$ , have been determined by error propagation of the uncertainties given by *Anderson and Sarmiento* [1994].

**Table 2.** Relative Error Contribution to  $\Delta C^*$

AOU, $\mu\text{mol kg}^{-1}$	$\sigma_{\Delta C^*}$ , $\mu\text{mol kg}^{-1}$	$\sigma_C$ , %	$\sigma_{C_{\text{eq}}}$ , %	$\sigma_{r_{C:O_2}}$ , %	$\sigma_{O_2}$ , %	$\sigma_{O_2^{\text{sat}}}$ , %	$\sigma_{Alk}$ , %	$\sigma_{Alk^0}$ , %	$\sigma_{r_{N:O_2}}$ , %
0	7.9	40	26	0	0	0	10	23	0
50	9.1	30	19	26	0	0	8	17	0
100	12.1	17	11	58	0	0	4	10	0
150	15.9	9	6	75	0	0	3	6	0
200	20.0	6	4	84	0	0	2	4	0

Error contribution is based on (24) for  $\sigma_C = 5 \mu\text{mol kg}^{-1}$ ;  $\sigma_{C_{\text{eq}}} = 4 \mu\text{mol kg}^{-1}$ ;  $\sigma_{r_{C:O_2}} = 0.092$ ;  $\sigma_{O_2} = 1 \mu\text{mol kg}^{-1}$ ;  $\sigma_{O_2^{\text{sat}}} = 4 \mu\text{mol kg}^{-1}$ ;  $\sigma_{Alk} = 5 \mu\text{eq kg}^{-1}$ ;  $\sigma_{Alk^0} = 11 \mu\text{eq kg}^{-1}$  and  $\sigma_{r_{N:O_2}} = 0.0081$ .



**Figure 3.** Estimated error of  $\Delta C^*$ ,  $\sigma_{\Delta C^*}$  plotted versus AOU ( $O_2^{\text{sat}} - O_2$ ) for two values of the error of  $\sigma_{r_{C:O_2}}$ . The line at  $\sigma_{\Delta C^*} = 9 \mu\text{mol kg}^{-1}$  denotes our chosen uncertainty for  $\Delta C^*$ .

Table 2 shows the relative contribution of the various terms in (24) (relative to the square of the total error, e.g.,  $\sigma_{\Delta C^*}^2$ ). The error due to  $\sigma_{O_2}$ ,  $\sigma_{O_2^{\text{sat}}}$ , and  $\sigma_{r_{N:O_2}}$  is always negligible. The other terms, except for the error due to  $\sigma_{r_{C:O_2}}$ , are all of the same order and lead to an error of  $7.9 \mu\text{mol kg}^{-1}$  for zero AOU. The error due to uncertainties in the  $C : O_2$  stoichiometric ratio,  $\sigma_{r_{C:O_2}}$ , becomes significant only for AOU greater than  $80 \mu\text{mol kg}^{-1}$ . Since most anthropogenic CO<sub>2</sub> will be found in waters with relatively low AOU, we estimate for  $\Delta C^*$  an error of the order of  $9 \mu\text{mol kg}^{-1}$  (equal to the error for an AOU of  $50 \mu\text{mol kg}^{-1}$ ).

The uncertainty of the amount of anthropogenic CO<sub>2</sub> in the ocean,  $\sigma_{\Delta C_{\text{ant}}}$ , is estimated by quadratic error addition of the error in  $\Delta C^*$  ( $\sigma_{\Delta C^*}$ ) and  $\Delta C_{\text{dis eq}}^*$  ( $\sigma_{\Delta C_{\text{dis eq}}}$ ). We estimated the latter to be about  $\pm 4 \mu\text{mol kg}^{-1}$  by taking the average  $\sigma_{\Delta C_{\text{dis eq}}}$  value of all density surfaces (see Table 3). This gives an uncertainty of  $\pm 10 \mu\text{mol kg}^{-1}$  for  $\Delta C_{\text{ant}}$ . The anthropogenic  $C$  content of the ocean ranges from 0 to about  $50 \mu\text{mol kg}^{-1}$ . The signal to noise (error) ratio of  $\Delta C_{\text{ant}}$  is therefore  $\approx 5$ .

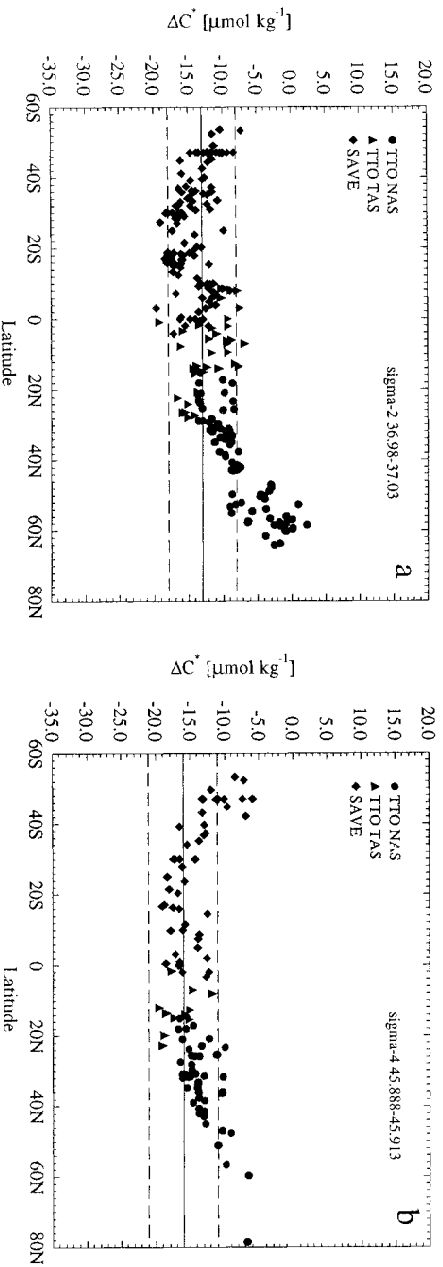
It was assumed above, for estimating the uncertainty of  $\Delta C^*$  and  $\Delta C_{\text{ant}}$ , that all errors are random and independent. However, some of the errors might be of systematic origin. We show in the appendices that these systematic errors are small for the use of the oxygen saturation concentration for preformed oxygen, for preformed alkalinity, as well as for inaccuracies in the determination of  $C$  and  $Alk$ . Even if these systematic errors are larger, they do not affect our anthropogenic CO<sub>2</sub> results, since  $\Delta C_{\text{ant}}$  is calculated by difference of the two quantities  $\Delta C^*$  and  $\Delta C_{\text{dis eq}}$ , which are equally affected by a systematic offset (see (17)) in these quantities.

With the reported precision of the modern coulometric  $C$  and titrimetric  $Alk$  data of  $\pm 1 \mu\text{mol kg}^{-1}$  and  $\pm 2 \mu\text{eq kg}^{-1}$ , respectively [Miller, 1995, Table I], the error of  $\Delta C^*$  for zero AOU is lowered to  $5 \mu\text{mol kg}^{-1}$ , with the largest contribution coming from  $\sigma_{Alk}$  and  $\sigma_{C_{\text{eq}}}$ . The influence of the uncertainty in the  $C : O_2$  stoichiometric ratio,  $\sigma_{r_{C:O_2}}$ , starts to dominate  $\sigma_{\Delta C^*}$  for AOU greater than  $45 \mu\text{mol kg}^{-1}$ . This implies that the uncertainty of  $\Delta C_{\text{ant}}$  is ultimately limited by the uncertainty of this stoichiometric ratio.

## Results and Discussion

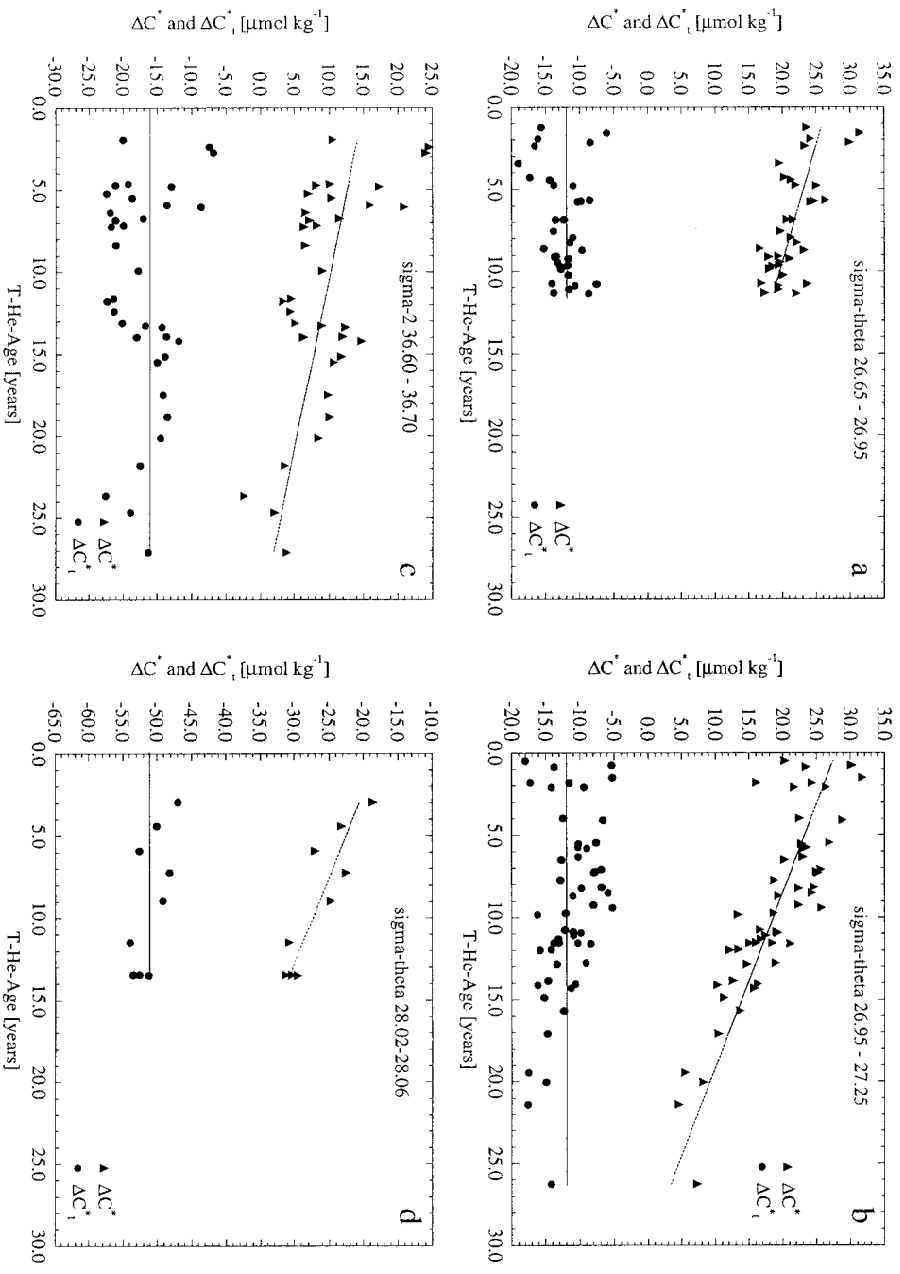
### $\Delta C^*$ and $\Delta C_f^*$

Figure 4 shows  $\Delta C^*$  as a function of latitude for 2 of the 10 deep isopycnal surfaces where we determined the air-sea disequilibrium by the first  $\Delta C^*$  method. These



**Figure 4.**  $\Delta C^*$  as a function of latitude from 60°S to 80°N along two deep isopycnal horizons in the Atlantic Ocean: (a) the  $\sigma_2$  interval from 36.98 to 37.03 which represents the core of the North Atlantic Deep Water (NADW) and (b) the  $\sigma_4$  interval from 45.888 to 45.913 which represents the boundary between the NADW and the Antarctic Bottom Water. The solid lines represents the average  $\Delta C^*$  in the region from 20°S to 20°N which corresponds to  $\Delta C_{\text{dis eq}}^*$ . The dashed lines are drawn at  $\pm 5 \mu\text{mol kg}^{-1}$  from the estimated  $\Delta C_{\text{dis eq}}^*$ , which is a little bit more than half of the estimated error of  $\Delta C^*$ . The upward trend near the outcrops in the south and the north is due to the invasion of anthropogenic CO<sub>2</sub>. Results from the TTO/NAS cruises are shown as circles; Results from the TTO/TAS cruises as are shown as triangles; and results from the SAVE program are shown as diamonds.

