Improvements on the back-calculation technique for estimating anthropogenic CO₂.

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ABSTRACT.

The back-calculation technique for evaluating the anthropogenic CO₂ (C_{ANT}) input corrects total inorganic carbon for the remineralization of organic matter and the dissolution of calcium carbonate, along with subtracting the pre-industrial equilibrium total inorganic carbon. This technique is mainly dependent on the estimation of the preformed values of total alkalinity, oxygen and partial pressure of CO₂ (pCO₂). A new approach for estimating the preformed alkalinity (TA⁰) in the North Atlantic Ocean is suggested. TA⁰ is parameterized as a function of the inorganic to organic carbon decomposition ratio in the water column in agreement with sediment trap data and a recent review by Milliman *et al.* (*Deep-Sea Research I*, 46, 1653-1669, 1999), which gives evidence for a considerable calcium carbonate dissolution in the upper 500-1000 m of the ocean, above the lysocline. We recalculated the C_{ANT} content in a section along the Eastern North Atlantic (OacesNAatlIIB-93) using this new TA⁰, the Mehrbach *et al.* (*Limnology and Oceanography*, 8, 897-907, 1973) CO₂ dissociation constants, and including the effect of water vapor pressure on estimation of the pre-industrial pCO₂. Our findings lead us to conclude that the CO₂ disequilibrium when water masses are formed is small and not significant. Direct and indirect evidence based on available high-quality CO₂ data taken in formation areas in late winter conditions support this argument.

Keywords: Anthropogenic Carbon, Preformed Alkalinity, North Atlantic Ocean, CO₂ Disequilibrium.

1. INTRODUCTION.

The oceans have taken up from one third to one half of the anthropogenic CO₂ emitted to the atmosphere (Siegenthaler and Sarmiento, 1993; Watson *et al.*, 1995). In this sense, the Atlantic Ocean is considered to be the most important CO₂ sink (Takahashi *et al.*, 1997). In particular, the North Atlantic Ocean is an area of deep-water formation where much of the CO₂ taken up is sequestered on centennial time scales because of the large scale meridional overturning circulation.

The gravitational settling of biogenic debris from the photic zone transports carbon to the deep ocean. This debris consists of soft-tissue organic compounds and hard siliceous and calcareous skeletons, and its remineralization in the water column contributes to the creation and maintainance of concentration gradients in the ocean. This process is known as the “biological pump”, divided into the “soft-tissue pump” and the “carbonate pump” (Volk and Hoffert, 1985).

The anthropogenic CO₂ uptake is calculated by correcting total inorganic carbon for these processes, regeneration of organic matter and dissolution of particulate carbonates, as independently proposed by Brewer (1978) and Chen and Millero (1979), and reformulated by Gruber *et al.* (1996) (hereinafter GSS'96) using tracer ages and a conservative tracer called C*, which is similar to the conservative parameter CAO earlier described by Ríos *et al.* (1989).

Several estimates of anthropogenic CO₂ have been performed in the North Atlantic Ocean using historical data sets such as GEOSECS or TTO (Chen, 1982; Gruber *et al.*, 1996). Recently, other inventories have been done relying on more accurate data sets (Körtzinger *et al.*, 1998; Wanninkhof *et al.*, 1999a).

In this work we analyse some of the caveats of the most widely used methodology for estimating anthropogenic CO₂, that proposed by GSS'96, with especial emphasis on the evaluation of preformed alkalinity by means of modelling the alkalinity pump using sediment trap data. Our analysis was performed using a publicly-available high-quality data set for CO₂ measurements from the North Atlantic Ocean Atmosphere Carbon Exchange Study. We selected the National Oceanic and Atmospheric Administration Cruise Leg IIB (OacesNatIIB-93, July/August, 1993) covering from 35°N to 63°N along 20°W (www.aoml.noaa.gov/ocd/oaces). The anthropogenic CO₂ inventory along this leg is calculated introducing improvements on the GSS'96 methodology, and finally the consistency of our results is discussed.

2. FORMULATION.

2.1. The back-calculation technique.

The back-calculation technique as formulated by GSS'96 uses a conservative parameter C*, which corrects total inorganic carbon for biological activity, both the soft-tissue and the carbonate pumps. C* can be expressed in terms of current or preformed variables:

$$C^*(\tau) = C_T + O_2/R_C - \frac{1}{2} (TA + O_2/R_N) = C_T^0(\tau) + O_2^0/R_C - \frac{1}{2} (TA^0 + O_2^0/R_N) \quad (1)$$

where C_T is the total inorganic carbon concentration, O_2 is dissolved oxygen, TA stands for alkalinity, R_C ($=-\Delta O_2/\Delta C$) and R_N ($=-\Delta O_2/\Delta N$) are stoichiometric coefficients and τ stands for the water mass age. $C^*(\tau)$, as NO or PO (Broecker, 1974), reflects the origin of the water mass, being independent of the biological activity accounted for since the water mass lost contact with the atmosphere (that is, τ) but containing the time-increasing CO₂ anthropogenic signal taken up by atmospheric contact at the outcrop region. $C_T^0(\tau)$ stands for the preformed inorganic carbon concentration the water mass acquires when formed at oxygen saturation (O_2^0) and preformed alkalinity (TA^0) conditions. Oxygen saturation is calculated from the equation of Benson and Krause (UNESCO, 1986). As alkalinity is not affected by the anthropogenic CO₂ increase in the atmosphere, present and pre-industrial alkalinity preformed values are equal and can be derived from contemporary winter measurements of surface TA . In this sense, TA^0 is usually calculated

from linear regressions using conservative properties such as salinity, potential temperature, PO or NO (Broecker, 1974). Different equations have been proposed for TA^0 (Chen and Pytkowicz, 1979; Chen *et al.*, 1990; GSS'96; Millero *et al.*, 1998; Sabine *et al.*, 1999; Wanninkhof *et al.*, 1999a).

GSS'96 states that there is an effective and time-independent CO_2 air-sea disequilibrium (ΔC_{Tdis}) when the water loses contact with the atmosphere, thus the same whether the water mass is formed at a certain time (τ) or in pre-industrial times (π):

$$\Delta C_{Tdis} = C_T^0(\tau) - C_T^{eq}(\theta, S, TA^0, pCO_2^\tau) = C_T^0(\pi) - C_T^{eq}(\theta, S, TA^0, pCO_2^\pi) \quad (2)$$

where C_T^0 are the preformed C_T values when the water mass is currently formed, $C_T^0(\tau)$, and in pre-industrial times, $C_T^0(\pi)$, calculated according to equation 1. C_T^{eq} are the C_T values in equilibrium with the atmospheric partial pressure of CO_2 when the water mass is currently formed (pCO_2^τ) and in pre-industrial times (pCO_2^π). C_T^{eq} are calculated from thermodynamic equations as a function of hydrographic variables, potential temperature (θ) and salinity (S), preformed alkalinity and the corresponding atmospheric pCO_2 (Neftel *et al.*, 1994). ΔC_{Tdis} reflects the CO_2 -air-sea disequilibrium in C_T when water masses are formed once carbon is corrected for biology.

