On the role of heat fluxes in the uptake of anthropogenic carbon in the North Atlantic

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[1] The influence of the overturning circulation on the anthropogenic carbon sink in the North Atlantic is investigated with a simple box model. The net air-sea flux of anthropogenic carbon in the North Atlantic is the result of two opposing fluxes: The first is the uptake caused by the disequilibrium between the rapidly rising atmospheric pCO_2 and the dissolved carbon content in the ocean, depending mainly on the water exchange rate between mixed layer and interior North Atlantic ocean. Superimposed is a second flux, related to the northward transport of heat within the Atlantic basin, that is directed out of the ocean, contrary to conventional wisdom. It is caused by a latitudinal gradient in the ratio of seawater alkalinity to total dissolved inorganic carbon that in turn is related to the cooling and freshening of surface water on its way north. This flux depends strongly on the vertical structure of the upper branch of the overturning circulation and on the distribution of undersaturation and supersaturation of CO_2 in Atlantic surface waters. A data-based estimate of anthropogenic carbon inventory in the North Atlantic is consistent with a dominance of the disequilibrium flux over the heat-flux-related outgassing at the present time, but, in our model, does not place a strong constraint on the net anthropogenic air-sea flux. Stabilization of the atmospheric pCO_2 on a higher level will change the relative role of the two opposing fluxes, making the North Atlantic a source of anthropogenic carbon to the atmosphere. We discuss implications for the interpretation of numerical carbon cycle models. *INDEX TERMS:* 1615 Global Change: Biogeochemical processes (4805); 1630 Global Change: Impact phenomena; 3210 Mathematical Geophysics: Modeling; 3339 Meteorology and Atmospheric Dynamics: Ocean/atmosphere interactions (0312, 4504); *KEYWORDS:* physical pump, anthropogenic carbon, North Atlantic, heat transport

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1. Introduction

[2] Mankind currently emits more than 6 petagrams of carbon (Pg C) per year into the atmosphere in the form of CO_2. Only about half of this carbon accumulates in the atmosphere, whereas the other half is taken up by the ocean and the land biosphere. Estimates of the net anthropogenic carbon uptake by the ocean differ considerably depending on the method used [*Ciais et al.*, 1995; *Heimann and Maier-Reimer*, 1996; *Takahashi et al.*, 1997; *Orr et al.*, 2001]. The range of uptake estimates for the decade 1980–1990 based on models of the global carbon cycle has narrowed recently from 2.0 ± 0.8 Pg C a^{-1} [*Siegenthaler and Sarmiento*, 1993] to 1.85 ± 0.35 Pg C a^{-1} [*Orr et al.*, 2001]. The regional distribution of the flux, however, is subject to much higher uncertainty [*Orr et al.*, 2001], possibly creating problems in attempts to determine the location of terrestrial anthropogenic carbon sinks from inverse atmospheric modeling [e.g., *Fan et al.*, 1998].

[3] In the North Atlantic, the increase in atmospheric CO_2 partial pressure (pCO_2) has led to a corresponding increase in dissolved inorganic carbon concentrations as compared to preindustrial values (anthropogenic carbon or C_{ant}) throughout the whole water column [*Gruber*, 1998; *Körtzinger et al.*, 1998; *Wanninkhof et al.*, 1999]. This is deeper than anywhere else in the world ocean. Does this imply that the flux of carbon from the atmosphere into the North Atlantic has increased over its preindustrial value? Observed differences in pCO_2 between the atmosphere and ocean surface waters show that the northern North Atlantic is a strong sink

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for atmospheric CO_2 [*Takahashi et al.*, 1997], but give no hint whether this flux has increased since preindustrial times. A strong uptake of C_{ant} (i.e., an additional carbon uptake compared to the preindustrial state) from the atmosphere by the North Atlantic is found in most numerical simulations of the marine carbon cycle [*Maier-Reimer and Hasselmann*, 1987; *Sarmiento et al.*, 1992, 1995; *Orr et al.*, 2001].