surfaces are the  $\sigma_2$  interval 36.98–37.03 which is the core of the middle North Atlantic Deep Water (NADW) (average depth 2500 m) and the  $\sigma_4$  interval 45.888–45.913 (average depth 4500 m) which represents the boundary between the Antarctic Bottom Water and the lower NADW.  $\Delta C^*$  near the outcrop regions of these deep surfaces in the north and south shows increasing values due to the uptake of anthropogenic CO<sub>2</sub>. The  $\Delta C^*$  away from the outcrops is remarkably uniform within the uncertainty of  $\Delta C^*$ . This supports our assumption that the effective CO<sub>2</sub> disequilibrium has stayed more or less constant over time. It furthermore shows that effective air-sea disequilibrium in the northern and southern outcrop region is very nearly the same. We chose the region from 20°S to 20°N as the region without anthropogenic CO<sub>2</sub> to determine  $\Delta C_{\text{dis eq}}^*$ . Limited information on water ages in that region from <sup>39</sup>Ar analysis [Rodriguez, 1993] confirm that most of these waters are older than 150 years. Weiss *et al.* [1985] showed, however, that CCl<sub>2</sub>F originating from the Labrador Sea has already penetrated deeply into the equatorial Atlantic within a well-defined deep western boundary undercurrent between 1000 and 2000 m. They estimated that this water has taken about 23 years to reach the equatorial region. Our determination of  $\Delta C_{\text{dis eq}}^*$  is not affected by these very young waters, since our boundary for switching between the  $\Delta C_f^*$  and the  $\Delta C^*$  method is at about 2000 m, at the lower boundary of the waters affected by this deep western boundary undercurrent. Furthermore, most of the stations used in the tropics lie



**Figure 5.**  $\Delta C_t^*$  (circles) and  $\Delta C^*$  (triangles) versus tritium-helium age along four isopycnal surface intervals in the North Atlantic. These surfaces include (a) the  $\sigma_\theta$  interval 26.65–26.95, (b) the  $\sigma_\theta$  interval 26.95–27.25 representing Subpolar Mode Water, (c) the  $\sigma_2$  interval 36.60–36.70 which lies within the Mediterranean Water Tongue, and (d) the  $\sigma_\theta$  interval 28.02–28.06 which occurs only in the Greenland and Norwegian Seas. The lines for  $\Delta C^*$  are drawn to emphasize the trend and have been obtained by linear regression. The lines for  $\Delta C_t^*$  represent the average.

well outside the region affected by this western boundary undercurrent.

Figure 5 shows  $\Delta C_t^*$  and  $\Delta C^*$  versus  $^3\text{H}$ - $^3\text{He}$  age for 4 of the 18 density surfaces where the  $\Delta C_t^*$  method has been used to estimate the CO<sub>2</sub> air-sea disequilibrium at the time the water last contact with the atmosphere. These surfaces are the  $\sigma_\theta$  interval 26.65–26.95 (average depth 500 m), the  $\sigma_\theta$  interval 26.95–27.25 (average depth 700 m) which represents the Subpolar Mode Water [McCartney and Talley, 1982], and the  $\sigma_2$  interval 36.60–36.70 (average depth 1200 m) lying within the Mediterranean Water, and the  $\sigma_\theta$  interval 28.02–28.06, which occurs only in the Greenland and Norwegian Seas.

In all surfaces,  $\Delta C^*$  decreases with increasing water age. This decrease reflects the uptake history of anthropogenic CO<sub>2</sub>, since atmospheric  $f\text{CO}_2$  was lower when the older water was last in contact with the atmosphere. After removing this effect from  $\Delta C^*$  by replacing  $C_{\text{eq}}$  with  $C_{\text{eq}}(t)$ , the resulting  $\Delta C_t^*$  has more or less con-

stant values within the uncertainties of the scatter of the data. This near constancy of  $\Delta C_t^*$  also confirms our a priori assumption that the effective air-sea disequilibrium in the outcrop region of a specific density surface has remained constant over time. We determined the final effective CO<sub>2</sub> air-sea disequilibrium,  $\Delta C_{\text{dis}}^*$  eq, finally by averaging all  $\Delta C_t^*$  values within the specified density surface interval using only values with water ages younger than 30 years.

#### Air-Sea Disequilibrium

A summary of the effective air-sea disequilibrium  $\Delta C_{\text{dis}}^*$  eq found on the isopycnal intervals is given in Table 3 and shown graphically in Figure 6. Also shown are the smoothing spline curves, which are used for the final estimate of  $\Delta C_{\text{ant}}^*$ . All investigated density surfaces have negative  $\Delta C_{\text{dis}}^*$  eq, which means that the outcrop region of these surfaces is undersaturated with respect to atmospheric CO<sub>2</sub>. This is due to the fact that all these surfaces outcrop in temperate- to high-latitude

**Table 3.** Mean Values of Temperature, Salinity, Preformed  $Alk$ ,  $\Delta C_t^*$ , and calculated  $\Delta fCO_2$  on Potential Density Surfaces in the North Atlantic

Potential Density	$\bar{T}$ , °C	$\bar{S}$ , psu	$\overline{Alk}^0$ , $\mu\text{eq kg}^{-1}$	$\Delta C_{\text{dis}}^{\text{eq}}$ , $\mu\text{mol kg}^{-1}$	$\sigma_{\Delta C_{\text{dis}}^{\text{eq}}}$ , $\mu\text{mol kg}^{-1}$	$N_{\Delta C_{\text{dis}}^{\text{eq}}}$ , #	method <sup>a</sup>	$\Delta fCO_2$ , $\mu\text{atm}$
<i><math>\sigma_\theta</math> Surfaces</i>								
25.30	23.7	37.06	2417	-19	5	5	2	-26
25.60	22.5	37.04	2417	-17	5	2	2	-24
25.90	20.8	36.82	2405	-13	8	6	2	-19
26.20	18.9	36.60	2393	-24	4	7	2	-35
26.50	17.3	36.42	2385	-22	5	52	2	-32
26.80	14.6	35.97	2364	-12	3	34	2	-20
27.10	11.3	35.50	2343	-12	3	53	2	-20
27.30	9.3	35.29	2333	-14	4	20	2	-25
27.40	8.8	35.31	2335	-17	4	13	2	-30
<i><math>\sigma_2</math> Surfaces</i>								
36.45	8.1	35.26	2341	-16	5	39	2	-29
36.55	7.4	35.25	2337	-15	5	34	2	-28
36.65	6.4	35.21	2334	-16	6	39	2	-29
36.75	5.5	35.13	2329	-18	5	60	2	-34
36.85	4.4	35.04	2325	-13	8	102	2	-26
36.95	3.8	35.00	2323	-10	4	106	1	-20
37.00	3.1	34.96	2322	-13	4	92	1	-27
37.05	2.7	34.93	2321	-16	3	94	1	-31
<i><math>\sigma_4</math> Surfaces</i>								
45.825	2.7	34.93	2321	-16	3	51	1	-32
45.850	2.5	34.92	2320	-16	4	49	1	-33
45.875	2.4	34.90	2320	-15	4	68	1	-31
45.900	2.2	34.89	2319	-16	3	39	1	-32
45.925	2.0	34.87	2318	-15	3	28	1	-31
45.950	1.8	34.89	2317	-15	3	15	1	-31
<i><math>\sigma_\theta</math> Surfaces in the Greenland and Norwegian Seas</i>								
27.92	2.1	34.91	2319	-36	5	8	2	-67
27.96	1.3	34.91	2318	-43	6	6	2	-80
28.00	0.4	34.90	2318	-41	5	6	2	-77
28.04	-0.4	34.90	2318	-51	3	9	2	-94
28.08	-0.9	34.91	2319	-56	2	34	2	-102

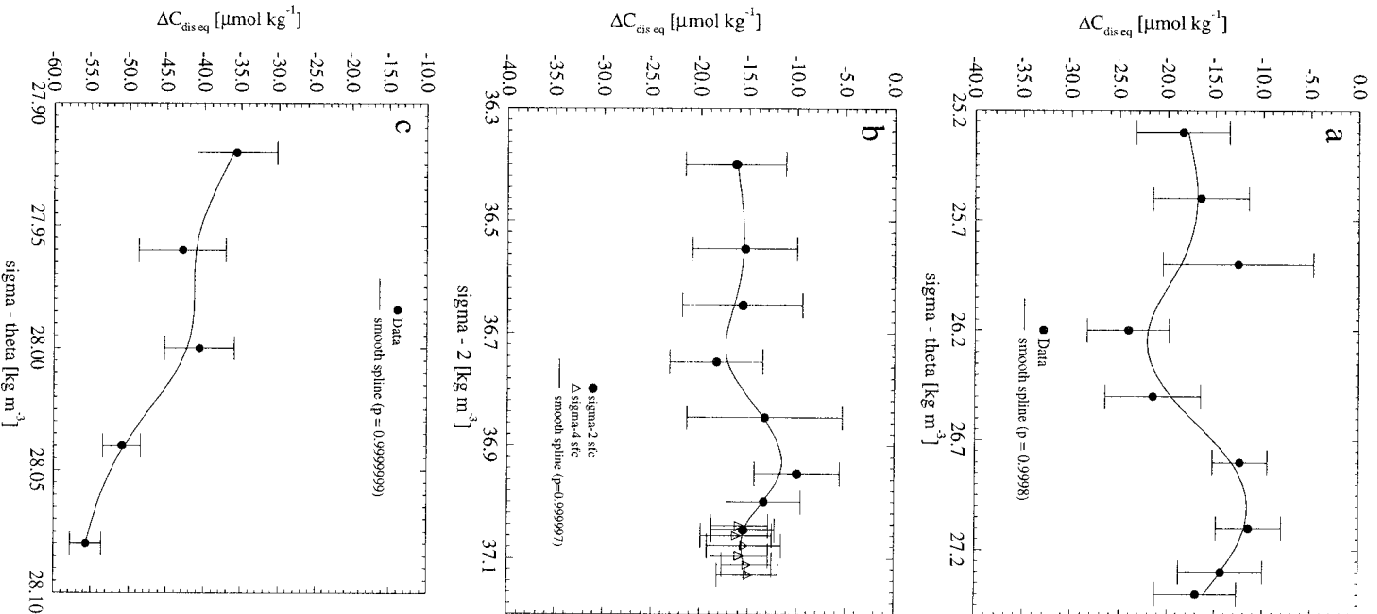
<sup>a</sup>  $\Delta C_t^*$  method indicated as 1;  $\Delta C_t^*$  method indicated as 2.

<sup>b</sup> Calculated from  $\bar{T}$ ,  $\bar{S}$ ,  $Alk^0$ , and  $\Delta C_{\text{dis}}^{\text{eq}}$  using thermodynamic relationships.

areas characterized by wintertime cooling. The air-sea disequilibrium does not vary greatly in the entire water column of the North Atlantic Ocean south of 60°N. The minimum is about -10  $\mu\text{mol kg}^{-1}$ , and the maximum is about -25  $\mu\text{mol kg}^{-1}$ .

In the main thermocline we find the largest  $\Delta C_{\text{dis}}^{\text{eq}}$  for the  $\sigma_\theta$  surfaces from 26.05-26.60. These surfaces outcrop in the region of Ekman convergence in the North Atlantic between 30°N and 40°N [Kawase and Sarmiento, 1985]. The deeper surfaces in the main thermocline ( $\sigma_\theta$  26.65-27.35) show a considerably smaller

air-sea disequilibrium. These surfaces also outcrop in the region of Ekman convergence in the North Atlantic but at higher latitudes (40°N - 50°N) [Kawase and Sarmiento, 1985]. The waters at the lower base of the thermocline ( $\sigma_2$  36.40-36.80) have a very uniform  $\Delta C_{\text{dis}}^{\text{eq}}$  of about -15  $\mu\text{mol kg}^{-1}$ . The source regions of these water masses are the Mediterranean, the Arctic Front and also partially the Antarctic Circumpolar Front (for the Antarctic Intermediate Water). The upper North Atlantic Deep Water (NADW) which is mainly composed of Labrador Sea Water ( $\sigma_2$

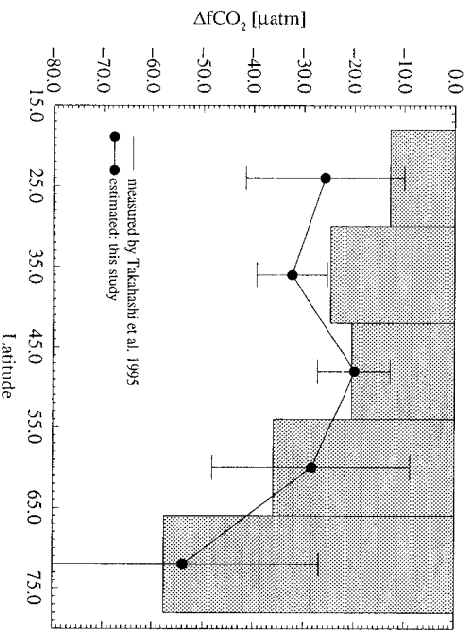


**Figure 6.** Plot of the estimated  $\Delta C_{\text{dis eq}}$  versus potential density for the different potential density intervals. (a) The  $\sigma_{\theta}$  surfaces 25.30–27.40 are shown; (b) the  $\sigma_2$  surfaces from 36.45–37.05 and the  $\sigma_4$  surfaces 45.825–45.950 (converted to the appropriate  $\sigma_2$  value) are shown; and (c) the  $\sigma_{\theta}$  surfaces 27.92–28.08 in the Greenland and Norwegian Seas are shown. Also depicted is a smoothing spline fit through the data. The chosen stiffness parameter  $p$  is also shown.