GSS'96 defined the conservative variable $\Delta C^*(\tau)$, which depends on the anthropogenic input, and thus the water mass age (τ), and includes the steady-state disequilibrium term:

$$\Delta C^*(\tau) = C_{ANT} + \Delta C_{Tdis} = C^*(\tau) - C^*(\pi) + \Delta C_{Tdis} \quad (3)$$

Combining 1 to 3:

$$\Delta C^*(\tau) = C_T - O_2/R_C - \frac{1}{2}(TA + O_2/R_N) - (C_T^0(\pi) + O_2^0/R_C - \frac{1}{2}(TA^0 + O_2^0/R_N)) + C_T^0(\pi) - C_T^{eq}(\theta, S, TA^0, pCO_2^\pi) = C_T - AOU/R_C - \frac{1}{2}(\Delta TA + AOU/R_N) - C_T^{eq\pi} \quad (4)$$

where $C_T^{eq\pi}$ denotes the $C_T^{eq}(\theta, S, TA^0, pCO_2^\pi)$ term, AOU denotes Apparent Oxygen Utilization and $\Delta TA = TA - TA^0$. Finally, recombining equation 3 and 4:

$$C_{ANT} = C_T - AOU/R_C - \frac{1}{2}(\Delta TA + AOU/R_N) - C_T^{eq\pi} - \Delta C_{Tdis} \quad (5)$$

The GSS'96 disequilibrium term is evaluated by density intervals employing two different methods but in both assuming that the air-sea disequilibrium has remained constant over time. In uncontaminated regions along isopycnals where no anthropogenic carbon is supposed, $\Delta C^*(\tau)$ reflects the effective air-sea disequilibrium. Therefore, ΔC_{Tdis} is calculated as the mean of $\Delta C^*(\tau)$ within a given isopycnal interval:

$$\Delta C_{Tdis} = \Delta C^*(\tau) \big|_{\sigma=cte} \quad (6)$$

On shallower surfaces with measurable tracer concentrations, the disequilibrium is estimated from the corresponding atmospheric CO_2 level matching a tracer-estimated age (pCO_2^τ). GSS'96

uses tritium-³He ages as an approximation to true ages, disregarding non-linear effects on the tracer age and assuming that the transport is mainly advective. The CO₂ disequilibrium is evaluated as:

$$\Delta C_{Tdis} = [C_T - AOU/R_C - 1/2 \cdot (\Delta TA + AOU/R_N) - C_T^{eq}(\theta, S, TA^0, pCO_2^\tau)] \big|_{\sigma=cte} \quad (7)$$

As a consequence of assuming steady-state in the disequilibrium term (equation 2), the intrinsic definition of C_{ANT} can also be expressed as:

$$C_{ANT} = C_T^0(\tau) - C_T^0(\pi) = C_T^{eq}(\theta, S, TA^0, pCO_2^\tau) - C_T^{eq}(\theta, S, TA^0, pCO_2^\pi) \quad (8)$$

The second half of equation 8 substituted in 5 yields equation 7, thus, equation 7 is a consequence of assuming a steady-state disequilibrium.

Summing up, the GSS'96 methodology assumes: i) total alkalinity is not significantly affected by the CO₂ increase in the atmosphere; ii) the effective CO₂ air-sea disequilibrium has stayed constant within the outcrop region of a particular isopycnal surface; iii) water transport is mainly along isopycnal surfaces.

According to equation 8, C_{ANT} can be directly derived as the difference between C_T in equilibrium with the atmospheric CO₂ content when the water mass is formed at a certain age (τ) and in pre-industrial (π) times, as calculated in Tait *et al.* (2000) and Thomas and Ittekkot (2001). This is not a shortcut, as stated by GSS'96, but a direct consequence of the assumption of a constant CO₂ disequilibrium with time. With equation 8 no C_T measurements are even necessary; the key factor is an exact knowledge of the water mass age. Although the individual C_T^{eq} calculations are affected by inaccuracies in the estimation of TA^0 and in the chosen set of thermodynamic constants, the final errors in C_{ANT} due to both sources of uncertainty practically cancel out, as both C_T^{eq} are modified in the same manner but with opposing sign.

2.2. Inorganic to Organic carbon decomposition Ratio (IOR).

The ratio between the carbon variation due to dissolution of calcium carbonate (ΔC_i) and that derived from the decomposition of organic matter (ΔC_o) can be expressed as:

$$IOR = \frac{\Delta C_i}{\Delta C_o} = \frac{1/2(TA - TA^0 + AOU/R_N)}{AOU/R_C} = R_C(\Delta TA/AOU + 1/R_N)/2 \quad (9)$$

where all the terms were explained previously. Thus, if IOR and AOU are known the variation of alkalinity due to redissolution of carbonates (ΔTA) is calculated as:

$$\Delta TA = (2 \cdot IOR/R_C - 1/R_N) \cdot AOU \quad (10)$$

The ratio between soft and hard material decomposition varies with depth. The upper ocean is supersaturated with calcium carbonate (Broecker and Peng, 1982; Takahashi *et al.*, 1981), and therefore the regeneration of inorganic carbon is predominantly by soft-tissue remineralisation in this upper layer (Honjo *et al.*, 1982; Honjo and Manganini, 1993). However, a recent review of the

global carbonate budget performed by Milliman *et al.* (1999) showed evidence that a considerable portion of surface-produced calcite, as much as 60-80%, dissolves in the upper 1000 m, above the lysocline, as a result of biological mediation. In deeper waters, the dissolution of hard material predominates because of the increased pressure, decreased temperature and the longer residence time (Broecker and Peng, 1982).

Broecker and Peng (1982), using GEOSECS data covering various oceans, estimated an IOR of 0.25 for the permanent thermocline and about 1 for deep waters. Takahashi *et al.* (1985) calculated IOR values for the North Atlantic from 0.09 to 0.15. In the Eastern North Atlantic Ocean Ríos *et al.* (1995) found an IOR of 0.16 for the upper 2300 m and 1.05 for deeper waters.

Silicon is also exported, as opal in biogenic debris (mostly as diatom frustules), and mainly redissolved in the deep ocean. As for calcium carbonate, most opaline silica dissolution takes place below the main thermocline. Thus, the high covariation between the alkalinity and the silicate fields (Brewer *et al.*, 1995; Broecker and Peng, 1982; Ríos *et al.*, 1995), probably exists because the dissolution of these hard structures is biologically stimulated in micro-environments such as marine snow, zooplankton guts, etc.

3. EVIDENCE FOR AN INACCURATE ESTIMATION OF TA^0 AND $C_T^{eq\pi}$.

In this section we demonstrate that the TA^0 parameterization proposed by GSS'96 and other authors contradicts the knowledge about calcium carbonate dissolution in the oceans. A new parameterization is introduced and validated. Likewise, several improvements are also introduced to estimate the C_T in equilibrium with the pre-industrial atmosphere, $C_T^{eq\pi}$.

3.1. The alkalinity pump, estimation of TA^0 .

As previously mentioned, there is a good covariation between the processes controlling alkalinity and silicate variability. In this sense, the silicate increase due to dissolution of opal (ΔSi) can be estimated by an approach similar to that used to determine the alkalinity variation due to dissolution of carbonate (ΔTA). As ΔTA is $TA - TA^0$, ΔSi is estimated as the difference between the current silicate concentration and the preformed value ($\Delta Si = Si - Si^0$). As an approximation to the winter mixed layer, and thus preformed, silicate concentrations, a linear relationship is obtained between silicate and potential temperature for the layer between 50 and 200 m using data from the OacesNatlIIB-93:

$$Si^0 \pm 0.93 = (10.2 \pm 0.5) - (0.67 \pm 0.05) \cdot \theta \quad r^2=0.69 \quad n=92 \quad (11)$$

where Si^0 is preformed silicate and θ is potential temperature. Equation 11 can be applied for waters with $\theta > 2^\circ C$, with no Antarctic influence; otherwise it would underestimate Si^0 .