[4] These model results are at odds with several recent calculations of meridional carbon transport in the Atlantic and its anthropogenic component [*Holfort et al.*, 1998; G. Rosón et al., Carbon distribution, fluxes and budgets in the subtropical North Atlantic (24.5°N), submitted to *J. Geophys. Res.*, 2001 (hereinafter referred to as Rosón et al., submitted manuscript, 2001); A. Macdonald et al., A 1998–1992 comparison of inorganic carbon and its transport across 24.5 N in the Atlantic, submitted to *Deep Sea Research II*, 2002 (hereinafter referred to as Macdonald et al., submitted manuscript, 2002)]. The transport calculations consistently show a strong northward transport of C_{ant} throughout the subtropical Atlantic (i.e., a weakening of the southward carbon transport since preindustrial times) that has about the same order of magnitude as the rate at which C_{ant} is accumulating within the North Atlantic basin. This implies only a small air-sea flux of C_{ant} within the North Atlantic (Rosón et al., submitted manuscript, 2001), in contrast to the numerical model results.

[5] The discrepancy between these data-based estimates of transport and accumulation and model-based estimates of air-sea fluxes may well be within the (fairly large) error limits of both approaches. Certainly the transport-based estimates are subject to significant error arising from a wide variety of sources. However, the errors on model-based estimates of regional uptake are rarely assessed, and it remains unclear to what extent problems with the calculated heat transport, vertical mixing and convection affect model-based regional C_{ant} uptake. It is fair to say that at present we also cannot tell whether the accumulation of C_{ant} in the North Atlantic is driven preferentially by local air-sea gas exchange or northward transport. In this paper we seek to gain intuition into some of the key factors controlling the air-sea flux of C_{ant} in the North Atlantic ocean using a very simple model.

[6] On a global scale the present net uptake of carbon by the ocean is driven by the disequilibrium between the rapidly increasing atmospheric pCO_2 and the pCO_2 of the surface ocean. Air-to-sea fluxes of C_{ant} are therefore expected to be large where water that has not been in contact with the atmosphere for a long time reaches the surface, i.e., in upwelling and convection regions.

[7] However, a major factor that can modulate the distribution of CO_2 uptake in the North Atlantic is heat flux. The relation between heat fluxes and the preanthropogenic (as opposed to C_{ant}) carbon flux in the Atlantic has been discussed by *Watson et al.* [1995]. It is based on the facts that the solubility of CO_2 in seawater, like that of most other gases, increases with decreasing temperature, and that the dissociation reactions of CO_2 in seawater are also temperature-dependent. This causes that surface water in the tropical Atlantic in equilibrium with the atmosphere contains less dissolved inorganic carbon (DIC) than in the subpolar Atlantic. The cooling associated with the northward transport in the upper limb of the overturning circulation therefore drives a natural oceanic uptake of CO_2 throughout the northern Atlantic (schematic illustration in Figure 1a) that is proportional to the temperature change within the North Atlantic and to the strength of the transport.

[8] As pointed out by Wallace [2001], however, the picture becomes more complicated when one considers the current anthropogenic increase of the CO_2 partial pressure in the atmosphere. The large background concentration of DIC, that is caused by the dissociation of H_2CO_3 in seawater, increases proportionally much less than pCO_2. This is conveniently described by the Revelle factor, which is defined as the quotient between relative changes in pCO_2 and DIC, or

$$Rf = \frac{\partial pCO_2}{\partial \mathrm{DIC}} \frac{\mathrm{DIC}}{pCO_2} \tag{1}$$

for infinitesimally small changes ∂pCO_2 and ∂DIC.

[9] Values for the Revelle factor in the ocean range between 8 and 15, mainly because the *Rf* depends strongly on DIC and total alkalinity (TA). The direct dependency of *Rf* on temperature (keeping TA and DIC constant), in contrast, is rather weak. However, for an analysis of the effect of heat fluxes on C_{ant} uptake, it is more appropriate to analyze the dependency of *Rf* on temperature keeping pCO_2 rather than DIC constant, as it is a constant atmospheric pCO_2 that a parcel of water experiences at the surface of the ocean. The difference between these two temperature dependencies is illustrated in Figure 2. The *Rf* decreases much stronger with temperature holding pCO_2 constant than holding DIC constant, because DIC decreases with increasing temperature (at constant pCO_2), which in turn decreases *Rf*. For brevity we will refer to this behavior as temperature related, although strictly speaking the dependency of *Rf* on temperature is mainly indirect and mediated by changes in the TA/DIC ratio.