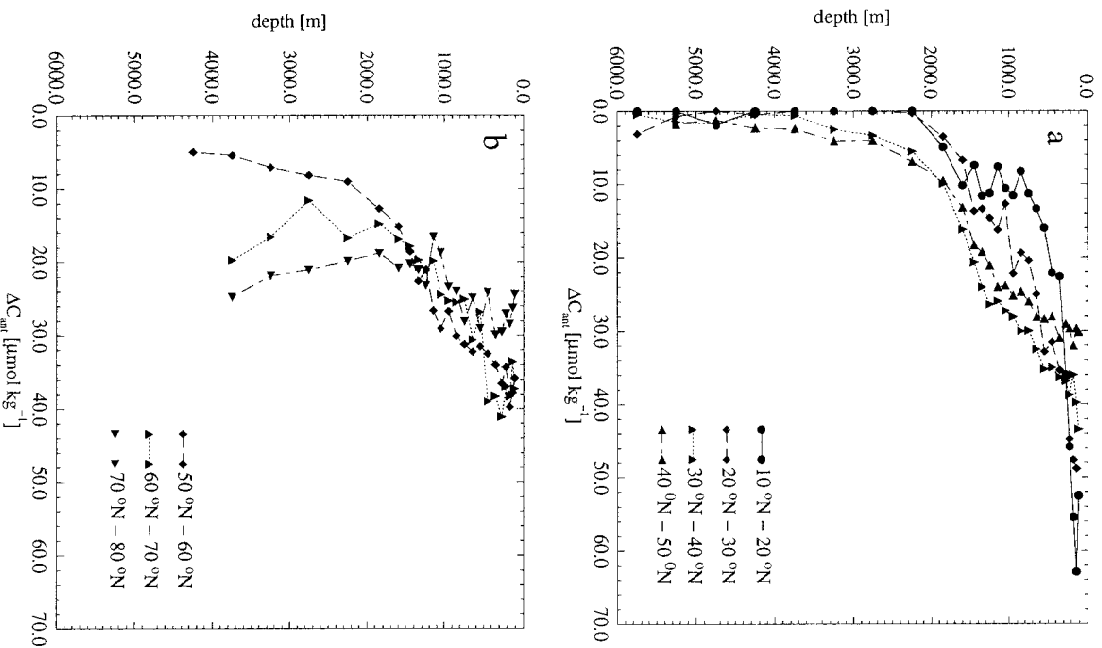
36.80–36.90) has a somewhat lower  $\Delta C_{\text{dis eq}}$  than the main body of the NADW (density surfaces  $\sigma_2$  36.85 to  $\sigma_4$  45.900) which has a remarkably uniform  $\Delta C_{\text{dis eq}}$  of about  $-15 \mu\text{mol kg}^{-1}$ . The middle NADW has its

source region mainly in the Greenland and Norwegian Seas [Swift, 1984a]. We find for the deep waters in these basins a very large  $\Delta C_{\text{dis eq}}$  in the range of  $-36$  to  $-56 \mu\text{mol kg}^{-1}$ , which is probably due to rapid cooling of surface waters and subsequent deep convection without enough time for CO<sub>2</sub> equilibration. However, the waters overflowing the sills in the Denmark Strait (Denmark Strait Overflow Waters), on Iceland-Faroe Ridge and on Faroe Bank Channel (Iceland Scotland Overflow Waters), which form the source waters for NADW, are not the product of deep convection but of intermediate water formation north of the Greenland-Scotland ridge [Dickson and Brown, 1994]. Although not investigated in more detail, one can conclude from the near uniform and relatively low air-sea disequilibrium found in the middle NADW that these intermediate waters in the Greenland and Norwegian Seas must have a much smaller  $\Delta C_{\text{dis eq}}$  than the deep waters in these basins.

Is this pattern of CO<sub>2</sub> air-sea disequilibrium consistent with what we know from direct observations of  $\Delta f\text{CO}_2$ ? We calculated  $\Delta f\text{CO}_2$  from  $\Delta C_{\text{dis eq}}$  and the mean values of temperature, salinity, and preformed  $\Delta k$  along the investigated density surfaces (see Table 3). The same thermodynamic relationships as used in appendix A were employed. In order to calculate zonal means of  $\Delta f\text{CO}_2$ , the outcrop latitudes of all surfaces were first determined from the NOAA Atlas [Levitus *et al.*, 1994; Levitus and Boyer, 1994]. Then all calculated  $\Delta f\text{CO}_2$ , which belong to a density surface outcropping within the specified latitude belt, were averaged. We compare our estimate of the zonal mean  $\Delta f\text{CO}_2$  with the direct wintertime observations of  $\Delta f\text{CO}_2$  (months December-February) by Takahashi *et al.* [1995, Table 1]. Figure 7 shows very good agree-



**Figure 7.** Comparison of the Atlantic Ocean zonal mean air-sea difference of  $f\text{CO}_2$ ,  $\Delta f\text{CO}_2$ , between the observational estimates of Takahashi *et al.* [1995] and our estimates based on  $\Delta C_{\text{dis eq}}$ . The direct observations are averages for the winter months December-February.



**Figure 8.** Horizontally averaged profiles of  $\Delta C_{\text{ant}}$  in seven latitude belts from 10°N to 80°N in the North Atlantic.

ment between our estimated  $\Delta f\text{CO}_2$ , based on data from the interior of the ocean and the direct observations. The observations confirm also the relative minimum in the latitude band from 42°N to 54°N and the strong increase of  $\Delta f\text{CO}_2$  north of 60°N. However, we generally overestimate the air-sea disequilibrium in the low latitudes, where we determine  $\Delta C_{\text{dis}}$  eq by the  $\Delta C_f^*$  method. In the high latitudes, where the second method employing  $\Delta C^*$  has been used, the opposite seems to be the case. This tendency is, however, not significant, given the large uncertainties of our estimates of  $\Delta f\text{CO}_2$  and the observations. This independent check of our approach to estimate the air-sea disequilibrium in the North Atlantic improves our confidence, not only in the determination of  $\Delta C_{\text{dis}}$  eq but also in our estimates of  $\Delta C_{\text{ant}}$ .

### Distribution of Anthropogenic CO<sub>2</sub> in the North Atlantic

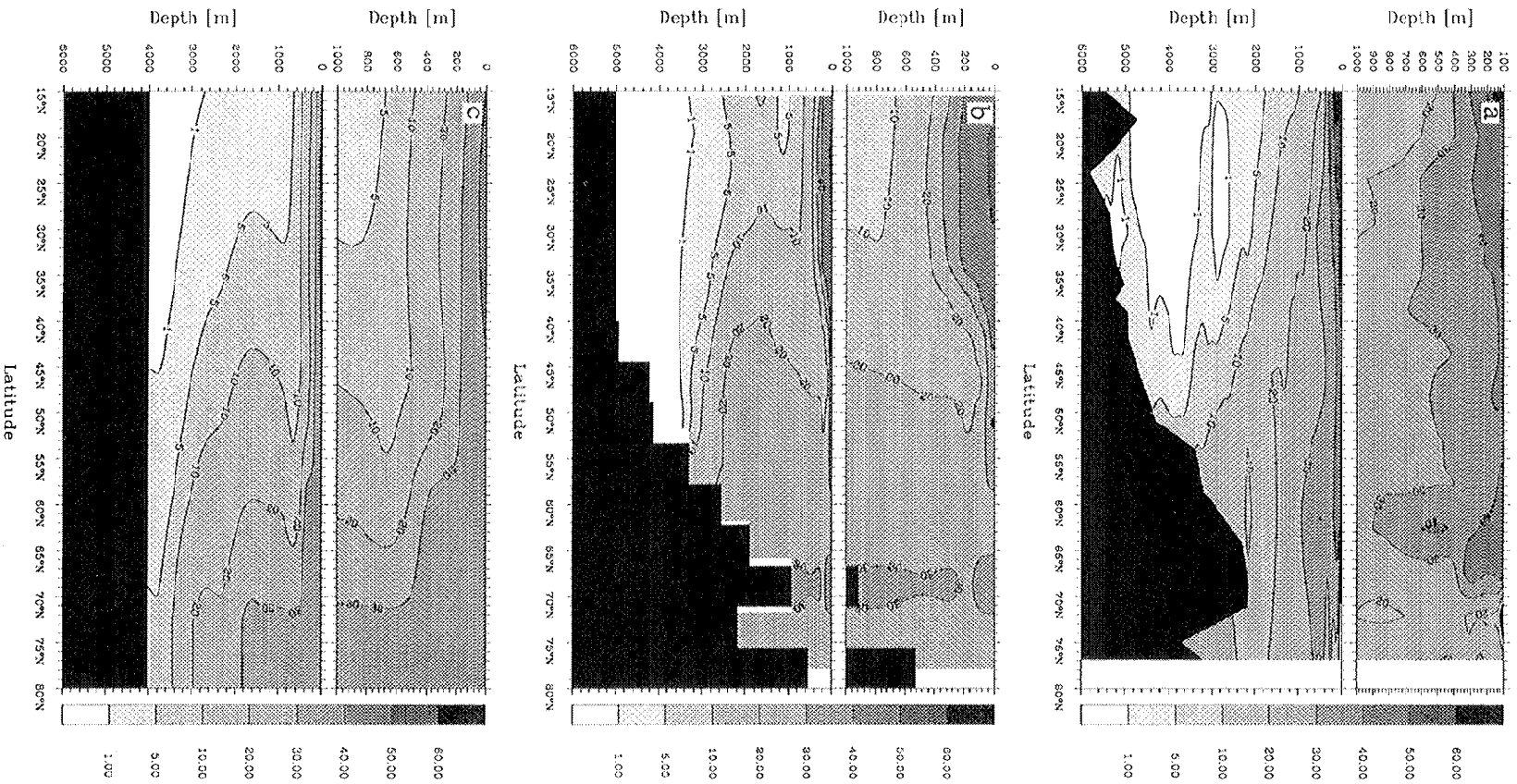
The results of our separation of the anthropogenic CO<sub>2</sub> component from  $C$  are shown in Figures 8 to 10.

Figure 8 shows the horizontally averaged profiles in seven latitude belts from 10°N to 80°N within the North Atlantic. Near the surface (note that we excluded the upper 100 m) the concentrations are in the range of 40 to 50  $\mu\text{mol kg}^{-1}$  in the low latitudes and around 30  $\mu\text{mol kg}^{-1}$  in the high latitudes. This is in agreement with what is expected based on thermodynamic considerations. If the ocean follows more or less the anthropogenic atmospheric CO<sub>2</sub> increase, we expect the cold surface waters (< 5°C) to contain about 30  $\mu\text{mol kg}^{-1}$  of anthropogenic CO<sub>2</sub> and the warm waters (> 20°C) to contain more than 40  $\mu\text{mol kg}^{-1}$  because of the temperature sensitivity of the CO<sub>2</sub> solubility and chemistry.