The relationship between the increase of silicate and alkalinity due to dissolution of opal and calcium carbonate, respectively, is shown in Figure 1. ΔSi was calculated from equation 11 and

ΔTA using different parameterizations for TA^0 : GSS'96, Millero *et al.* (1998) and Wanninkhof *et al.* (1999a). The GSS'96 TA^0 function was obtained from top 100 m data from the whole Atlantic Ocean and reported with an uncertainty of $11 \mu\text{mol}\cdot\text{kg}^{-1}$. The Millero *et al.* (1998) TA^0 function was obtained from surface data from the whole North Atlantic Ocean (30°N - 80°N), reported with an uncertainty of $5 \mu\text{mol}\cdot\text{kg}^{-1}$. The Wanninkhof *et al.* (1999a) TA^0 parameterization was obtained from the particular data set obtained along about $25/32^\circ\text{W}$ from 43°S to 62°N , occupied as part of NOAA-OACES during July 1991 and July/August 1993, this TA^0 parameterization was calculated with top 100 m data and reported with an uncertainty of $5.2 \mu\text{mol}\cdot\text{kg}^{-1}$.

The first two parameterizations give systematic negative values of ΔTA despite the net increase of silicate from 0 to $10 \mu\text{mol}\cdot\text{kg}^{-1}$. However, the Wanninkhof *et al.* (1999a) TA^0 function yields positive ΔTA in the former range. As mentioned previously, there is an increasing amount of evidence suggesting a considerable dissolution of calcium carbonate above the chemical lysocline (Milliman *et al.*, 1999; Mintrop *et al.*, 1999; Yu *et al.*, 2001). Hence, the first two TA^0 parameterizations seem questionable. This fact is also suggested by the variability with depth of the IOR values calculated by substituting TA^0 from GSS'96 in equation 9 (Figure 2). Once again there exists a systematic shift to negative values of IOR in the upper 2000 m, indicating precipitation of calcium carbonate contrary to the conclusions of Milliman *et al.* (1999) and the previously cited values for IOR in the upper water column [0.25 from Broecker and Peng (1982), 0.16 from Ríos *et al.* (1995)].

The Millero *et al.* (1998) TA^0 parameterization is based on surface measurements of TA all over the North Atlantic Ocean, expressed as a function of temperature. Most of this data was collected in summer or spring. Consequently, they do not reflect the winter-time conditions, being affected by seasonal warming. Accordingly, TA^0 values are overestimated because of the shift to higher temperatures in the TA^0 function.

The GSS'96 TA^0 empirical function relies on data from the top 100 m and depends on the conservative parameters salinity and PO (Broecker, 1974). This parameterization was also obtained from data collected primarily during summer conditions. However, it should yield reliable results for winter, as salinity normalized alkalinity has a small seasonal cycle (Takahashi *et al.*, 1993), as also argued by GSS'96. We speculate that the GSS'96 TA^0 function must suffer from biases in the initial TA data set: the precision of TA measurements during GEOSECS (1972-1978) and TTO-NAS (1981) was low (± 9 and $\pm 5 \mu\text{mol}\cdot\text{kg}^{-1}$, respectively, Brewer *et al.*, 1986) compared to current measurements (less than $1 \mu\text{mol}\cdot\text{kg}^{-1}$, Mintrop *et al.*, 2000). It may also suffer from the influence of high TA values due to the predominance of South Atlantic samples in the GSS'96 analysis and finally of a bias in the data values for alkalinity, oxygen, phosphate and salinity, as taken from the seasonal thermocline, especially oxygen which is affected by outgassing.

The TA^0 function proposed by Wanninkhof *et al.* (1999a) also uses TA, salinity and NO data from top 100 m but in contrast to Millero *et al.* (1998) and GSS'96 TA^0 functions yields positive values for ΔTA in the upper layer. Therefore it is presumably a correct model for the TA^0 of water masses in the North Atlantic.

In order to avoid the use of any TA^0 parameterization, we adjusted IOR as a polynomial function with depth. This polynomial was obtained as the best fit, in a least square sense, for the IOR values calculated from equation 9, where ΔTA is calculated as $m \cdot \Delta Si$, ($\Delta Si = Si - Si^0$, Si^0 from equation 11). Therefore, the polynomial equation and m are calculated iteratively until the best fit to the data is obtained. The final polynomial expression for IOR with depth was obtained with $m=1.42$, thus:

$$IOR \pm 0.03 = 0.003117 \cdot z^5 - 0.04608 \cdot z^4 + 0.2313 \cdot z^3 - 0.4457 \cdot z^2 + 0.3489 \cdot z + 0.0371$$

$$r^2=0.94 \quad n=549 \quad (12)$$

where z is depth in km. The individual values of IOR and their fit (equation 12) are shown in Figure 2. The error finally incurred in ΔTA is evaluated by an error propagation analysis in equation 10. IOR and AOU initial values are modified in ± 0.03 and $\pm 2 \mu\text{mol} \cdot \text{kg}^{-1}$ intervals with a normally distributed random number, then IOR is recalculated. This modification is performed a hundred times over the whole set of samples. The standard deviation of the difference between the initial and modified ΔTA ($\pm 1.4 \mu\text{mol} \cdot \text{kg}^{-1}$) is considered to be the uncertainty of our ΔTA estimation. Considering a maximum error in TA of $\pm 2 \mu\text{mol} \cdot \text{kg}^{-1}$, the final uncertainty in TA^0 is $\pm 3.4 \mu\text{mol} \cdot \text{kg}^{-1}$.

The IOR values are in the range within 0.12-0.60, in agreement with sediment trap data from the North Atlantic and hydrological water mass analysis (Broecker and Peng, 1982; Honjo and Manganini, 1993; Martin *et al.*, 1993; Ríos *et al.*, 1995; Takahashi *et al.*, 1985). On the other hand, $\Delta TA / \Delta Si = 1.42$ implies a mean $\text{CaCO}_3:\text{SiO}_2$ ratio for the whole water column of 0.71. The open ocean calcite and opal decomposition in the water column, according to Milliman *et al.* (1999) and Tréguer *et al.* (1995), are $47 \cdot 10^{12} \text{ mol} \cdot \text{y}^{-1}$ and $90.9 \cdot 10^{12} \text{ mol} \cdot \text{y}^{-1}$ respectively, thus, a mean $\text{CaCO}_3:\text{SiO}_2$ decomposition ratio of 0.52, value in reasonable agreement with our estimation.

According to Berger and Herguera (1992) a $\text{CaCO}_3:\text{SiO}_2$ ratio of 0.71 is expected for an area with a mean organic carbon flux of $10 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, which is in close agreement with their productivity value for the Eastern North Atlantic Ocean (Martin *et al.*, 1993). Higher $\text{CaCO}_3:\text{SiO}_2$ ratios, around 0.95, were measured in sediment traps deployed at the NABE site below 3100 m (Newton *et al.*, 1994).

With the aim of validating our proposed parameterization for ΔTA (equation 10 as a function of equation 12) we proposed a simple 1D steady state model simulating the biological pump, thus, the decomposition of hard and soft-tissue biogenic matter. As a proxy for the whole North Atlantic Ocean, it has been applied over the OacesNAtlIIB-93 data set and validated against sediment trap

profile data obtained by Martin *et al.* (1993) at the NABE site. Thus, the decomposition ratios (IOR) are adjusted with the ratio between organic and inorganic matter accumulated in sediment traps (rain ratios).

The decomposition of biogenic debris between two horizontal layers produces a gain of AOU and ΔTA in time:

$$-\frac{\partial F_{Co}}{\partial z} = \frac{\rho}{R_C} \cdot \frac{dAOU}{dt} \quad -\frac{\partial F_{Ci}}{\partial z} = \rho \cdot \frac{d\Delta TA}{dt} \quad (13)$$

where F_{Co} and F_{Ci} are the organic and inorganic carbon fluxes, respectively, z is depth, t is time, ρ is seawater density and R_C the stoichiometric $-\Delta O_2/\Delta C$ ratio. The transport equation in three dimensions for a non-conservative variable (NCV, AOU or ΔTA , in this case) may be written as:

$$\frac{dNCV}{dt} = \frac{\partial NCV}{\partial t} + v_z \frac{\partial NCV}{\partial z} + v_x \frac{\partial NCV}{\partial x} + v_y \frac{\partial NCV}{\partial y} - K \nabla^2 NCV \quad (14)$$

where K is the eddy diffusivity and v are the different components of the velocity.