[10] With respect to the anthropogenic perturbation, a higher *Rf* implies a lower C_{ant} for the same anthropogenic increase of pCO_2. The anthropogenic increase of DIC concentration is thus larger in warmer water than in cold water (Figure 1b), although DIC concentrations remain higher in colder water; that is, cooling continues to drive carbon uptake. Considering the difference between present and preindustrial state (Figure 1c) shows that cooling can drive outgassing of C_{ant}, or, which is the same, less uptake of DIC than in preindustrial times. Due to the buffering C_{ant} can be considered like a hypothetical gas with a solubility that increases with increasing temperature. Note, however, that this behavior is due to the carbonate buffer system rather than the CO_2 solubility itself. This behavior is quite different from that of freons, which are often used as proxies for C_{ant}.

[11] These effects are not easy to consider: Carbonate system behavior and C_{ant} uptake can be counterintuitive. Hence the primary aim of the present paper is to contribute to a qualitative understanding of the role that heat transport

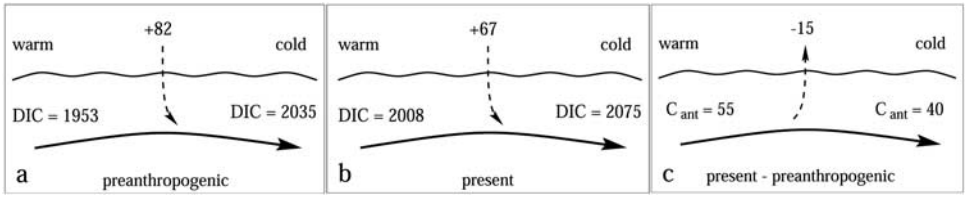

Figure 1. Schematic illustration of the effect of heat fluxes on fluxes of dissolved inorganic carbon and of anthropogenic carbon. Equilibrium DIC concentrations given in the figures for preanthropogenic and present pCO_2 are in mol kg^{-1}. They have been calculated using typical surface temperatures, salinities, and alkalinities for the tropical and subpolar Atlantic.

and net C_{ant} accumulation play in determining the uptake of anthropogenic carbon in the North Atlantic. This is attempted by investigating the dependency of the air-sea fluxes on the strength and vertical structure of the overturning circulation and on the vertical exchange of water within an idealized box model. In this model the overturning circulation is reduced to mass exchanges between a few boxes that characterize different water masses at the surface and within the interior of the Atlantic ocean. This simplification of the circulation pattern, as opposed to the use of an ocean general circulation model, allows us to separate the different processes contributing to the uptake of anthropogenic carbon, at the price of losing a ''realistic'' picture of gradients and processes. We investigate whether the anthropogenic carbon inventory as determined by *Gruber* [1998] can be used to constrain the anthropogenic carbon uptake in the box model sufficiently to resolve the apparent contradiction between data-based transport estimates and model-based air-sea fluxes.

[12] A simple box model certainly cannot give more accurate quantitative predictions than a carbon model coupled to a full general circulation model. But the identification of key processes contributing to the uptake of anthropogenic carbon in the Atlantic and their sensitivities might help to assess whether some of the usual deficiencies in numerical models, such as a too low northward heat transport in the Atlantic, are likely to be significant to the estimation of anthropogenic carbon uptake.

2. Box Model and Circulation Schemes

[13] The meridional surface gradient of C_{ant} concentrations in the Atlantic [*Gruber*, 1998; *Wanninkhof et al.*, 1999] can largely be explained by the temperature-related (see above) gradient of the Revelle factor. In the interior of the Atlantic the relatively high concentrations of C_{ant} within the northwestern North Atlantic and the ventilated thermocline [*Gruber*, 1998; *Körtzinger et al.*, 1998; *Wanninkhof et al.*, 1999] reflect the surface properties, but also, mainly, differences in ventilation timescales reaching from years (mode waters and the source region of North Atlantic Deep Water) to centuries (North Atlantic Deep Water in the South Atlantic).