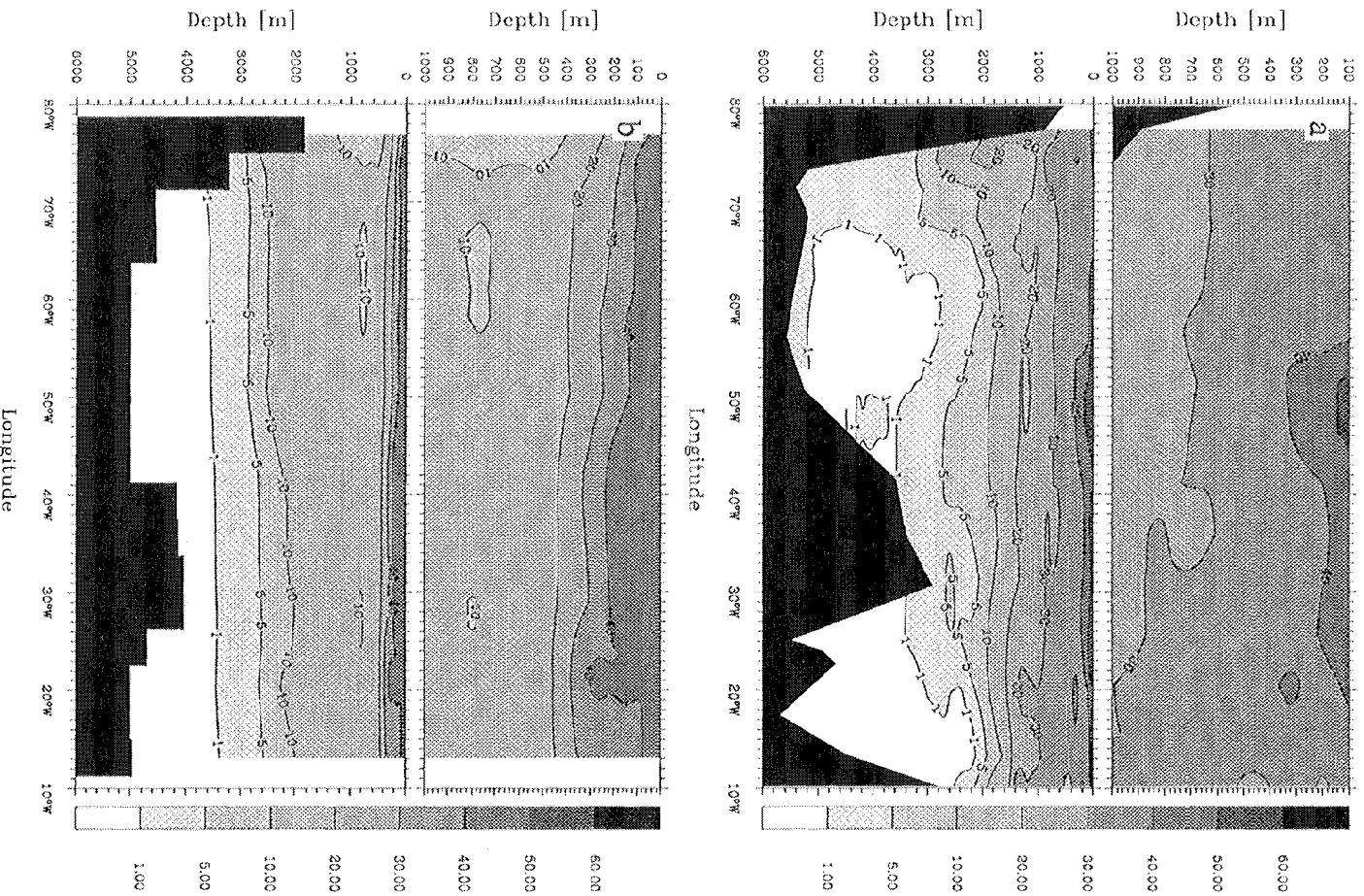
In the latitude belt from 10°N to 20°N,  $\Delta C_{\text{ant}}$  rapidly decreases downward from the surface to about 10  $\mu\text{mol kg}^{-1}$  at 1000 m depth and to below 2  $\mu\text{mol kg}^{-1}$  at about 2000 m. Going northward, the anthropogenic CO<sub>2</sub> penetrates more and more deeply, which is evident from the increase of  $\Delta C_{\text{ant}}$  at 1000 m and the progressively greater depth at which  $\Delta C_{\text{ant}}$  goes below 2  $\mu\text{mol kg}^{-1}$ . The average profile in the subtropics between 30°N and 40°N shows nearly a linear decrease of  $\Delta C_{\text{ant}}$  between the upper ocean and a depth of about 1500 m. At this depth,  $\Delta C_{\text{ant}}$  is still above 25  $\mu\text{mol kg}^{-1}$ . It then decreases rapidly and goes below 2  $\mu\text{mol kg}^{-1}$  at about 3500 m. The profile in the 40°N to 50°N latitude belt has the same structure as the latitudinal belt to the south. The thermocline, however, contains less anthropogenic CO<sub>2</sub>, but there are slightly higher concentrations of  $\Delta C_{\text{ant}}$  in the waters below 2000 m. This trend is confirmed in the latitudinal belt from 50°N to 60°N where  $\Delta C_{\text{ant}}$  stays above 5  $\mu\text{mol kg}^{-1}$  at the greatest depths. The structure of the zonal mean profiles of  $\Delta C_{\text{ant}}$  in the North Atlantic south of 60°N are consistent with our expectation based on the current knowledge of thermocline structure and ventilation [*Rooth and Ostlund, 1972; Sammieito et al., 1982*] and the circulation of the lower limb of the thermohaline overturning. [*Doney and Jenkins, 1994; Fine, 1995*].

In the latitude belts north of 60°N,  $\Delta C_{\text{ant}}$  shows high concentration down to the bottom. These two latitude belts comprise mainly the Greenland and Norwegian Seas, where the deep water has been shown to be fairly young. *Schlosser et al.* [1995] estimated a tritium-helium age of about 17 years for the Greenland Sea and 30 years for the Norwegian Sea, in good agreement with *Smetnie et al.* [1988], who estimated residence times between about 10 and 35 years based on chlorofluoromethane measurements.

Figure 9a depicts a meridional section of  $\Delta C_{\text{ant}}$  from



**Figure 9.** Meridional sections of  $\Delta C_{ant}$  ( $\mu\text{mol kg}^{-1}$ ) from 15°N to 80°N in the North Atlantic. (a) observations along the line shown in Figure 2; (b) results from the three-dimensional ocean general circulation biogeochemistry model of *Sarmiento et al.* [1995] along the same line within the resolution of the coarse resolution model; and (c) zonally averaged results from the 2.5-dimensional model of *Stocker et al.* [1994]. The model results are the average values for the year of 1982.



**Figure 10.** Zonal sections of  $\Delta C_{\text{ant}}$  ( $\mu\text{mol kg}^{-1}$ ) from  $80^\circ\text{W}$  to  $10^\circ\text{W}$  in the North Atlantic at approximately  $30^\circ\text{N}$ . (a) observations along the line shown in Figure 2 and (b) results from the three-dimensional OGCM biogeochemistry model of *Sarmiento et al.* [1995] for the year of 1982 along the same line within the resolution of the coarse resolution model.

$15^\circ\text{N}$  to  $80^\circ\text{E}$  in the western Atlantic (see Figure 2 for track). The concentration of anthropogenic  $\text{CO}_2$  in the upper 1000 m is rather uniform between  $20^\circ\text{N}$  and  $60^\circ\text{N}$ . South of  $20^\circ\text{N}$ , anthropogenic  $\text{CO}_2$  decreases more rapidly with increasing depth than to the north. Below 1000 m, large differences exist between high and

low latitudes. The southward spreading of relatively young NADW, which takes with it anthropogenic  $\text{CO}_2$ , is clearly visible by the downward slope of  $\Delta C_{\text{ant}}$  north of  $40^\circ\text{N}$ . Waters below 3000 m and south of  $40^\circ\text{N}$  contain essentially no anthropogenic  $\text{CO}_2$ . Recent advancement in the understanding of the lower



limb of the thermohaline circulation (see *Fine* [1995] for a review) by the use of transient tracers showed that the deep western boundary undercurrent (DWBC) is transporting freshly formed water in the high latitudes within decades to the tropics [*Doney and Jenkins*, 1994]. Along its pathway it constantly exchanges water with the interior abyssal ocean. We therefore expect to see elevated concentrations of  $\Delta C_{\text{ant}}$  in the western deep Atlantic compared to the eastern basin. Figure 10a shows a zonal section of  $\Delta C_{\text{ant}}$  from 80°W near the North American continent to 10°W close to the Iberian Peninsula at a latitude of approximately 30°N (see Figure 2 for track). A significant downward slope of the isolines by about 1000 m can be identified near the western boundary below 1000 m. The DWBC at that latitude is split into a shallow core centered at about 1200 m and a deep core centered at about 3500 m [*Fine*, 1995]. Our data do not permit us to discern two separated cores, but the observation of elevated  $\Delta C_{\text{ant}}$  concentration in that region in our section is consistent with our expectation.

This meridional section also reveals a deeper penetration of  $\Delta C_{\text{ant}}$  in the eastern thermocline compared to the west. This pattern reflects primarily the anticyclonic gyre transport, where anthropogenic CO<sub>2</sub>, much like bomb tritium, is subducted into the thermocline in the northeast [*Sarmiento et al.*, 1982].

#### Anthropogenic CO<sub>2</sub> Inventories

On the basis of TTO NAS and TTO TAS data, we now estimate the ocean inventory of anthropogenic CO<sub>2</sub> at the time of these surveys (1981-1983). We determine the inventory of each latitudinal belt between latitude  $\varphi_1$  and  $\varphi_2$ ,  $\text{INV}(\varphi_1, \varphi_2)$ , by vertically integrating the area-weighted mean of  $\Delta C_{\text{ant}}$  in that latitude belt,  $\overline{\Delta C_{\text{ant}}}(\varphi, z)$ ,

$$\text{INV}(\varphi_1, \varphi_2) = \int_{\text{bottom}}^{\text{sfc}} A(\varphi, z) \overline{\Delta C_{\text{ant}}}(\varphi, z) dz, \quad (25)$$

where  $A(\varphi, z)$  is the horizontal area of the latitude belt  $\varphi$  between  $\varphi_1$  and  $\varphi_2$  as a function of depth as determined from a 1° global topography [*Gates and Nelson*, 1975]. The concentration of  $\Delta C_{\text{ant}}$  in the surface 100 m is estimated from the averaged concentration between 100 and 200 m. We also calculate the specific inventories in the latitude belts ( $\text{INV}_{\text{spec}}(\varphi_1, \varphi_2)$ ) by

$$\text{INV}_{\text{spec}}(\varphi_1, \varphi_2) = \frac{\text{INV}(\varphi_1, \varphi_2)}{A(\varphi, z = 0 \text{ m})}. \quad (26)$$

The results are shown in Table 4. We obtain for the North Atlantic Ocean between 10°N and 80°N a total inventory of about  $16.3 \cdot 10^{14}$  mol C or about 19.6 Gt C and a specific inventory of about 41 mol C m<sup>-2</sup>. We estimate the error of the inventory (1- $\sigma$  of the mean) to be about  $3.3 \cdot 10^{14}$  mol C or 4 Gt C (20%) based on the previously estimated signal to noise ratio of  $\Delta C_{\text{ant}}$ . The inventories of the different latitude belts vary greatly because of the strongly varying volumes of these regions in the North Atlantic. The Atlantic Ocean from 10°N to 40°N contains about 64% of the anthropogenic CO<sub>2</sub> inventory, whereas the region from 40°N to 80°N holds the remaining 36%. The reason for this is that the volume of the region from 10°N to 40°N is about 76% of the total volume in the investigated region in the North Atlantic.

We turn therefore to the specific inventories as a better representation of the regions where anthropogenic CO<sub>2</sub> has accumulated. Although most of the effect of ocean topography has been removed, the distribution of the specific inventories is far from being uniform (see Figure 11). The highest specific inventory is found in the subtropical region between 30°N and 40°N with almost 60 mol C m<sup>-2</sup>. The tropics and the high latitudes have significantly lower specific inventories. The explanation for this pattern is related to the wind-driven meridional circulation. Anthropogenic CO<sub>2</sub> entering the ocean in the equatorial regions and subpolar gyres,

**Table 4.** Summary of the Estimated Water Column Inventory of Anthropogenic CO<sub>2</sub> in the North Atlantic Ocean by Latitude Belt

Latitude Belt, deg	Surface Area, 10 <sup>12</sup> m <sup>2</sup>	Volume, 10 <sup>16</sup> m <sup>3</sup>	Number of stations	Specific Inventory, mol C m <sup>-2</sup>	Inventory, 10 <sup>14</sup> mol C	Inventory, Gt C
10°N - 20°N	8.0	3.1	41	34	2.7	3.3
20°N - 30°N	8.9	3.6	53	41	3.6	4.3
30°N - 40°N	7.0	2.9	85	59	4.2	5.0
40°N - 50°N	5.3	1.6	26	43	2.3	2.8
50°N - 60°N	4.8	0.9	60	40	1.9	2.3
60°N - 70°N	3.7	0.4	22	28	1.0	1.2
70°N - 80°N	2.3	0.2	14	25	0.6	0.7
Total	40.0	12.6	301	41 (mean)	16.3	19.6

which are dominated by upwelling, is laterally transported by Ekman transport to the subtropical gyre where it accumulates in the main thermocline, which is at its deepest at these latitudes [Sarmiento *et al.*, 1992, Figures 5 and 6]. Note also the large accumulation of anthropogenic CO<sub>2</sub> in upper NADW below the main thermocline to a depth of about 3000 m (Figure 9) and in the deep western boundary current (DWBC) (Figure 10). The thermocline shallows and mean ocean depth decreases north of 45°N, both of which gradually reduce the specific inventory. The shallowness of the ocean is the major factor north of 60°N, where the specific inventory is small despite the high deep ocean concentrations.