Considering the relatively scarce information about horizontal variability in the sediment trap profiles, we assume the rain ratios reported at the NABE site as representative of the North Atlantic. Consequently, the 3D model simplifies to 1D by basin-scale integration. Thus, subduction and vertical mixing are considered as the main processes ventilating subsurface waters. Moreover, if the mean AOU and ΔTA along OacesNAtlIIB-93 are regarded as representative of the whole North Atlantic and in steady state, their temporal variation can be related to their vertical gradient by:

$$\frac{dNCV}{dt} = v_z \frac{\partial NCV}{\partial z} - K \nabla^2 NCV \quad (15)$$

Substituting equation 15 in equations 13 and integrating between two different depths we finally obtain:

$$F_{Co_{z_2}} = F_{Co_{z_1}} - \frac{\rho}{R_C} \left\{ v_z \cdot (AOU_{z_2} - AOUs_{z_1}) - K_z \left(\frac{dAOU}{dz} \Big|_{z_2} - \frac{dAOU}{dz} \Big|_{z_1} \right) \right\} \quad (16)$$

$$F_{Ci_{z_2}} = F_{Ci_{z_1}} - \rho \left\{ v_z \cdot (\Delta TA_{z_2} - \Delta TA_{z_1}) - K_z \left(\frac{d\Delta TA}{dz} \Big|_{z_2} - \frac{d\Delta TA}{dz} \Big|_{z_1} \right) \right\} \quad (17)$$

Therefore, the flux of organic and inorganic carbon at a given depth layer can be calculated from the corresponding initial fluxes at the above layer and the variation of AOU and ΔTA between both of them, if the vertical turnover velocity and vertical diffusivity are known. In this sense, v_z was parameterized as $v_z = 0.4 \cdot (z/100)^{-0.3}$ (v_z in $m \cdot d^{-1}$ and z is depth in km) in order to adjust our

organic carbon fluxes calculated from the mean vertical profile of AOU (obtained from the OacesNAtIIIB-93 data) with those measured by Martin *et al.* (1993) (Table 1). The vertical diffusive terms, using typical K_z values between 0.001 and 0.0002 $\text{m}\cdot\text{s}^{-2}$, are negligible compared to the advective terms. Predicted values for v_z (from 0.16 to 0.36 $\text{m}\cdot\text{d}^{-1}$) are in agreement with typical rates of subduction and entrainment given by Marshall *et al.* (1993) for the North Atlantic, and also with the decreasing meridional water flux in the mixed layer with increasing density (*i.e.* depth) (Huang, 1989).

Dissolution of calcium carbonate at the NABE site, as representative for the northern North Atlantic, is calculated as $\Delta\text{Ci} = \text{IOR}\cdot\text{AOU}/R_C$ with our IOR equation (equation 12) and as $\Delta\text{Ci} = \frac{1}{2}\cdot(\text{TA}-\text{TA}^0 + \text{AOU}/R_N)$ using the TA^0 formula from GSS'96 (See Table 1 and Figure 3). In the former approximations the AOU and TA mean profiles along the OacesNAtIIIB-93 are used along with the R_C and R_N from Anderson and Sarmiento (1994). Both the organic and inorganic carbon fluxes estimated using our model present a good agreement with those measured by Martin *et al.* (1993) (See Table 1 and Figure 3). The inorganic carbon flux calculated with TA^0 from GSS'96 agrees with the measured and modelled results in the upper 500 m (Table 1 and Figure 3). At deeper levels the inorganic carbon flux using the TA^0 from GSS'96 is notably overestimated, indicating a low dissolution rate of calcium carbonate. Although sediment trap data could be affected by hydrodynamic and other factors, leading to a significant “over/undertrapping” (Yu *et al.*, 2001), the inorganic and organic fluxes are both affected in the same manner. It must also be taken into account that water masses integrate the dissolution of biogenic material over time and space, hence attenuating the high variability of the rain ratios seen in the sediment trap data. Therefore, we consider that trap biases not relevant when measured and calculated rain ratios are compared.

3.2. Effect of the alkalinity pump and new improvements on $C_T^{\text{eq}\pi}$.

Having obtained a better parameterization of TA^0 as a function of IOR (equations 10 and 12), we proceed to address its effect on the estimation of the pre-industrial equilibrium total inorganic carbon, $C_T^{\text{eq}\pi}$. Additional improvements on $C_T^{\text{eq}\pi}$ are proposed.

$C_T^{\text{eq}\pi}$ is calculated from TA^0 , the pre-industrial level of atmospheric partial pressure of CO_2 (Neftel *et al.*, 1994) and using a given set of CO_2 constants. GSS'96 used their TA^0 parameterization, a constant value for pre-industrial $p\text{CO}_2$ equal to 280 μatm and the set of thermodynamic constants from Goyet and Poisson (1989). We have already shown that their TA^0 parameterization gives rather high values. On the other hand, atmospheric $p\text{CO}_2$ is a function not only of the molar fraction of CO_2 but also of the water vapor partial pressure and total atmospheric pressure (DOE, 1994; Wanninkhof and Thoning, 1993). Takahashi *et al.* (1993) showed that the best set of CO_2 thermodynamic constants is that by Mehrbach *et al.* (1973). Recently, other

thermodynamical and field studies (Johnson *et al.*, 1999; Lee *et al.*, 2000; Ríos and Pérez, 1999; Ríos *et al.*, 2001; Tapp *et al.*, 2000; Wanninkhof *et al.*, 1999b) reached the same conclusion.

In order to clearly show the variation of $C_T^{eq\pi}$ under different conditions, TA^0 parameterization, pCO_2^π calculation and set of thermodynamic constants, we calculated $C_T^{eq\pi}$ for the OacesNAtIIB-93 data set following these combinations:

- TA⁰ from GSS'96, a constant value for pCO_2^π equal to 280 μatm and the Goyet and Poisson (1989) constants. This is the GSS'96 option.
- TA⁰ from GSS'96, pCO_2^π calculated as a function of a molar fraction of 278.2 ppm (Neftel *et al.*, 1994; Sarmiento *et al.*, 1995), water vapor pressure and the constants of Goyet and Poisson (1989).
- The same as before but with the Merzbach *et al.* (1973) constants.
- TA⁰ obtained from our equations 10 and 12, pCO_2^π calculated as a function of a molar fraction of 278.2 ppm, water vapor pressure and the Merzbach *et al.* (1973) constants.

Figure 4 shows salinity-normalised $C_T^{eq\pi}$ ($NC_T^{eq\pi}$) values for the previous sets of combinations against potential temperature. Option (a) $NC_T^{eq\pi}$ present the highest values for the whole temperature range. Including the effect of water vapor in the calculation of pCO_2^π (option b) reduces $NC_T^{eq\pi}$ by an average of $5 \pm 1 \mu\text{mol}\cdot\text{kg}^{-1}$, with a maximum effect of $-10 \mu\text{mol}\cdot\text{kg}^{-1}$ at high temperatures, 15°C. Including the set of constants from Merzbach *et al.* (1973) (option c) gives $NC_T^{eq\pi}$ values that are $14 \mu\text{mol}\cdot\text{kg}^{-1}$ lower than GSS'96 values at low temperatures. On the other hand at high temperatures the effect of including the Merzbach *et al.* (1973) constants counteracts half of the effect due to including the water vapor pressure in the formulation. Finally, if our parameterization for TA^0 is included (option d) the $NC_T^{eq\pi}$ values are lower than those obtained with the GSS'96 option, the difference ranging from $-26 \mu\text{mol}\cdot\text{kg}^{-1}$ at 2°C to $-2 \mu\text{mol}\cdot\text{kg}^{-1}$ at 15°C.