[14] To represent these processes in a simple manner we describe the Atlantic Ocean by six boxes, similar to a recent box model used by *Toggweiler* [1999]. Three of these boxes (SH, TR, NH box) stand for surface water (directly exchanging carbon with the atmosphere) of different temperature, salinity, and alkalinity. The three interior boxes are used to represent the different ventilation time-scales of intermediate and thermocline waters (IW box), as opposed to the northern part of the deep North Atlantic (ND box) and the remaining deep Atlantic (D box). The lateral boundaries between the boxes have been drawn relatively arbitrarily at 30°S and at 48°N, the latter boundary approximately coinciding with the boundary between the subtropical and subpolar gyres. The depth of the surface boxes is 300 m for the two high latitude boxes (the approximate average depth of the winter mixed layer north of 48°N) and 150 m for the tropical box. The IW box extends to a depth of 1000 m below the TR box, and the ND box fills the North Atlantic North of 48°N below 300 m. Temperature, salinity, and total alkalinity of the surface boxes influence the exchange of CO_2 with the atmosphere; they are not modeled explicitly, but have been obtained by averaging over the sea surface temperatures and salinities in the climatology of *Reynaud et al.* [1998]. Alkalinity in the surface boxes has been esti-

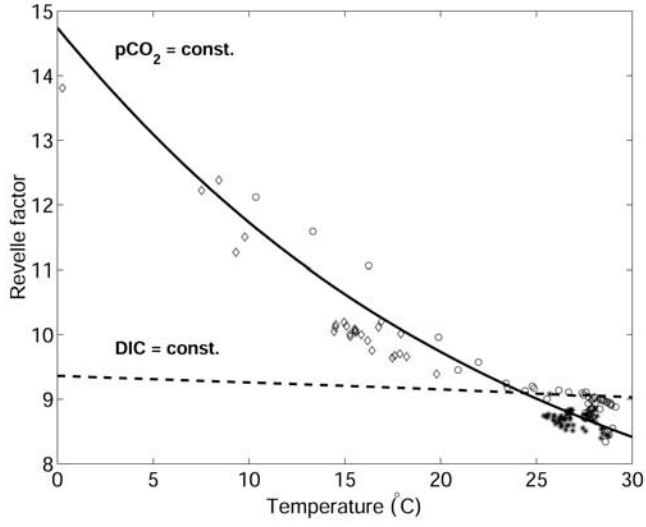

Figure 2. Temperature dependency of the Revelle factor in surface (<30 m) samples from WOCE sections A02b (diamonds), A20 (circles) and A06 (stars) in the equatorial and north Atlantic. Also shown are the theoretical curves for a total alkalinity of 2339 μM and a salinity of 35.48, holding either DIC constant at 2001 μM (dashed line) or pCO_2 constant at 365.1 atm (solid line).

Table 1. Properties of the Six Model Boxes

Box	Volume, 10^{15} m^3	Surface, 10^{13} m^2	Temperature, °C	Salinity	Alkalinity, μmol/kg
SH	8.8	3.08	7.89	34.39	2276
TR	8.0	5.53	23.74	35.91	2354
NH	2.8	1.12	7.45	34.16	2262
IW	43.0				
ND	15.2				
D	269.2				

mated from temperature and salinity, using the empirical relation by *Lee et al.* [1997] and then averaged. Table 1 lists the box properties.