### Comparison With Model Estimates

We compare our estimates of anthropogenic CO<sub>2</sub> in the North Atlantic Ocean with the results of the 2.5-dimensional circulation model of *Stocker et al.* [1994] (SBW) and with the Princeton three-dimensional ocean general circulation biogeochemistry model of *Sarmiento et al.* [1995](SML).

The 2.5-dimensional SBW model is a zonally averaged ocean model, where the world ocean is represented by three ocean basins (Atlantic, Pacific, and Indian) which are connected via a Southern Ocean south of 40°S. An inorganic carbon cycle model has been added representing the solubility pump. The “best tuned” (with respect to temperature and salinity) steady state circulation (state A) is used for the simulations. The inorganic carbon model differs slightly from the model described by *Stocker et al.* [1994], since the surface mean alkalinity [Takahashi *et al.*, 1981] has now been taken as the reference alkalinity instead of the ocean mean value.

The three-dimensional SML model is a coarse resolution model based on the nonseasonal circulation model of *Toggweiler et al.* [1989a]. A full natural carbon cycle model is included, namely, the solubility pump, the soft-tissue pump, and the carbonate pump.

The two models differ in their representation of the carbon cycle. However, since anthropogenic CO<sub>2</sub> can essentially be treated as a conservative tracer which is not involved in biological processes, the representation of the soft-tissue pump and carbonate pumps is not a necessary requirement for the prediction of the uptake of anthropogenic CO<sub>2</sub> [Broecker, 1991; Sarmiento *et al.*, 1992].

Both models have been spun up to a preindustrial steady state with an atmospheric CO<sub>2</sub> concentration of 280  $\mu\text{atm}$  for the SML model and 278.9  $\mu\text{atm}$  for the SBW model. To simulate the uptake of CO<sub>2</sub> over the industrial era, the model integrations start in 1767, and atmospheric CO<sub>2</sub> is prescribed for both models by the same smoothing spline through atmospheric CO<sub>2</sub> data

obtained from direct observations after 1958 [Keeling *and Whorf*, 1994] and ice-core data before 1958 [Neftel *et al.*, 1994]. Model results are analyzed for the year 1982, which is the middle year of the observations (1981-1983).

The results of these uptake experiments are shown in Tables 5 to 7 and Figures 9 to 11 together with the observations. The agreement between the model inventories in the North Atlantic from 10°N to 80°N (18.7 Gt C for SBW and 18.4 Gt C for SML) and the observed inventory of  $20 \pm 4$  Gt C is very good. The SBW model predicts a 7% higher global uptake rate and 7% higher global inventory than the SML model for the year 1982. However, inventories within the Atlantic from 10°N to 80°N differ by only 1% between the two models. They both slightly underestimate the North Atlantic inventory derived from observations by about 5% to 7%, which is within the uncertainty. The anthropogenic CO<sub>2</sub> inventory is mainly determined by ocean transport [Siegenthaler and Joos, 1992; Sarmiento *et al.*, 1992]. The SML model is known to have a too sluggish thermocline ventilation [Sarmiento *et al.*, 1992; Toggweiler *et al.*, 1989b]. However, this seems not to have a great impact on the calculated CO<sub>2</sub> inventory in the North Atlantic. The vertical exchange in the SBW model is too strong in the Southern Ocean because of excessive convection and too weak in the midlatitudes probably because of too little ventilation of the wind-driven gyre [Stocker *et al.*, 1994, p. 117-118]. In the high northern latitudes of the Atlantic the vertical exchange in the SBW model seems to be simulated properly. These two effects counterbalance each other in the Atlantic, causing good agreement between modeled and observed inventories. Note that the SBW model state A was not tuned using radiocarbon data but is rather that state that shows closest agreement of the zonal averages of temperature and salinity in each of the three ocean basins.

Does this good agreement of the anthropogenic CO<sub>2</sub> inventories for the entire North Atlantic also hold regionally? We turn to Figure 9 which shows observed and model calculated meridional sections of  $\Delta C_{\text{ant}}$  in the North Atlantic. Both the SML and the SBW model show qualitative agreement, but there are important differences between them and our reconstruction from the observations. Both models contain significantly less anthropogenic CO<sub>2</sub> in the low-latitude thermocline than predicted by the observations. The isolines are too shallow by about 600 m (SML) and about 400 m (SBW), compared to observations. A particularly large deficiency of anthropogenic CO<sub>2</sub> shows up in the SML model between 40°N and 50°N at depths between 200 and 500 m. This low  $\Delta C_{\text{ant}}$  water is due to artificial upwelling of deep water containing little anthropogenic CO<sub>2</sub> on the landward side of the Gulf Stream [Togg-

weiler et al., 1989b, p. 8249]. Veronis [1975] pointed out that this artificial upwelling might be due to the strictly horizontal orientation of lateral mixing in the models. Isopycnal mixing helps to reduce this artificial upwelling and also enhances  $\Delta C_{\text{ant}}$  penetration in the thermocline [Danabasoglu et al., 1994]. The 2.5-dimensional SBW model does not show such a depression of  $\Delta C_{\text{ant}}$  in the thermocline of the temperate latitudes, but the deficiency of  $\Delta C_{\text{ant}}$  in the entire thermocline is even larger than in the SML model. The thermocline ventilation process in the 2.5-dimensional model is parameterized by an increased horizontal diffusion. Our result here may indicate that an even higher horizontal diffusion is necessary to account for the high anthropogenic CO<sub>2</sub> present in the thermocline of the temperate latitudes.

Both models simulate the downward depression of the isolines in the high latitudes due to the southward progression of anthropogenic CO<sub>2</sub> bearing NADW. In the SML model the maximum penetration of the NADW does not go below model layer 10 (2935 m) [Toggweiler et al., 1989a], since denser water of Antarctic origin spreads to the north in levels 11 and 12, filling up the entire deep North Atlantic. This water is very weakly ventilated by flow from the south and by vertical mixing and hence contains no anthropogenic CO<sub>2</sub>. The SML model overpredicts the concentration of  $\Delta C_{\text{ant}}$  in the NADW (see 10 and 20  $\mu\text{mol kg}^{-1}$  isolines), compensating for the underprediction in the thermocline.

Differences of  $\Delta C_{\text{ant}}$  in the deep ocean between the 2.5-dimensional SBW model and the observations can mainly be attributed to the simplified basin topography. Strong vertical overturning in the northernmost grid-cell at 72.5°N transports large quantities of anthropogenic CO<sub>2</sub> to the model's bottom at 4000 m depth, whereas in the real ocean and the three-dimensional

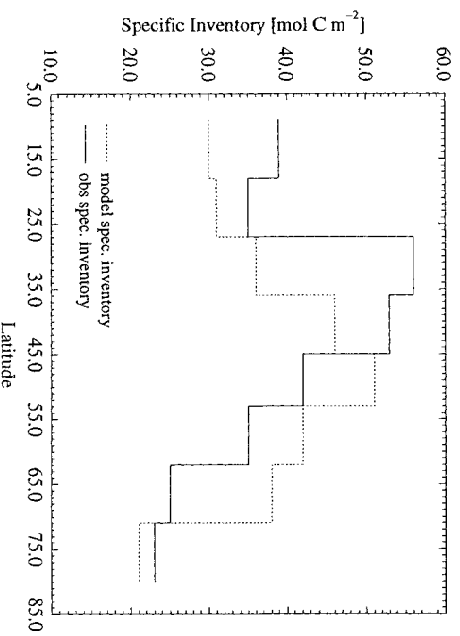
model this deep penetration is prevented by the topography.

Similar success and deficiency of the SML model can be found in a comparison between a simulated and observed zonal section of  $\Delta C_{\text{ant}}$  in the North Atlantic at about 30°N (see Figure 10). As in the observations, the SML model does not show large zonal gradients in  $\Delta C_{\text{ant}}$  at this latitude. Also, very evident is the too shallow penetration of the 30  $\mu\text{mol kg}^{-1}$  isoline and the too deep 10  $\mu\text{mol kg}^{-1}$  isoline. Contrary to the observations, no sign of elevated concentrations near the western boundary can be discerned, although the SML model has a clearly developed western boundary current. The artificial upwelling at the landward side of the western boundary currents is probably responsible for obscuring such a signal.

The too low concentrations in the upper 1000 m between 30°N and 45°N in the SML model are also evident in a more detailed comparison of the model predicted and the observed specific inventories (Table 5 and Figure 11). The model underpredicts the specific inventory in the subtropics from 27°N to 36°N by more than 35%. The total inventory between 10°N and 80°N, however, agrees well, since the overprediction of the specific inventories by the model in the temperate and subtropical regions compensates for this. Comparison of the specific inventories between observations and the SBW model in Table 6 shows large differences in the different latitude belts, which compensate each other, yielding a very good overall agreement. The model calculated specific inventory is only half as large in the tropical to temperate latitudes but almost 4 times larger in the high latitudes. As has been already stated above, the large overprediction of the high-latitude specific inventory can mainly be attributed to the simplified topogra-

**Table 5.** Comparison of the Estimated Water Column Inventory of Anthropogenic CO<sub>2</sub> in the North Atlantic With Estimates From the Sarmiento et al. [1995] (SML) Three-Dimensional Model for the Year 1982 by Latitude Belt

Latitude Belt,	SML Model			Observations		
	Surface Area, 10 <sup>12</sup> m <sup>2</sup>	Inventory, Gt C	Specific Inventory, mol C m <sup>-2</sup>	Surface Area, 10 <sup>12</sup> m <sup>2</sup>	Inventory, Gt C	Specific Inventory, mol C m <sup>-2</sup>
9°N - 18°N	6.8	2.4	30	7.0	3.3	39
18°N - 27°N	8.0	3.0	31	8.0	3.3	35
27°N - 36°N	7.1	3.1	36	7.0	4.7	56
36°N - 45°N	5.4	3.0	46	5.5	3.5	53
45°N - 53°N	4.1	2.5	51	4.0	2.0	42
53°N - 62°N	4.4	2.2	42	4.8	2.0	35
62°N - 71°N	3.1	1.4	38	2.8	0.8	25
71°N - 80°N	3.3	0.8	21	1.8	0.5	23
Total	42.2	18.4	36 (mean)	40.9	20.1	41 (mean)



**Figure 11.** Comparison between observed and OGCM-calculated specific inventories of anthropogenic CO<sub>2</sub> in the North Atlantic. The calculated inventories are from the three-dimensional OGCM biogeochemistry model of *Sarmiento et al.* [1995] and refer to the year of 1982.

phy of the model, whereas the too small specific inventory in the low latitudes is due to a too weak thermocline ventilation. The SBW model has primarily been designed for simulation of the thermohaline circulation and its variability over long timescales, and therefore a detailed comparison of such a 2.5-dimensional model on a regional basis is probably beyond feasibility.

### Comparison With Chen's Estimate

Recently, *Chen* [1993] summarized all of his calculations and attempted to estimate a global inventory of the amount of excess CO<sub>2</sub> in the oceans. He found a global inventory of  $82.3 \pm 16.0$  Gt C which is considerably smaller than the two model estimates shown in Table 7. For the North Atlantic ocean from 0° to 65°N he calculated an inventory of  $21.5 \pm 4.5$  Gt C for the year 1972 based on his earlier work [*Chen*, 1982]. He also presented an inventory of  $0.85 \pm 0.2$  Gt C for the Greenland and Norwegian Seas for the year 1982 mak-

ing use of the study of *Chen et al.* [1990]. Adding these two estimates for the North Atlantic together, disregarding the 10-year difference between them, he finds a total inventory of  $22.4 \pm 4.5$  Gt C between 0°N and 80°N. This is in good agreement with our estimate of  $20 \pm 4$  Gt C for the 10°N to 80°N band, particularly, if one takes into consideration that the 0° to 10°N band has an additional 2–3 Gt C. However, we consider this agreement to be fortuitous because of inherent problems in the Chen approach, as discussed in the introduction, and because of insufficient data coverage. Chen's estimate in the North Atlantic south of Iceland is based on GEOSSECS *C* and *Alk* data. However, because of problems with the titrators, no reliable carbon data north of 40°N could be obtained during the Atlantic GEOSSECS program, and Chen therefore had to extrapolate from data south of 40°N to cover the entire North Atlantic. For his estimate in the Greenland and Norwegian Seas he used winter/summer measurements obtained during the Hudson expedition in 1982. However, it was not possible with his technique to find the preindustrial reference level in these basins directly, since anthropogenic CO<sub>2</sub> has penetrated into the whole water column [*Chen et al.*, 1990, p. 1460]. It is therefore unclear to us how *Chen* [1993] was able to estimate an inventory in the Greenland and Norwegian Seas.