Briefly, at 2°C the inclusion of water vapor pressure in calculating pCO_2^π , the use of Merzbach *et al.* (1973) constants, and our new TA^0 parameterization independently reduce $NC_T^{eq\pi}$ by -6 , -8 and $-12 \mu\text{mol}\cdot\text{kg}^{-1}$, respectively, whereas at 15°C the corresponding contributions are -10 , $+6$, $+2 \mu\text{mol}\cdot\text{kg}^{-1}$. Hence, GSS'96 greatly overestimate $NC_T^{eq\pi}$ and consequently $C_T^{eq\pi}$ in deep waters.

4. CASE STUDY: REVALUATION OF C_{ANT} ALONG THE OacesNAtIIB-93 LINE.

Using the OacesNAtIIB-93 data we calculated C_{ANT} from equation 5, with our new approach for TA^0 (equations 10 and 12) and option (d) for estimating $C_T^{eq\pi}$. R_N and R_C are respectively equal to 10.6 and 1.45 according to Anderson and Sarmiento (1994). In addition, we calculated the apparent age of each water sample from the equilibrium partial pressure of CFC_{11} ($pCFC_{11}$) based on the solubility function of Warner and Weiss (1985) and the reconstructed

history of atmospheric pCFC₁₁ from Walker *et al.* (2000) as described by Bullister (1984) and Doney and Bullister (1992).

The ΔC_{Tdis} is evaluated by density intervals as in GSS'96, here explained in the Formulation section (equations 7 and 8). Some of the assumptions used by GSS'96 in the calculation of the former term are the following: first of all, that the ΔC_{Tdis} has remained constant over time and that tracer age is equal to the true water age. The first assumption has recently been verified by the analysis of CO₂ time-series data, showing that surface seawater CO₂ has kept pace with the atmospheric CO₂ increase (Bates *et al.*, 1996; Bates, 2001; Feely *et al.*, 1999) over the last four decades. The second assumption holds true for tritium-³He ages, as explained by GSS'96 and Gruber (1998), if the transport is mainly advective. In the case of CFCs, true age equals CFC age if the water parcel was saturated with CFC in the formation area and if mixing is mainly along isopycnals, without mixing between waters with significantly different CFC concentrations. In this case, the age method (equation 8) is used for surfaces lighter than $\sigma_4=45.81 \text{ kg}\cdot\text{m}^{-3}$, which have a CFC₁₁ concentration higher than $0.1 \text{ pM}\cdot\text{kg}^{-1}$.

The ΔC_{Tdis} by density intervals is shown in Table 2 in terms of carbon and pCO₂, along with the mean depth and CFC₁₁ age. Density layers with $\sigma_2 \leq 36.5 \text{ kg}\cdot\text{m}^{-3}$ have a CFC₁₁ age lower than 15 years. Up to this age, according to Doney *et al.* (1997), CFC-derived and corrected tritium-³He ages are linearly related with a small positive offset of 1-2 years in the CFC ages. Despite this, both tracers are good estimators for the ideal ventilation age in the main thermocline (Thiele and Samiento, 1990). A recent study compares CFC and ideal ages obtained from a simple, highly idealised model of the CFC uptake in the thermocline (Sonnerup, 2001) and concludes that CFC ages less than 15 years agree with the ideal age being to within 25%. CFC ages older than 15 years are significantly higher than the corrected tritium-³He ages, and both diverge from the ideal ventilation time-scales (Doney *et al.*, 1997; Sonnerup, 2001). The more rapid exchange rate for ³He and the non-linear mixing effects at greater tracer ages are the most likely reasons for this discrepancy.

Surface layers with $\sigma_0 \leq 27 \text{ kg}\cdot\text{m}^{-3}$ tend to be slightly undersaturated, and waters from $\sigma_0 = 27.1 \text{ kg}\cdot\text{m}^{-3}$ to $\sigma_2 = 36.5 \text{ kg}\cdot\text{m}^{-3}$ are slightly oversaturated in CO₂. These results contrast with those from GSS'96: their ΔC_{Tdis} range from -22 to $-16 \text{ }\mu\text{mol}\cdot\text{kg}^{-1}$ and from -30 to $-20 \text{ }\mu\text{atm}$ in pCO₂. The deepest layers, where no C_{ANT} contamination is expected, present a small positive disequilibrium (about $4 \text{ }\mu\text{mol}\cdot\text{kg}^{-1}$ and $5 \text{ }\mu\text{atm}$, Table 2), in contrast with the negative values proposed by GSS'96 ($-16 \text{ }\mu\text{mol}\cdot\text{kg}^{-1}$ and $-33 \text{ }\mu\text{atm}$) or the strong negative ΔC_{Tdis} obtained by Wanninkhof *et al.* (1999a) ($-40 \text{ }\mu\text{mol}\cdot\text{kg}^{-1}$). Intermediate layers also present low and negative ΔC_{Tdis} values, smaller than those obtained by GSS'96 and Wanninkhof *et al.* (1999a).

The aforementioned comments about the ΔC_{Tdis} estimation method and assumptions combined with our results lead us to doubt the existence of a significant air-sea disequilibrium

term. In the main thermocline where the apparent age approximates true age with a high degree of reliability, the mean ΔC_{Tdis} is $0 \pm 5 \mu\text{mol} \cdot \text{kg}^{-1}$. At intermediate levels we also obtained low disequilibrium values. However, they are subject to a greater uncertainty in the estimation of the age as mentioned previously. Thus, we disregard these results in our analysis. At the deepest density intervals, where no significant anthropogenic CO_2 signal is expected, the ΔC_{Tdis} values are very low as well ($3 \pm 1 \mu\text{mol} \cdot \text{kg}^{-1}$), and in agreement with the low values obtained in the main thermocline layer.

Figure 5 shows the relationship between $\Delta C^*(\tau)$ calculated with our improvements and that applying GSS'96 against the apparent CFC_{11} age. The inset in Figure 5 shows both $\Delta C^*(\tau)$ but against depth. The mean $\Delta C^*(\tau)$ for the upper 200 m are 41 ± 3 and $45 \pm 4 \mu\text{mol} \cdot \text{kg}^{-1}$ from GSS'96 and this work, respectively, and the corresponding means below 3500 m are -13 ± 2 and $4 \pm 3 \mu\text{mol} \cdot \text{kg}^{-1}$. GSS'96 gives disequilibria of -12 and $-16 \mu\text{mol} \cdot \text{kg}^{-1}$ for the upper and deep layers, respectively. Thus, the C_{ANT} according to GSS'96 for these two layers would be 53 ± 3 and $3 \pm 2 \mu\text{mol} \cdot \text{kg}^{-1}$. Neglecting the CO_2 disequilibrium, our C_{ANT} would be 45 ± 4 and $4 \pm 3 \mu\text{mol} \cdot \text{kg}^{-1}$.

The expected increase in surface C_T up to 1993 is $50 \mu\text{mol} \cdot \text{kg}^{-1}$, estimated from TA^0 (a mean value of $2330 \mu\text{mol} \cdot \text{kg}^{-1}$ at 15°C and salinity of 35) and the atmospheric pCO_2 increase. Given the uncertainty in the back-calculation method for estimating C_{ANT} the previous theoretical increase agrees with the calculated C_{ANT} according to GSS'96 ($53 \pm 3 \mu\text{mol} \cdot \text{kg}^{-1}$) and this work ($45 \pm 4 \mu\text{mol} \cdot \text{kg}^{-1}$). Correspondingly, in deeper layers where an insignificant anthropogenic CO_2 concentration is expected, both estimations of C_{ANT} agree, 3 ± 2 and $4 \pm 3 \mu\text{mol} \cdot \text{kg}^{-1}$ from GSS'96 and this work, respectively.