[15] The model solves the mass balance equations for DIC in the six model boxes; the DIC concentrations are influenced by mass exchange with the neighboring boxes and in the surface boxes by gas exchange with the atmosphere. The vertical transport of particulate organic matter derived from algal primary production at the ocean surface is usually believed to have no strong influence on anthropogenic carbon distribution and uptake [*Sarmiento et al.*, 1995], and is therefore neglected in our model. Model integrations are performed by first integrating the model over a few thousand years into a steady state with a prescribed preanthropogenic pCO_2 of 278 μatm, followed by integration over the time period between 1765 and 1990, using pCO_2 values from a spline fit [*Enting et al.*, 1994] to ice core data and recent direct measurements. Projections beyond 1990 were made using the IPCC stabilization scenario S650 [*Houghton et al.*, 1995]. Anthropogenic concentrations and fluxes are calculated as the difference between the final and 1765 values.

[16] The mass fluxes between the boxes can be separated into two parts: Firstly a caricature of the overturning circulation within the Atlantic, and secondly bidirectional vertical mass exchange between surface boxes and the boxes underneath. The overturning circulation consists of a deep southward flowing NADW branch of strength T and a northward return flow in the TR and IW box. Northward spreading of Antarctic Bottom Water is neglected. Two model parameters describe the vertical structure of the northward flow in the model: The fraction α of the total overturning that enters the TR box from the SH box at 30°S, and the fraction β that upwells from the IW box into the TR box (see Figure 3). As we are interested in the North Atlantic only, we close the conveyor belt circulation by upwelling in the Atlantic sector of the Southern Ocean. This shortcut of the conveyor belt has no significant effect on the model results for the NH box. A fraction γ of the total upwelling can enter the IW box without prior contact with the atmosphere.

[17] It is to be expected that the partitioning of the northward return flow into surface and intermediate waters has a strong effect on the anthropogenic carbon balance in the North Atlantic, because only the part that is in direct contact with the atmosphere fully experiences the temperature-related (see above) differences in Revelle factor. *Schmitz and McCartney* [1993] estimate that at 30°S the northward flow is distributed equally between 7 Sverdrup (Sv, 1 Sv equals 10^6 m^3 s^{-1}) of surface water and 7 Sv of intermediate and thermocline water. At 24°N the flow is partitioned into 9 Sv of surface water and 5 Sv of intermediate and thermocline water; that is, there is a net upwelling of 2 Sv around the equator. *Keeling and Peng* [1995], on the other hand, concluded that the phosphate balance of the North Atlantic requires only that not less than 3 Sv of the northward flow at the equator are surface water. We assume that these two circulation scenarios bracket the real structure of the overturning circulation in the upper subtropical Atlantic. To investigate the sensitivity of the model results we therefore performed model integrations with values of α and β corresponding to these scenarios. Scenario A uses $\alpha = 7/14$ and $\beta = 2/14$, while scenario B uses $\alpha = 3/14$ and $\beta = 0$. Variations of γ had almost no effect

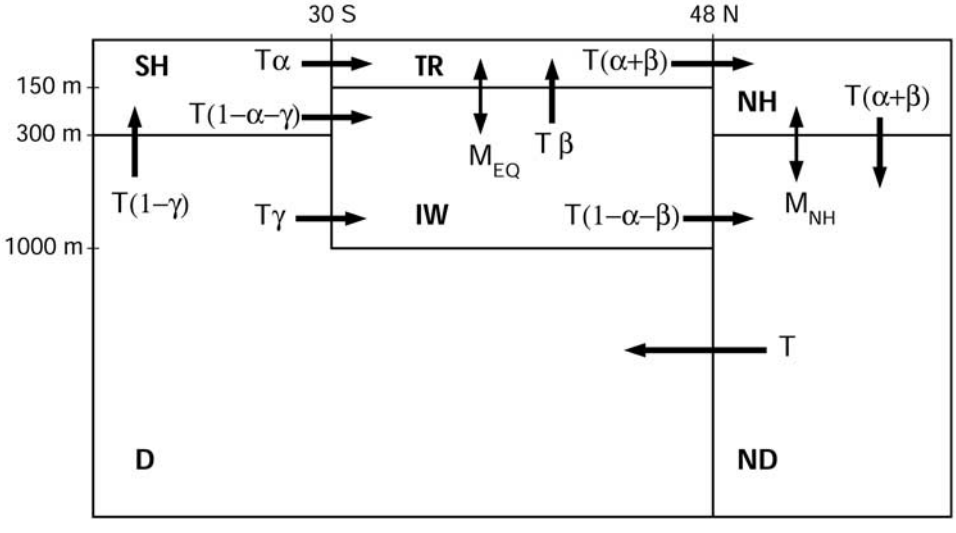

Figure 3. Unidirectional (proportional to T) and bidirectional (M_{TR} and M_{NH}) volume fluxes in the box model.

on model outcomes in the NH box; all model results shown here were obtained with $\gamma = 0$.