### Summary and Conclusions

On the basis of three information sources, (1) concurrent measurements of *C*, *Alk*, dissolved oxygen, temperature, and salinity on a specific ocean water sample, (2) information about the water age from measurements of tritium and helium isotopes, and (3) the history of the increase of atmospheric CO<sub>2</sub> over the last 200 years, it is possible to separate the anthropogenic CO<sub>2</sub> signal from the large background variability of *C* in the ocean. This method involves the important assumption of constant *C* : O<sub>2</sub> and *N* : O<sub>2</sub> stoichiometric ratios which is necessary to define a new quasi-conservative tracer  $\Delta C^*$

**Table 6.** Comparison of the Estimated Water Column Inventory of Anthropogenic CO<sub>2</sub> in the North Atlantic With Estimates From the *Stocker et al.* [1994] (SBW) 2.5 Dimensional Model for the Year 1982 by Latitude Belt

Latitude Belt,	SBW Model			Observations		
	Surface Area, 10 <sup>12</sup> m <sup>2</sup>	Inventory, Gt C	Specific Inventory, mol C m <sup>-2</sup>	Surface Area, 10 <sup>12</sup> m <sup>2</sup>	Inventory, Gt C	Specific Inventory mol C m <sup>-2</sup>
deg						
9°N - 36°N	21.4	5.8	23	22.0	11.3	43
36°N - 62°N	14.6	7.6	43	14.3	7.5	44
62°N - 80°N	5.0	5.4	90	4.6	1.3	24
Total	41.0	18.7	38 (mean)	40.9	20.1	41 (mean)

**Table 7.** Comparison of the Total Estimated Water Column Inventory of Anthropogenic CO<sub>2</sub> in the North Atlantic With Model Estimates (Year 1982)

	Global Uptake Rate, Gt C yr <sup>-1</sup>	Global Inventory, Gt C	North Atlantic <sup>a</sup> Inventory, Gt C
Observations (this study)			20 ± 4
<i>Stocker et al.</i> [1994]	1.99	113	18.7
<i>Sarmiento et al.</i> [1995]	1.86	106	18.4

<sup>a</sup> Atlantic Ocean between 10°N and 80°N.

from the information of source 1. This tracer reflects only the uptake of anthropogenic CO<sub>2</sub> and the air-sea disequilibrium when the water parcel last contact with the atmosphere, plus residual effects due to our choice of oxygen and alkalinity end-members, since the effects of the soft-tissue and carbonate pumps have been removed. Assuming that the ocean has been operating in a steady state and that the effective air-sea disequilibrium has not changed over time, the effective air-sea disequilibrium can be estimated directly from the interior for deep potential density surfaces not entirely affected by anthropogenic CO<sub>2</sub>. For the shallower potential density surfaces, information from sources 2 and 3 is used to reconstruct the effective air-sea disequilibrium. This permits us then to identify the anthropogenic CO<sub>2</sub> signal.

We applied this method to carbon and other tracer data from the North Atlantic Ocean sampled as part of the TTO NAS and TAS cruises in 1981 to 1983. The anthropogenic CO<sub>2</sub> distribution in the North Atlantic obtained in this way reflects the pathways of ocean uptake and consequent redistribution within the ocean. Highest concentrations of anthropogenic CO<sub>2</sub> are found in the shallow subtropical thermocline. Vertical penetration is small in the subtropical and temperature latitude but is large in the high latitudes, because of deep convection and downward transport associated with the NADW. We estimate a North Atlantic anthropogenic CO<sub>2</sub> inventory from 10°N to 80°N of 20 ± 4 Gt C.

We use anthropogenic CO<sub>2</sub> as a constraint to test the performance of two ocean models of different complexity (2.5-dimensional and three-dimensional model) to estimate the uptake of anthropogenic CO<sub>2</sub>. The agreement of the total inventory in the investigated region in the North Atlantic is excellent (18.7 Gt C and 18.4 Gt C, respectively), but a regional breakdown reveals important differences, mostly related to known deficiencies in the models.

Our method can be modified and extended easily, by using different methods to estimate the CO<sub>2</sub> air-sea disequilibrium at the time a water parcel was last in contact with the atmosphere. First, there is a possibility

to use chlorofluorocarbon observations to derive water ages, since the tritium-helium method fails in the southern hemisphere because of the very small tritium input into this region. Second, the rapidly increasing data set of wintertime measurements of  $\Delta f\text{CO}_2$  can be used to estimate the CO<sub>2</sub> air-sea disequilibrium more directly.

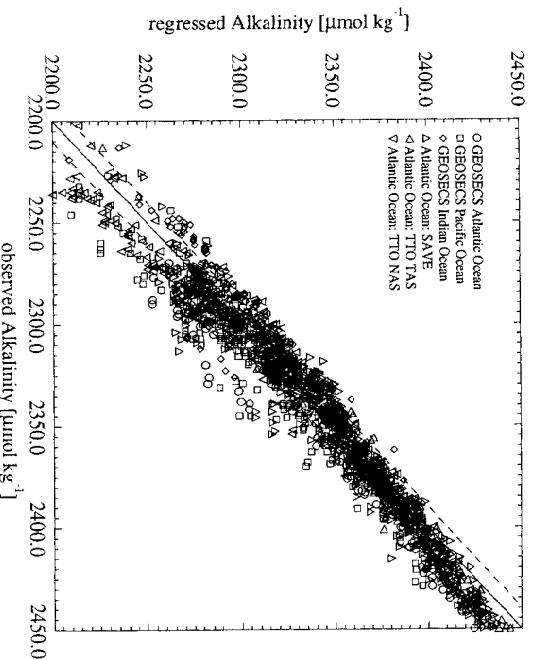
The strength of this new method will increase when data from the ongoing World Ocean Circulation Experiment (WOCE) will become available in the future. First the high quality carbon data will considerably lower the uncertainty associated with  $\Delta C^*$  and hence the estimate of anthropogenic CO<sub>2</sub>, and second, the global coverage (including transient tracers) will eventually make it possible to calculate a global inventory of anthropogenic CO<sub>2</sub>. Repeated surveys in certain regions, where good quality data are already available (Atlantic Ocean) would also permit determination of the increase of the anthropogenic CO<sub>2</sub> over time. These are very powerful constraints for any ocean model employed to estimate the uptake of anthropogenic CO<sub>2</sub>.

## Appendix A: Performed Concentrations

### Performed Alkalinity

Our estimate of performed *Alk* assumes that the anthropogenic transient has not affected the surface alkalinity in the oceans. The invasion of anthropogenic CO<sub>2</sub> affects the degree of equilibrium between *C* and calcite and aragonite, respectively. However, since surface waters are highly supersaturated with respect to these carbonates [Takahashi et al., 1981], the invasion of anthropogenic CO<sub>2</sub> does not lead to any calcite or aragonite dissolution, which would affect alkalinity.

We estimate performed *Alk* from a multiple linear regression model using the conservative tracers salinity (*S*) and *PO* as independent variables. *PO* is defined as  $PO = O_2 - r_{O_2}P$  [Broecker, 1974]. We chose an *O*<sub>2</sub> : *P* ratio of -170 as given by Anderson and Sarmiento [1994] rather than Broecker's [1974] original value of -135 or later value of -175 [Broecker et al., 1985b]. Using upper ocean *Alk* data (< 100 m) from the GEOSECS,



**Figure A1.** Plot of regressed alkalinity versus observed alkalinity for the world surface oceans. Regressed alkalinity is based on the multiple regression using salinity and the conservative tracer “ $PO$ ” [Broecker, 1974] (see (A1)). The dashed curves depict the estimated  $1\text{-}\sigma$  uncertainty of the multiple regression ( $11\ \mu\text{eq kg}^{-1}$ ). The multiple regression underpredicts the alkalinity at very high alkalinity concentrations. However, alkalinities of over  $2400\ \mu\text{mol kg}^{-1}$  occur only in the subtropical South Atlantic, and therefore only a small water mass (Subtropical Underwater) is affected.

TTO NAS, TTO TAS, and the SAVE programs gives the following relationship:

$$Alk^o = (367.5 + 54.9\ \text{psu}^{-1} \cdot S + 0.074\ \text{kg}\ \mu\text{mol}^{-1} \cdot PO)\ \mu\text{eq kg}^{-1};\ r^2 = 0.96, \quad (\text{A1})$$

where  $S$  and  $PO$  are in the appropriate units (practical salinity units and micromoles per kilogram, respectively). The standard error of the estimated  $Alk^o$  is  $11\ \mu\text{eq kg}^{-1}$  (see Figure A1). This relationship holds for the entire surface ocean as covered by the above cruises. These data have been collected primarily during summer conditions. However, studies at time-series locations in subtropical regions at station “S” and at the Hawaii Ocean Time-Series station (HOT) [Keeling, 1993] and high-latitude areas at stations around Iceland [Takahashi et al., 1993] showed that alkalinity, after normalization to constant salinity, reveals little seasonal cycle. The relationship (A1) should therefore yield good results for winter as well as summer conditions.

Takahashi et al. [1980] discussed in detail the alkalinity trends in the surface GEOSECS alkalinity data. For most of the warm waters of the oceans, surface alkalinity is primarily determined by the water balance at the sea surface, yielding very strong correlations with salinity.

Waters from the Southern Oceans and the North Pacific show a different trend which is caused by the upwelling of alkalinity rich deep waters produced by dissolution of calcium carbonates [Takahashi et al., 1980, p. 312 ff]. Since these waters also have high  $PO$ , inclusion of this tracer as an independent variable greatly improves the predictive value of the regression. Our regression systematically underpredicts the performed alkalinity at very high alkalinities ( $Alk^o > 2400\ \mu\text{eq kg}^{-1}$ ) (see Figure A1). These high alkalinities occur only in the subtropical South Atlantic Ocean, where alkalinity rich water from the south is undergoing strong evaporation thereby increasing  $Alk$  even more. Inclusion of temperature or silicate as independent variables does not help to solve this systematic underprediction. However, the affected water masses occur only in the upper 200 m in the subtropical South Atlantic, and therefore this deficiency does affect our analysis of anthropogenic CO<sub>2</sub> in the North Atlantic.

Chen and Pytkowicz [1979], Chen and Millero [1979], and later studies used temperature instead of  $PO$  as an independent variable. However, no single relationship was found for the entire ocean surface. This approach represents a large drawback because this introduces serious problems when waters originating from sources with a different relationship are mixed. No such problem exists in our relationship using  $PO$ .

### Performed O<sub>2</sub>

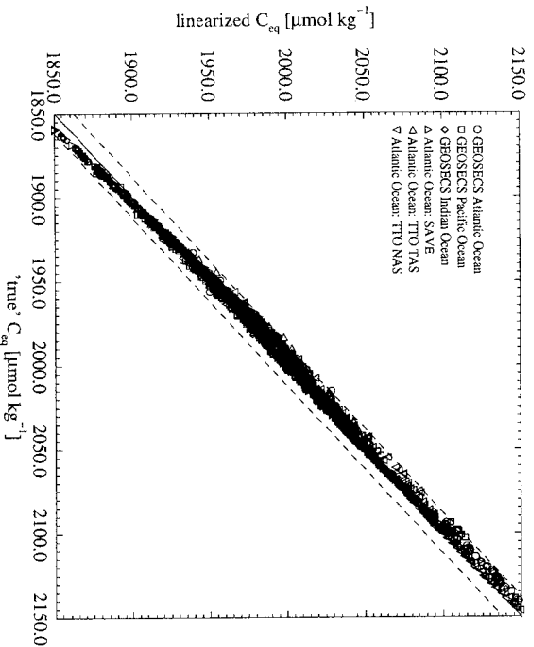
We assumed in (15) in the main text that dissolved oxygen in the ocean is in equilibrium with the atmosphere when the water parcel loses its contact with the atmosphere, and therefore set  $O_2^0$  equal to  $O_2^{\text{sat}}$ . Although air-sea exchange of oxygen is rather rapid, the surface waters of the ocean are often supersaturated or undersaturated. Broecker et al. [1985a] combined GEOSECS, NORPAX, and TTO surface data and found an average surface supersaturation of  $7\ \mu\text{mol kg}^{-1}$ . However, all these measurements were obtained during the summer period. Measurements obtained at time-series stations in subtropical regions (station “S” and HOT) show that the oxygen disequilibrium has a strong seasonality [Jenkins and Goldman, 1985; Emerson et al., 1993]. Supersaturation is highest in spring and summer when photosynthesis near the ocean surface is adding oxygen to the surface mixed layer. During the winter months, when most of the deeper waters are formed, O<sub>2</sub> is very close to its saturation value. Time series stations in the subarctic (station “P” and stations around Iceland) show the same seasonal behavior [Emerson, 1987; Takahashi et al., 1985b; Takahashi et al., 1993]. Wintertime measurements during the Hudson cruise in the Norwegian and Greenland Seas also showed oxygen concentration near saturation [Chen et al., 1990]. We therefore conclude that the average

supersaturation found by *Broecker et al.* [1985a] is an upper limit because it is summer-biased and that the average deep water formed during the winter season is near saturation for oxygen. However, to account for possible disequilibria, we assign an uncertainty of about 4  $\mu\text{eq kg}^{-1}$  (1-2%) to  $\text{O}_2^{\text{sat}}$  based on the results of the lime - series stations and the Hudson cruise.