These results could be misleading, as both methods, that developed by GSS'96 and the improvements proposed here, yield the same quantities at particular deep layers, but start from divergent assumptions. We arise the question about the existence of a significant air-sea disequilibrium term.

5. DISCUSSION.

The back-calculation technique for estimating anthropogenic CO_2 introduced by Chen and Millero (1979) and Brewer (1978) and recently reviewed by GSS'96, was developed on the same principles as the conservative parameters NO or CAO (Broecker, 1974; Ríos *et al.*, 1989). The work by GSS'96 renewed the attention on estimating the C_{ANT} inventory in the ocean as a way to constrain global ocean circulation and biogeochemical models. The GSS'96 procedure suffers from some sources of error, among which we have evaluated the most important: the estimation of TA^0 , the effect of water vapor pressure on calculating pre-industrial pCO_2 and the CO_2 dissociation constants. Their impact on $\Delta C^*(\tau)$ is of great significance, especially in deep waters where errors in

the preformed estimates can lead to anomalous values, which GSS'96 ascribed to a disequilibrium term.

TA^0 has been generally parameterised as an empirical function of conservative parameters in order to correct for mixing effects and biological activity. Despite its being a very reasonable approximation, the lack of wintertime measurements of surface TA prevents it from being put into practice. Most of the oceanic CO_2 data have been collected in summer or spring, when seasonal warming, phytoplankton activity and oxygen outgassing take place. Therefore, temperature-parameterised TA^0 values are overestimated because of the shift to higher temperatures in the initial TA^0 values. Moreover, using PO or NO does not counteract this effect because they do not correct for the oxygen outgassing. Empirical relations between high quality alkalinity data and salinity and other conservative parameters such as NO or PO obtained during wintertime in formation areas will be excellent for modelling the preformed alkalinity values. However, another potential procedure would be the analysis of data not affected by seasonal warming or freshwater flux variations, that is, data from the homogenous layer below the seasonal thermocline as an approximation for the winter mixed layer (e.g. Wanninkhof *et al.*, 1999a and Körtzinger *et al.*, 2001). Preformed alkalinity values obtained in this manner should also be consistent with the decomposition of organic and inorganic matter in the water column.

Recently, the dissociation constants by Mehrbach *et al.* (1973) have been confirmed to be the most suitable for calculating C_T from TA and pCO_2 . This set of constants was the only one determined on natural seawater, thus including the interferences of all its acid-base components, even those derived from organic matter.

After applying our proposed improvements: the TA^0 parameterization, including the water vapor effect on pre-industrial pCO_2 calculation and using the Mehrbach *et al.* (1973) constants, we question the existence of a disequilibrium term as high as that concluded by GSS'96. From their point of view, this term is a “cul-de-sac” accumulating the air-sea disequilibrium in CO_2 , any residual effects due to the selection of the TA^0 and oxygen end-members, as well as the uncertainty in data and parameters. In deep waters, this disequilibrium is an artefact to correct negative values of their $\Delta C^*(\tau)$ (our C_{ANT}) to zero where no anthropogenic contamination is expected, and originates mainly from an inaccurate estimation of the alkalinity pump and the set of constants used, and therefore the $C_T^{eq\pi}$. In the main thermocline, where the age uncertainty (2 years as maximum) is much lower than at depth, the ΔC_{Tdis} proposed by GSS'96 (from -12 to $-24 \mu mol \cdot kg^{-1}$, corresponding to -19 to $-35 \mu atm$) seems unrealistically high and would arise (equation 7) from the overestimation of TA^0 , affecting also the calculation of $C_T^{eq}(\theta, S, TA^0, pCO_2^s)$, which is also affected by the choice of dissociation constants and the effect of water vapor pressure on pCO_2^s . Between very young and ancient water masses, the disequilibrium stems mainly from the

bias towards younger ages of the tracer apparent ages (Beining and Roether, 1996; Doney *et al.*, 1997; Sonnerup, 2001), leading to an overestimation of $p\text{CO}_2^\tau$ from the tracer age.

The non-existence of significant ΔC_{Tdis} when the water masses are formed can be directly corroborated only with winter measurements of CO_2 parameters on formation areas. Peng *et al.* (1987) reported seasonal variations of carbon dioxide, nutrients and oxygen in the Irminger Sea surface water from 1983 to 1985, showing surface water nearly in equilibrium with atmospheric oxygen and CO_2 during the winter months. Only their winter values with mixed layer depths exceeding 300 m are reproduced in Table 3. $C_T^0(\tau)$ calculated as in equation 1 from C_T and AOU minus $C_T^{\text{eq}}(\theta, S, \text{TA}^0, p\text{CO}_2^\tau)$ represent the ΔC_{Tdis} according to equation 2. ΔC_{Tdis} are slightly negative for the three isopycnals (from 0 to $-2 \mu\text{mol}\cdot\text{kg}^{-1}$), expressed in terms of $p\text{CO}_2$ from 0 to $-3 \mu\text{atm}$. In conclusion, wintertime measurements of CO_2 and oxygen in the Irminger Sea point to the same degree of air-sea disequilibrium in both tracers, mutually compensated.

More recently, Takahashi *et al.* (1993) collected CO_2 and nutrient data in high-latitude oceans in order to study their seasonal cycle. Around Iceland they found $p\text{CO}_2$ air-sea gradients during winter months ranging from 10 to $-30 \mu\text{atm}$, being about $-12 \mu\text{atm}$ in the Eastern North Atlantic. No oxygen values were reported, but presumably these slight CO_2 disequilibria are partially compensated by AOU during these short deep winter mixing events.

More evidence supports our proposal of a low level of disequilibrium. A completely independent and comprehensive data set was collected between 30° and 60°N along 20°W during summer 1996, practically the same track as the OacesNAtlIIB-93 line. The high quality CO_2 data collected is presented and analysed in Körtzinger *et al.* (2001). Following a procedure described in Takahashi *et al.* (1985) they calculated the wintertime C_T concentrations by isopycnals (Table 3). C_T once biologically corrected, $C_T^0(\tau)$, practically corresponds with C_T^{eq} in 1996. ΔC_{Tdis} ranges from -5 to $2 \mu\text{mol}\cdot\text{kg}^{-1}$, in $p\text{CO}_2$ terms from -9 to $3 \mu\text{atm}$, supporting our assumption of a negligible CO_2 disequilibrium.

Labrador sea data taken in July-August 1996, kindly provided by Mintrop and Körtzinger (CARINA web page, <http://www.ifm.uni-kiel.de/ch/carina/index.htm>), also support our proposal of a small air-sea disequilibrium when water masses are formed. CO_2 and oxygen data were selected to characterise an homogenous layer of Labrador Sea Water (LSW) (from 200 to 1800 m), whose mean and standard deviation characteristics are shown in Table 3. The mean age of this homogenous layer was 9 ± 2 years, estimated from CFC_{11} , giving $C_T^0(\tau)$ very close to $C_T^{\text{eq}}(\theta, S, \text{TA}^0, p\text{CO}_2^\tau)$ (Table 3). The analysis of this data reinforces our concept of the same degree of air-sea disequilibrium in oxygen and CO_2 , and even CFC_{11} , when water masses are formed, resulting in a negligible effective CO_2 disequilibrium. This means that the three gases (CO_2 , O_2 , CFC_{11}) were at the same degree of air-sea disequilibrium when the LSW was last in contact with the atmosphere.