[18] The direct exchange between surface and deep ocean within the North Atlantic is represented by a mass exchange M_{NH} between the NH and ND boxes. We will refer to this term in the following as 'high latitude mixing'. An upper limit for this mixing may be estimated from the annual cycle of the mixed layer depth within the North Atlantic, using the *Levitus and Boyer* [1994] monthly climatology. From the difference between the maximum and minimum mixed layer depth we may estimate an exchange rate of about 50 Sv, compared to a strength of the overturning circulation of 15 ± 2 Sv [*Ganachaud and Wunsch*, 2000]. However, most of the water remaining after by the shallowing of the mixed layer in late spring is entrained again in the next winter, making the effective exchange rate with "older" water probably much lower than this. For example, *Sarmiento and Toggweiler* [1984] estimate the total amount of mixing between the high-latitude surface oceans and the deep ocean boxes from the ocean radiocarbon inventory to lie between 30 and 75 Sv, with most of this probably occurring in the Southern Ocean.

[19] A second mixing term is introduced between the TR and IW boxes. It represents two different processes: The first is the equatorial upwelling, which is at least partly compensated by the downward Ekman pumping over the subtropical gyres. The strength of this exchange is estimated to lie between 7 Sv [*Wunsch*, 1984] and 11–12 Sv [*Gouriou and Reverdin*, 1992]. The second process is the subduction of subtropical mode water at the northern edge of the North Atlantic subtropical gyre that contributes at least another 13 Sv [*Qiu and Huang*, 1995], such that the total vertical exchange M_{TR} is of the order of 20–30 Sv. In the following calculations we fixed M_{TR} at 23 Sv.

[20] Gas exchange in the uppermost model boxes is assumed to be proportional to the pCO_2 difference between box and atmosphere, using a constant gas transfer velocity. In some model runs we assumed an infinite gas transfer velocity. In this case gas exchange is calculated diagnostically as the difference between the carbon accumulation rate within the box minus the divergence of the advective carbon fluxes into the box.

3. Results

[21] An expression for the air-to-sea flux of C_{ant} in the North Atlantic surface box ($F_{ant,NH}$, positive into the ocean) can be obtained from the mass balance equation for DIC, taking the difference between the actual and the preindustrial state. It consists of three terms: net advection (or advective flux divergence), vertical mixing, and accumulation (or storage) within the NH box:

$$F_{ant,NH} = (\alpha+\beta)T\left(C_{ant,NH} - C_{ant,TR}\right) + M_{NH}\left(C_{ant,NH} - C_{ant,ND}\right) + V_{NH}\frac{dC_{ant,NH}}{dt} \quad (2)$$

Here, $(\alpha + \beta)T$ is the fraction of the total overturning T that passes through the NH box, M_{NH} is the vertical mixing rate between the NH and ND boxes, and V_{NH} is the volume of the NH box.

[22] The advective flux divergence term is the heat-transport-related flux of anthropogenic carbon; it is proportional to the overturning and to the difference in C_{ant} concentrations between the warm and cold surface boxes. The second and third terms on the right hand side of equation (2), on the other hand, reflect the disequilibrium flux of C_{ant} into the NH and ND boxes, driven by the rate of change of pCO_2 in the atmosphere.

[23] To avoid complexities resulting from undersaturation and supersaturation in the surface boxes, we first analyze model runs with an infinite gas transfer velocity, forcing the surface boxes into instantaneous equilibrium with the atmosphere. In this limiting case, C_{ant} concentrations in the surface boxes depend only on pCO_2, temperature, salinity, and alkalinity, not on the circulation. For a pCO_2 of 354 μatm, reached in the year 1990, we obtain a C_{ant} concentration of 54.8 μmol kg^{-1} in the TR box and 41.7 μmol kg^{-1} in the NH box; the difference between the boxes is mainly due to the temperature-related (see above) difference of *Rf*, to a lesser degree to the alkalinity difference.