### Calculation of $C_{\text{eq}}$

In order to keep the definition of  $\Delta C^*$  conservative, we linearize  $C_{\text{eq}}$  around ocean mean values of temperature, salinity, and alkalinity. The equilibrium concentration of  $C$  with respect to an atmospheric  $\text{CO}_2$  fugacity of 280  $\mu\text{atm}$  was first calculated using the dissociation constants for carbonic acid of *Goyet and Poisson* [1989], the dissociation constant for boric acid of *Dickson* [1990], the dissociation constant for water in seawater of *Dickson and Riley* [1979a], the dissociation constants for phosphoric acid of *Dickson and Riley* [1979b], and the  $\text{CO}_2$  solubility of *Weiss* [1974]. The linearization of  $C_{\text{eq}}$  yields

$$\begin{aligned} C_{\text{eq}}(S, T, Alk) \Big|_{f_{\text{CO}_2} = 280 \mu\text{atm}} = & \\ [2072.0 - 8.982^\circ\text{C}^{-1} \cdot (T - 9.0^\circ\text{C}) & \\ - 4.931 \text{ psu}^{-1} \cdot (S - 35.0 \text{ psu}) & \\ + 0.842 \text{ kg } \mu\text{eq}^{-1} \cdot (Alk - 2320.0 \text{ } \mu\text{eq kg}^{-1})] & \quad (\text{A2}) \\ \mu\text{mol kg}^{-1}, & \end{aligned}$$



**Figure A2.** Plot of linearized  $C$  equilibrium concentration  $C_{\text{eq}}(S, T, Alk)$  (see (A2)) versus directly calculated  $C$  equilibrium concentration using the full carbon chemistry equations. These equilibrium concentrations are for an atmospheric  $f_{\text{CO}_2}$  of 280  $\mu\text{atm}$ . This plot is based on surface ( $< 100$  m) temperature, salinity, and alkalinity data from the GEOSECS, TTO, and SAVE cruises. The dashed curves represent the the estimated 1- $\sigma$  uncertainty of 4  $\mu\text{mol kg}^{-1}$ .

where  $T$  denotes the temperature (degrees Celsius),  $S$  denotes the salinity (practical salinity units), and  $Alk$  denotes the alkalinity ( $\mu\text{eq kg}^{-1}$ ). Using the observed temperature, salinity, and alkalinity data of the GEOSECS, TTO and SAVE cruises, the 1- $\sigma$  standard deviation of the difference between the linearized equilibrium concentration  $C_{\text{eq}}$  and the directly calculated  $C_{\text{eq}}$  is found to be about 3  $\mu\text{mol kg}^{-1}$  (see Figure A2). However, for waters with a very low or very high  $C_{\text{eq}}$ , the discrepancy can be as large as 8  $\mu\text{mol kg}^{-1}$ . To account for this, we increase the uncertainty of the linearized equilibrium concentration  $C_{\text{eq}}$  to 4  $\mu\text{mol kg}^{-1}$ . When  $C_{\text{eq}}$  is used in context of (15),  $Alk$  is replaced by  $Alk^0$ .

## Appendix B: Data Considerations

### Measurement Methods, Precision, and Accuracy

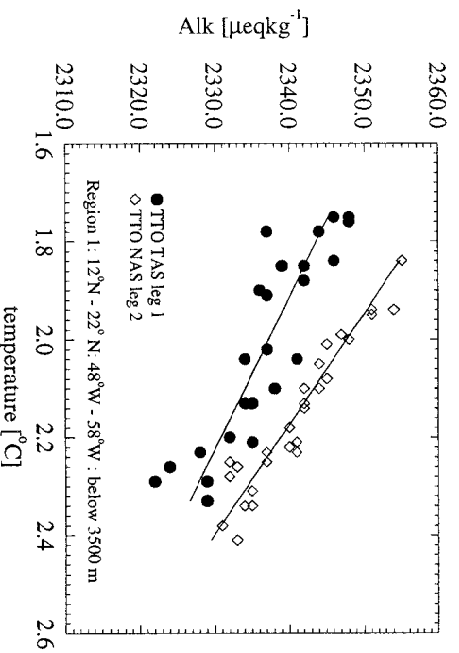
The  $C$  and  $Alk$  determinations during the GEOSECS program employed a potentiometric titration technique followed by a Gran type processing of the titration output [*Bradshaw et al.*, 1981]. The precision of the  $Alk$  data is estimated to be about  $\pm 9 \mu\text{eq kg}^{-1}$ , and for  $C$  it is about  $\pm 10 \mu\text{mol kg}^{-1}$  [*Brewer et al.*, 1986]. The  $Alk$  data during the TTO NAS and TAS cruises were obtained by a slightly revised potentiometric technique [*Brewer et al.*, 1986] which resulted in an improved precision of about  $\pm 5 \mu\text{eq kg}^{-1}$ . The  $C$  data were also obtained from the titration, but in the case of the TTO NAS cruise these were not used in our study. Instead, the  $C$  data were calculated from the  $Alk$  and  $f_{\text{CO}_2}$  measurements using thermodynamic relationships [*Takahashi and Brewer*, 1986]. The precision of this recalculated  $C$  data is probably similar to the precision of the potentiometric  $C$  determinations during the TTO/TAS cruise and of the order of  $\pm 5 \mu\text{mol kg}^{-1}$ . During the SAVE cruise, only  $f_{\text{CO}_2}$  and  $C$  were measured. The  $C$  determinations were done conventionally with a precision of about 2  $\mu\text{mol kg}^{-1}$  (T. Takahashi, personal communication, 1995). The  $Alk$  data were calculated from  $C$  and  $f_{\text{CO}_2}$ . We estimate for  $Alk$  a precision of about  $\pm 4 \mu\text{eq kg}^{-1}$ .

### Internal Consistency

We have applied the following corrections (in micromoles per kilogram) to the GEOSECS  $C$ ,  $Alk$ , and  $P$  data as summarized by *Anderson and Sarmiento* [1994]:

stations 28-34	$C$ -17	[ <i>Bainbridge</i> , 1981b, p. 2]
Pacific: $C$ and $Alk$	various	[ <i>Craig et al.</i> , 1981, p. 2]
stations 201-454	$C$ -15	[ <i>Takahashi</i> , 1983, p. 5]
various corrections to $P$		[ <i>Broecker et al.</i> , 1985b]

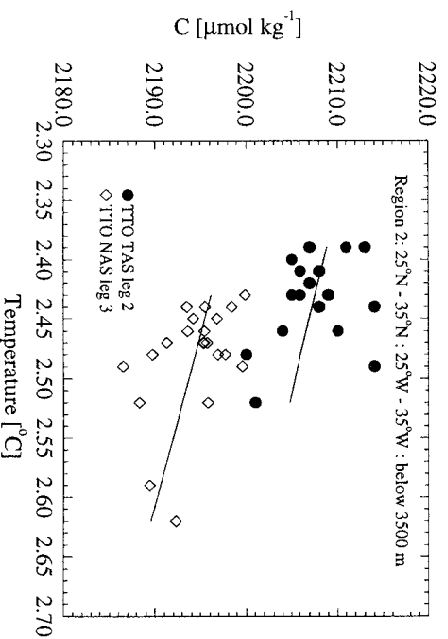
The internal consistency of the Atlantic data sets was investigated by determining deep ocean ( $> 3500$  m)  $C$



**Figure A3.** Alkalinity versus temperature in the region from 12°N to 22°N and from 48°W to 58°W and for depths below 3500 m in the North Atlantic. Values for TTO TAS leg 1 are shown by circles and for TTONAS leg 2 by diamonds. The lines represent the results of linear regressions. A mean difference of 9  $\mu\text{eq kg}^{-1}$  has been found between the two cruises.

and *Alk* trends versus temperature in 10° by 10° areas which have been repeatedly sampled by different legs or cruises. We identified four regions for the TTO NAS, two regions for the TTO TAS, and seven regions for the SAVE program. The revised carbon data from the TTONAS cruise showed good internal consistency. However, systematic offsets for TTONAS and SAVE data have been identified.

Comparison of the trends of *Alk* versus temperature in the region from 12°N to 22°N and from 48°W to 58°W and below 3500 m show that the TTONAS leg 1

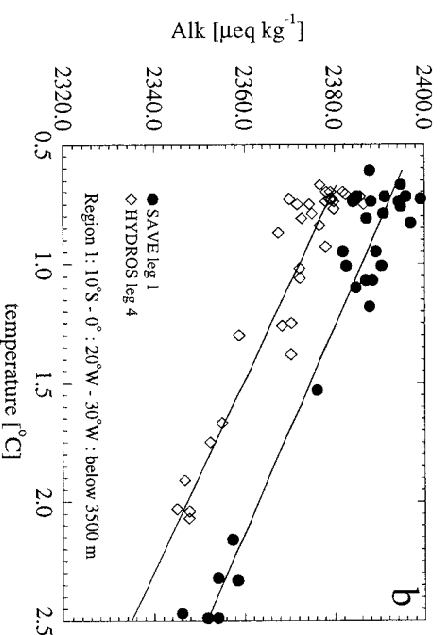
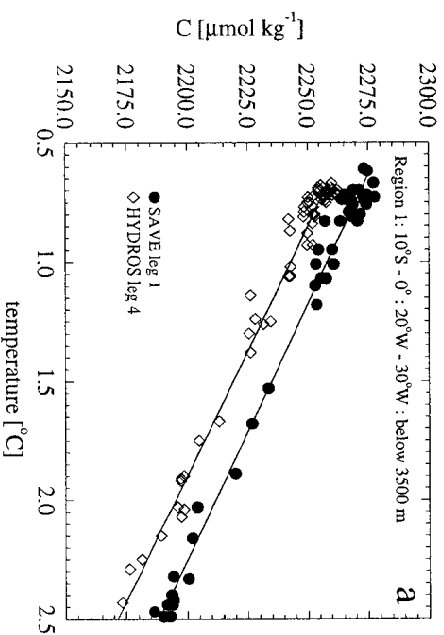


**Figure A4.** *C* versus temperature in the region from 25°N to 35°N and from 25°W to 35°W and for depths below 3500 m in the North Atlantic. Values for TTONAS leg 2 are depicted by circles and for TTONAS leg 3 by diamonds. The lines represent the results of linear regressions. The mean difference between the two cruises amounts to 13  $\mu\text{mol kg}^{-1}$ .

measurements are systematically lower by about 9  $\mu\text{eq kg}^{-1}$  than the TTONAS determinations (see Figure A3). This is almost twice the estimated precision of the *Alk* measurements. Comparison of *C*, salinity, and nutrient data show no such offset. We therefore conclude that this offset is due to analytical problems and should be corrected for.

A similar offset was identified for the *C* data of TTONAS leg 2. In Figure A4, *C* data from the region from 25°N to 35°N and from 25°W to 35°W and below 3500 m are plotted versus temperature. We calculated a significant mean offset of 13  $\mu\text{mol kg}^{-1}$  between the TTONAS leg 2 and the TTONAS *C* data, with the TTONAS being higher. No such difference is found in the other tracers analyzed, and we are therefore forced to conclude that this offset is probably not “real”.