The calculated disequilibrium stems mainly from the mixing between newly formed vintages of LSW and those ventilated in the preceding winters.

GSS'96 showed a good latitudinal correlation between $\Delta p\text{CO}_2$ estimated from their ΔC_{Tdis} and winter zonal $\Delta p\text{CO}_2$ mean values given by Takahashi *et al.* (1997). The strong natural $\Delta p\text{CO}_2$ at northern latitudes derives from surface cooling. In this connection, remember the strong bias of ΔC_{Tdis} toward low values at low temperatures due to inaccuracies in the back-calculation technique. The effective ΔC_{Tdis} would be set when water loses its contact with the atmosphere, reaching maximum winter mixing depths under very severe weather conditions. Although under these strong wind conditions the air-sea exchange is strongly enhanced (Nightingale *et al.*, 2000; Wanninkhof and McGillis, 1999), rapid deep mixing with underlying CO_2 -loaden and oxygen poor waters also takes place, finally resulting in a winter mixed layer slightly oversaturated in CO_2 and undersaturated in oxygen (see Table 3). These conditions take place in late winter or early spring. Presumably zonal averages of winter $\Delta p\text{CO}_2$ values are not representative of $\Delta p\text{CO}_2$ when the water mass loses contact with atmosphere. Furthermore, the outcrop of water masses is a spatially localised phenomenon, occurring at specific areas where the stability of the surface layer is reduced. So, we think the agreement between mean zonal $\Delta p\text{CO}_2$ from GSS'96 and Takahashi *et al.* (1997) is somehow spurious and fortuitous.

In summary, we showed evidence for some significant deficiencies in the estimation of the anthropogenic CO_2 uptake in the oceans. The estimation of TA^0 as a function of AOU and IOR, the addition of water vapor pressure in the calculation of pre-industrial $p\text{CO}_2$ and the selection of the appropriate carbonic acid dissociation constants (Merzbach *et al.*, 1973) stand out as key factors in the back-calculation technique for C_{ANT} . These improvements yielded consistent results in the estimation of C_{ANT} along a section in the Eastern North Atlantic Ocean, with practically no anthropogenic input in deep and bottom waters and reasonable C_{ANT} concentrations in the upper water column. We conclude that there does not exist a significant CO_2 disequilibrium when water masses are formed, previous claims of such a disequilibrium being based on an artefact arising from the inaccuracy in estimating preformed TA^0 , pre-industrial equilibrium C_{T} and the water masses true age, which is estimated from transient tracers.

Our improvements on C_{ANT} can be applied for any other ocean basin, except for the parameterization of TA^0 , which is specific for the North Atlantic Ocean. Similar procedures for other ocean basins where long-term average rain ratios are available could be developed. Despite the proposed improvements, uncertainties still remain in the estimation of C_{ANT} : the respiratory quotient for sinking organic matter, the mixing problem, but overall the verification of preformed values of oxygen, alkalinity, $p\text{CO}_2$ and nutrients at the winter mixed layer.

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FIGURE CAPTIONS.

Figure 1. Relationship between dissolution of opal ($\Delta\text{Si}=\text{Si}-\text{Si}^0$ in $\mu\text{mol}\cdot\text{kg}^{-1}$) and carbonate ($\Delta\text{TA}=\text{TA}-\text{TA}^0$ in $\mu\text{mol}\cdot\text{kg}^{-1}$). Si^0 has been calculated from equation 11, and TA^0 from GSS'96 (open squares, $\text{TA}^0 = 367.5 + 54.9\cdot\text{S} + 0.074\cdot\text{PO}$, where S is salinity and $\text{PO} = 170\cdot\text{PO}_4 + \text{O}_2$), Millero *et al.* (1998) (dark squares, $\text{TA}^0 = \text{S}/35\cdot[2291 - 2.69\cdot(\theta-20) - 0.046\cdot(\theta-20)^2]$, where θ is temperature and S salinity), Wanninkhof *et al.* (1999b) (open circles, $\text{TA}^0 = 278.4 + 57.91\cdot\text{S} + 0.0074\cdot\text{NO}$, where S is salinity and $\text{NO} = 10.6\cdot\text{NO}_3 + \text{O}_2$) and our new parametrization from equations 10 and 12 (dark circles).

Figure 2. Inorganic to Organic carbon decomposition Ratio (IOR) versus depth. IOR was calculated from equation 9 with TA^0 from GSS'96 (open squares) and TA^0 as a function of the opal dissolution (dark circles) ($\Delta\text{TA} = 1.42\cdot\Delta\text{Si}$, $\Delta\text{Si} = \text{Si}-\text{Si}^0$, where Si^0 has been calculated from equation 11). The solid line is the polynomial fit for the previous IOR data, as expressed in equation 12.

Figure 3. Measured (dotted line) and modeled (solid line) profiles of organic (circles) and inorganic (squares) carbon fluxes at the NABE site. The inorganic carbon flux calculated based on TA^0 from GSS'96 is also shown (crosses). Note the reversed scale for the inorganic carbon flux axis.

Figure 4. Salinity-normalized pre-industrial equilibrium total inorganic carbon ($\text{C}_T^{\text{eq}\pi}$ in $\mu\text{mol}\cdot\text{kg}^{-1}$) versus potential temperature (θ in $^{\circ}\text{C}$) based on different approximations. Dark squares (option a, see text) stand for $\text{C}_T^{\text{eq}\pi}$ calculated with TA^0 from GSS'96, a constant value for pre-industrial pCO_2 of 280 μatm and the Goyet and Poisson (1989) constants. Open circles (option b) denote $\text{C}_T^{\text{eq}\pi}$ calculated with TA^0 from GSS'96, pre-industrial pCO_2 calculated as a function of a molar fraction of 278.2 ppm and water vapor pressure (WV) and the constants of Goyet and Poisson (1989). Crosses (option c) indicate $\text{C}_T^{\text{eq}\pi}$ calculated the same as before but with the Mehrbach *et al.* (1973) constants (Mehr). Dark circles (option d) represent $\text{C}_T^{\text{eq}\pi}$ calculated with TA^0 obtained from our equations 10 and 12, pre-industrial pCO_2 calculated as a function of a molar fraction of 278.2 ppm, water vapor pressure and the Mehrbach *et al.* (1973) constants (New approach).

Figure 5. $\Delta C^*(\tau)$ (in $\mu\text{mol}\cdot\text{kg}^{-1}$) calculated according to GSS'96 (open circles) and our improvements on the back-calculation technique (black circles) versus CFC_{11} age in years. The inset shows both $\Delta C^*(\tau)$ versus depth. $\Delta C^*(\tau)$ is equivalent to C_{ANT} disregarding the disequilibrium term in equation 3.

TABLES.

Table 1. Organic (Co) and inorganic (Ci) carbon fluxes at different depth layers measured by Martin *et al.* (1993) in sediment traps deployed at the NABE site and results from the 1D model proposed in this work. “Mean” refers to the mean profile of Apparent Oxygen Utilisation (AOU) and dissolution of calcium carbonate (ΔCi) using data from the OacesNAtIIIB-93. ΔCi is calculated as: a) $\Delta\text{Ci} = \text{IOR} \cdot \text{AOU} / R_C$, where IOR is calculated from equation 12 and b) $\Delta\text{Ci} = \frac{1}{2} \cdot (\text{TA} - \text{TA}^0 + \text{AOU} / R_N)$, using TA^0 from GSS’96. R_C and R_N are stoichiometric coefficients from Anderson and Sarmiento (1994). v_z stands for the water turnover velocity in $\text{m} \cdot \text{d}^{-1}$. Depth is expressed in km, AOI and ΔCi in $\mu\text{mol} \cdot \text{kg}^{-1}$ and the Co and Ci fluxes in $\text{mol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$.