[24] The relative role of heat-transport-related and disequilibrium fluxes of anthropogenic carbon in the North Atlantic is best understood by analyzing the dependency of the air-sea flux of C_{ant} on overturning strength T and high-latitude mixing M_{NH}. This parameter dependency is shown in Figure 4 for the two circulation scenarios (i.e., for higher and lower fractions of the overturning passing through the NH box).

[25] Several things can be noted here. Firstly, increasing the overturning always decreases the air-sea flux of C_{ant}, because $C_{ant,TR}$ is larger than $C_{ant,NH}$, making the first term on the right-hand side of equation (2) negative. The net advective gain depends on the fraction of the overturning T $(\alpha + \beta)$ passing through the NH box, and is therefore smaller for scenario B than for scenario A. If there is no or little vertical mixing M_{NH}, and if the net advective gain is larger than the accumulation of C_{ant} in the NH box, the air-sea flux becomes negative; that is, the North Atlantic can return C_{ant} to the atmosphere, as suggested by *Wallace* [2001] (lower right corner in Figure 4a). For an infinite gas transfer rate, the accumulation of C_{ant} in the NH box does not depend on T and M_{NH}, but only on the volume of water that is in direct contact with the atmosphere (i.e., on the model box depth), and on the rate of change of the atmospheric pCO_2.

[26] Increasing the high latitude mixing, on the other hand, always increases the air-to-sea flux, because more older deep-ocean water containing little C_{ant} is exposed to the atmosphere. While the net advective gain is independent of the mixing term, the converse does not hold: The concentration of C_{ant} in the ND box increases with increasing overturning, making the mixing term less effective in transporting C_{ant} into the deep ocean. This explains the slight positive curvature of the isolines in Figures 4a and 4b.

[27] Things become more complicated, but more realistic, if we take into account that air-to-sea gas exchange is not infinitely fast, but driven by partial pressure disequilibrium