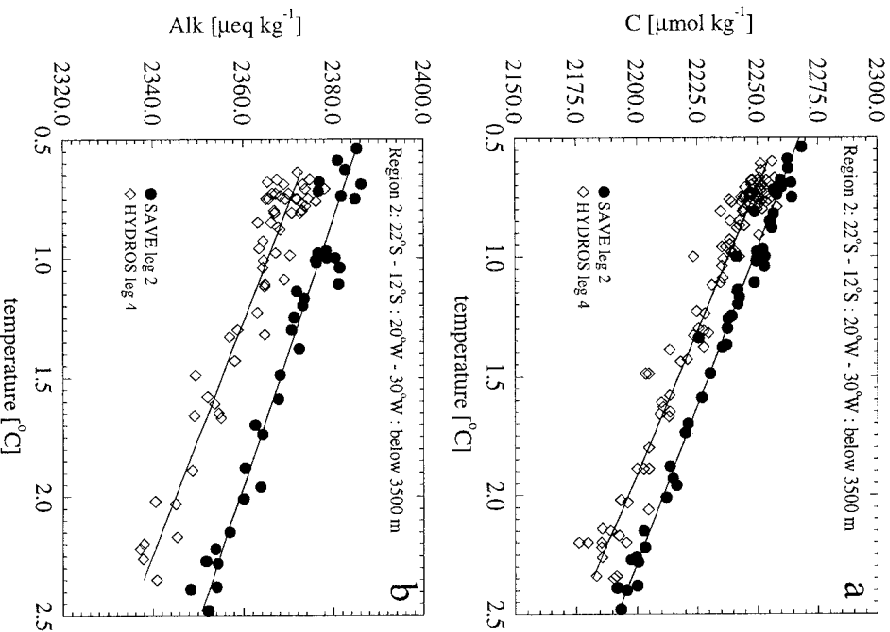
Comparison of *C* versus temperature in the region from 10°S to the equator and from 20°W to 30°W and



**Figure A5.** (a) *C* versus temperature in the region from 10°S to 0° and from 20°W to 30°W and for depths below 3500 m in the Equatorial Atlantic. Values for SAVE leg 1 are shown by circles and for HYDROS leg 4 (equals SAVE leg 6) by diamonds. The lines represent the results of linear regressions. A mean difference of 15  $\mu\text{mol kg}^{-1}$  is found between the two legs. (b) The same for *Alk*. The difference for *Alk* is 19  $\mu\text{eq kg}^{-1}$ .



below 3500 m shows a significant systematic difference between SAVE leg 1 and HYDROS leg 4 (equals SAVE leg 6) of approximately  $15 \mu\text{mol kg}^{-1}$  (Figure A5a). Since the SAVE  $Alk$  has been calculated from  $C$  and  $f\text{CO}_2$  determinations, this offset should also be evident in the  $Alk$  versus temperature trend from the same region. As shown in Figure A5b,  $Alk$  data from SAVE leg 1 is indeed systematically higher by about  $19 \mu\text{eq kg}^{-1}$ , confirming our expectation. We found a similar problem with the  $C$  and  $Alk$  data of SAVE leg 2. Figure A6a shows  $C$  versus temperature in the region from  $22^\circ\text{S}$  to  $12^\circ\text{S}$  and from  $20^\circ\text{W}$  to  $30^\circ\text{W}$  and for depths below  $3500 \text{ m}$ .  $C$  data from SAVE leg 2 are consistently higher than data from HYDROS leg 4 (SAVE leg 6) by approximately  $13 \mu\text{mol kg}^{-1}$ . The  $Alk$  data of SAVE leg 2 from the same region also show a systematic offset of about  $12 \mu\text{eq kg}^{-1}$ , as expected (Figure A6b). A comparison of HYDROS leg 4 with the other SAVE legs



**Figure A6.** (a)  $C$  versus temperature in the region from  $22^\circ\text{S}$  to  $12^\circ\text{S}$  and from  $20^\circ\text{W}$  to  $30^\circ\text{W}$  and for depths below  $3500 \text{ m}$  in the Equatorial Atlantic. Values for SAVE leg 2 are shown by circles and for HYDROS leg 4 (equals SAVE leg 6) by diamonds. The lines represent the results of linear regressions. A mean difference of  $13 \mu\text{mol kg}^{-1}$  is found between the two legs. (b) The same for  $Alk$ . The difference for  $Alk$  is  $12 \mu\text{eq kg}^{-1}$ .

(except leg 1 and 2) and the corrected TTO TAS data reveals no additional inconsistencies in the  $C$  and  $Alk$  data. Investigation of the trends of the other tracers (salinity and nutrients) do not show consistency problems, so that temporal variability can be excluded as a cause. We conclude therefore that the  $C$  determinations of SAVE leg 1 and 2 have a consistent offset, which then also affected the calculated  $Alk$  data.

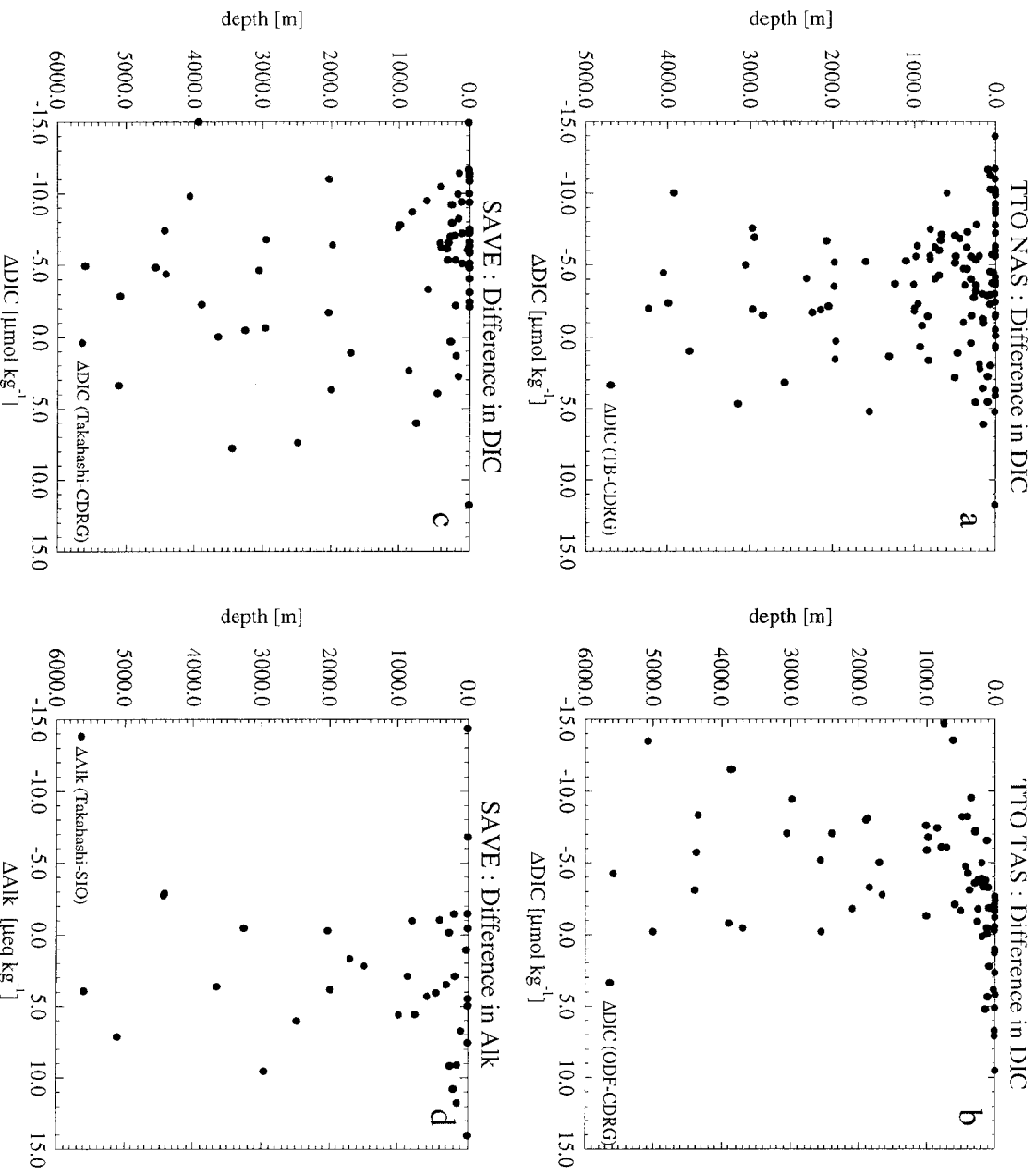
In summary, we found and applied the following corrections to the carbon data:

TTO TAS leg 1 (1-54)	$Alk_{corr} = Alk + 9 \mu\text{eq kg}^{-1}$
TTO TAS leg 2 (55-94)	$C_{corr} = C - 13 \mu\text{mol kg}^{-1}$
SAVE leg 1 (1-43)	$C_{corr} = C - 15 \mu\text{mol kg}^{-1}$
SAVE leg 1 (1-43)	$Alk_{corr} = Alk - 19 \mu\text{eq kg}^{-1}$
SAVE leg 2 (44-105)	$C_{corr} = C - 13 \mu\text{mol kg}^{-1}$
SAVE leg 2 (44-105)	$Alk_{corr} = Alk - 12 \mu\text{eq kg}^{-1}$

### Accuracy Assessment

We assessed possible inaccuracies of the corrected Atlantic data by comparing them with the shore-based  $C$  and  $Alk$  measurements obtained by the Carbon Dioxide Research Group (CDRG) at the Scripps Institution of Oceanography (C.D. Keeling, personal communication, 1994). The CDRG  $C$  data were measured employing a cryogenic vacuum extraction method with a reported precision of about  $\pm 0.5 \mu\text{mol kg}^{-1}$  and accuracy of about  $\pm 1 \mu\text{mol kg}^{-1}$  (T.J. Lueker et al., Inorganic carbon variations in surface waters near Bermuda, submitted to the *Journal of Marine Chemistry*, 1996) (Hereinafter referred to as Lueker et al., submitted manuscript, 1996).  $Alk$  was determined using a potentiometric titration with an estimated precision of  $\pm 2 \mu\text{eq kg}^{-1}$  and accuracy of about  $\pm 5 \mu\text{eq kg}^{-1}$  (Lueker et al., submitted manuscript, 1996)

For TTO NAS and TTO TAS,  $C$  data from CDRG and from Brewer et al. [1986] were available from the same bottles. In the case of SAVE,  $C$  and  $Alk$  from CDRG and from Oceanographic Data Facility [ODF, 1992a; ODF, 1992b, T. Takahashi, personal communication, 1995] were available for the same bottles. The revised TTO NAS  $C$  data no longer have the depth dependency that was described by Bradshaw and Brewer [1988], but there is still a substantial amount of scatter in the difference between the Brewer et al. [1986] TTO NAS revised  $C$  data and the CDRG data (see Figure A7a). The mean difference is  $-3.4 \pm 5.1 \mu\text{mol kg}^{-1}$  (number of samples (N) = 126). The difference between the PCODF [1986b] TTO TAS and the CDRG  $C$  data is approximately the same (Figure A7b). The mean difference for all depths is  $-3.6 \mu\text{mol kg}^{-1}$  with a standard deviation of  $5.7 \mu\text{mol kg}^{-1}$  (N = 77). However, all differences below  $200 \text{ m}$  are negative, and the mean difference for the data below  $1500 \text{ m}$  is  $-5.3 \pm 3.7$



**Figure A7.** (a) Difference between the *Takahashi and Brewer* [1986] revised TTO NAS and the Carbon Dioxide Research Group (CDRG) TTO NAS  $C$  data sets. (b) Difference between the *PCODF* [1986b] TTO TAS and CDRG TTO TAS  $C$  data sets. (c) Difference between the corrected T. Takahashi (personal communication, 1995) SAVE and CDRG SAVE  $C$  data sets. (d) Difference between the corrected T. Takahashi (personal communication, 1995) SAVE and CDRG SAVE  $Alk$  data sets. All samples were drawn from the same bottles.

$\mu\text{mol kg}^{-1}$  ( $N = 20$ ). Although this is a significant systematic difference at the 5% confidence level, we applied no correction to the PCODF/TTO/TAS data, since this difference is close to the measurement accuracy of these data.

Figure A7c shows the difference between the corrected (T. Takahashi, personal communication, 1995) SAVE and the CDRG  $C$  data. The upper ocean Takahashi (personal communication, 1995)  $C$  data seem to be systematically lower by approximately  $8 \mu\text{mol kg}^{-1}$ , whereas below 1500 m the difference is  $-2.9 \mu\text{mol kg}^{-1}$  with a standard deviation of  $5.6 \mu\text{mol kg}^{-1}$  ( $N = 21$ ).

The mean difference for all depths is found to be  $-5.1 \pm 5.4 \mu\text{mol kg}^{-1}$  ( $N = 74$ ) which is significant at the 5% level. However, no further correction has been applied to the SAVE data, since this difference is in the range of the accuracy of the  $C$  determinations during this cruise.  $Alk$  in Figure A7d shows a mean difference over all depths of  $3.4 \pm 5.6 \mu\text{eq kg}^{-1}$  ( $N = 38$ ). This comparison shows that no systematic differences exist between the TTO NAS, TTO TAS, and SAVE  $C$  and  $Alk$  data sets. However, the CDRG  $C$  data seem to be consistently higher by  $2\text{--}3 \mu\text{mol kg}^{-1}$ . The reason for this discrepancy is presently not known.

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