Source	Fitted	Mean	Mean ^a	Mean ^b	Traps	Traps	Model	Model ^a	Model ^b
Depth	v_z	AOU	ΔCi	ΔCi	Co flux	Ci flux	Co flux	Ci flux	Ci flux
0.00					14.35	2.44	14.35	2.44	2.44
0.15	0.35	11.4	0.6	-2.9	10.50	1.97	11.09	2.16	1.91
0.30	0.29	31.1	2.3	-2.1	4.83	1.57	6.75	1.63	1.67
0.50	0.25	48.1	4.2	-1.5	3.25	1.22	3.65	1.13	1.54
0.75	0.22	58.3	5.3	-1.5	3.00	1.23	2.02	0.87	1.54
1.00	0.20	60.6	5.3	-1.9	1.62	0.93	1.69	0.85	1.62
1.50	0.18	63.4	5.6	-2.5	1.08	0.77	1.33	0.81	1.73
2.00	0.16	68.0	7.7	-1.5	1.04	0.49	0.79	0.45	1.55

Table 2. Mean values of pressure (in db), CFC₁₁ age (in years), air-sea disequilibrium in terms of carbon (ΔC_{Tdis} in $\mu\text{mol}\cdot\text{kg}^{-1}$) and pCO₂ ($\Delta p\text{CO}_{2dis}$ in μatm) on potential density surfaces along the OacesNAtIIB-93. SDM stands for the standard deviation weighted by the number of determinations (n). $\Delta C^*(\tau)$ is calculated from equation 4, C_{ANT} GSS'96 (in $\mu\text{mol}\cdot\text{kg}^{-1}$) stands for the calculation of the anthropogenic carbon according to Gruber *et al.* (1996), *i.e.*, $C_{ANT} = \Delta C^*(\tau) - \Delta C_{Tdis}$.

Density ($\text{kg}\cdot\text{m}^{-3}$)	Press. (db)	CFC ₁₁ age	$\Delta C_{Tdis} \pm \text{SDM}$ (n)	$\Delta p\text{CO}_{2dis} \pm \text{SDM}$	$\Delta C^*(\tau)$	C_{ANT} GSS'96	Method
σ_θ Surfaces							
26.9-27	194	6	-3.7 ± 1.7 (7)	-6.3 ± 2.9	42	46	Eq.3.7
27-27.1	239	6	0.0 ± 0.7 (19)	0.1 ± 1.3	45	45	Eq.3.7
27.1-27.2	304	7	3.3 ± 0.5 (35)	6.2 ± 0.9	46	43	Eq.3.7
27.2-27.3	420	10	4.9 ± 0.5 (31)	9.4 ± 1.0	44	39	Eq.3.7
27.3-27.4	458	13	2.8 ± 0.7 (30)	5.6 ± 1.3	40	37	Eq.3.7
$\sigma_\theta - \sigma_2$ Surfaces							
27.4-36.5	573	13	3.2 ± 0.6 (51)	6.7 ± 1.3	39	36	Eq.3.7
σ_2 Surfaces							
36.5-36.6	801	17	-0.4 ± 0.6 (30)	-0.5 ± 1.2	32	33	Eq.3.7
36.6-36.7	892	18	-3.6 ± 0.5 (19)	-6.7 ± 0.9	27	31	Eq.3.7
36.7-36.8	1087	20	-4.7 ± 0.4 (28)	-8.6 ± 0.7	25	29	Eq.3.7
36.8-36.9	1372	21	-4.9 ± 0.4 (39)	-9.2 ± 0.8	23	28	Eq.3.7
36.9-37	1939	25	-7.4 ± 0.5 (53)	-13.7 ± 0.9	18	26	Eq.3.7
$\sigma_2 - \sigma_4$ Surfaces							
37-45.81	2422	32	-12.9 ± 0.9 (10)	-23.2 ± 1.6	10	23	Eq.3.7
σ_4 Surfaces							
45.81-45.88	2715	33	3.0 ± 0.9 (8)	4.9 ± 1.4	3	0	Eq.3.8
45.88-45.95	3925	39	3.8 ± 0.5 (36)	6.3 ± 0.8	4	0	Eq.3.8

Table 3. Estimations of the air-sea disequilibrium in terms of carbon (ΔC_{Tdis}) and pCO_2 (ΔpCO_{2dis}) from total inorganic carbon (C_T), partial pressure of CO_2 (pCO_2), alkalinity (TA^0) and Apparent Oxygen Utilization (AOU) data collected by different authors. ΔC_{Tdis} (equation 2) is calculated as the difference between preformed total inorganic carbon ($C_T^0(\tau)$, equation 1) and that in equilibrium with the corresponding atmospheric CO_2 ($C_T^{eq}(\tau)$). Correspondingly, ΔpCO_{2dis} is the difference between preformed pCO_2 ($pCO_2^{0\tau}$) and that in the atmosphere (pCO_2^{air}). CARINA stands for the CARbon dioxide In the North Atlantic ocean program and MLD for Mixed Layer Depth. * stands for measured and + for calculated CO_2 initial variables. All the C_T variables, TA^0 and AOU are in $\mu mol \cdot kg^{-1}$, pCO_2 variables are in μatm .

Area / Time		σ_θ / σ_2	θ / S	AOU	TA^0	C_T	pCO_2	$C_T^0(\tau)$	$C_T^{eq}(\tau)$	ΔC_{Tdis}	$pCO_2^{0\tau}$	pCO_2^{air}	ΔpCO_{2dis}	Data source and characteristics
Irminger Sea. March 1983-85		27.59/36.61	4.96 / 35.08	12.0	2301 ⁺	2122 [*]	360 [*]	2114	2114	0.1	345	344	0.2	Peng <i>et al.</i> (1987) Data with MLD>300 m
		27.67/36.72	5.52 / 35.08	13.0	2302 ⁺	2130 [*]	364 [*]	2121	2122	-0.7	347	348	-1.3	
		27.74/36.81	6.28 / 35.09	-7.0	2283 ⁺	2101 [*]	329 [*]	2106	2108	-2.0	337	341	-3.4	
Eastern North Atlantic, 30°-60°N along 20°W. Summer 1996.		26.95/35.67	13.9 / 35.96	4.9	2359 [*]	2105 [*]	353 ⁺	2102	2106	-4.7	355	355	-8.4	Körtzinger <i>et al.</i> (2001) Isopycnal analysis in the Eastern North Atlantic.
		27.00/35.74	13.3 / 35.86	5.0	2354 [*]	2109 [*]	358 ⁺	2106	2108	-2.3	355	355	-4.1	
		27.05/35.82	12.5 / 35.72	5.1	2347 [*]	2110 [*]	357 ⁺	2106	2109	-2.6	356	356	-4.9	
		27.10/35.89	11.8 / 35.61	5.2	2341 [*]	2116 [*]	366 ⁺	2112	2111	1.8	356	356	3.4	
		27.20/36.06	10 / 35.32	5.4	2327 [*]	2117 [*]	362 ⁺	2113	2114	-0.7	356	356	-1.4	
		27.30/36.20	8.9 / 35.21	5.5	2322 [*]	2124 [*]	368 ⁺	2120	2118	1.9	357	357	3.9	
Labrador Sea (n=127) Summer 1996	Mean	27.76/36.92	3.06 / 34.85	25.1	2298 [*]	2152 [*]	383 ⁺	2134	2136	-1.3	343	345	-1.5	CARINA data base. Mintrop/Körtzinger
	STD	0.02	0.13 / 0.01	3	2	2	3	2	2	3.8	3	1	6.9