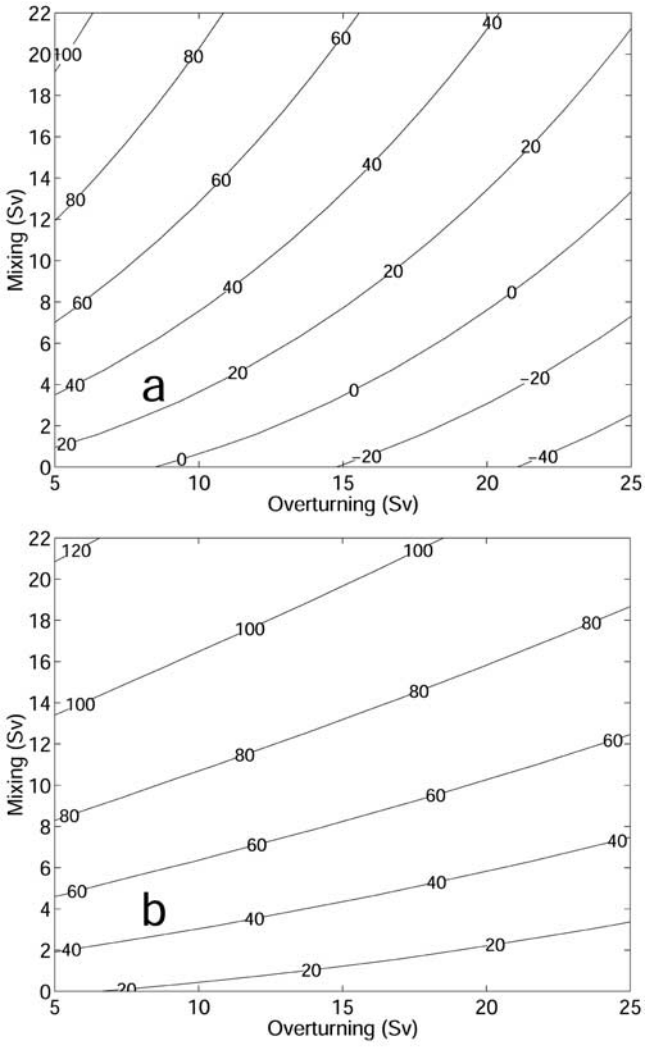

Figure 4. Atmosphere-ocean flux of anthropogenic carbon in the NH box in 1990 (in Teragrams of carbon per year, Tg C a^{-1}) over a range of overturning and mixing strengths, assuming infinite gas transfer velocity. (a) Circulation scenario A. (b) Circulation scenario B.

between atmosphere and ocean. CO_2 gas exchange can be parameterized by

$$\text{gas exchange} = \text{kA}\left(\text{s}\ \text{pCO}_2^{\text{atm}} - [\text{CO}_2]\right) \quad (3)$$

with gas transfer velocity k, box surface area A, CO_2 solubility s, and a CO_2 concentration $[CO_2]$ that is a function of DIC, TA, and temperature. The observed pattern of uptake and outgassing of carbon in the Atlantic requires undersaturation in the northern North Atlantic and a slight supersaturation in the subtropical and equatorial Atlantic [*Takahashi et al.*, 1997]. The present-day (1990) undersaturation in the NH box in our model is somewhat lower (-27 or -20 μatm for the two scenarios, assuming an overturning strength T of 15 Sv, and a mixing strength M_{NH} of 10 Sv) than the average of the *Takahashi et al.* [1997] estimate (-48 μatm north of 48°N). The difference in relation to *Takahashi et al.* [1997] may be caused by neglecting the biological pump, and/or by choosing too small values of T and M_{NH}. The agreement is better in the subtropical and tropical Atlantic, where both model and data show only a slight supersaturation (2 or 1 μatm in the TR box, and 2.6 μatm in the *Takahashi et al.* [1997] estimate between 30°S and 48°N).

[28] Figures 5a and 5b show the dependency of the air-sea flux of C_{ant} in the NH box again as a function of overturning strength and high latitude vertical mixing, but now calculated with a finite gas transfer velocity of 0.2 m h^{-1}, which is close to the global average estimated by *Broecker et al.* [1986] on the basis of GEOSECS radiocarbon data. It is evident that the slope of the isolines is smaller than in Figures 4a and 4b, and even becomes negative for some values of T and M_{NH} in Figure 5a; that is, the air-sea flux is less sensitive to the strength of the overturning than for the infinite gas transfer velocity case. This is caused by a reduced C_{ant} concentration difference between the TR and NH boxes, compared to the model run with infinite gas transfer velocity. The main cause of this reduced concentration difference is the nonlinearity of the buffering of the carbonate system: The Revelle factor (at constant TA) increases with increasing DIC content; that is, the more DIC sea water already contains, the more resistance it exerts to a further increase. The pCO_2 undersaturation in the northern North Atlantic implies a lower DIC content compared to equilibrium conditions, and thus facilitates uptake of C_{ant}; vice versa for the equatorial Atlantic. In contrast to the case with infinite gas transfer velocity, the C_{ant} concentration difference between the TR and NH boxes therefore decreases and can even change sign with increasing overturning strength, due to increasing under-saturation in the NH box.

[29] Qualitatively we may therefore state that the heat-flux-related C_{ant} flux is reduced by the distribution of undersaturation and supersaturation of CO_2 in Atlantic surface waters. This distribution cannot be reproduced very well by a simple box model; in our model however, and for the set of parameter values chosen here, we find no negative air-sea C_{ant} fluxes within the range of T and M_{NH} chosen in Figure 5.

[30] Can we use the data-based estimate of the total C_{ant} inventory within the North Atlantic by *Gruber* [1998] to constrain the circulation in the box model and thereby constrain the air-sea flux of C_{ant}? *Gruber* [1998] gives a total C_{ant} inventory of 5.3 Pg C north of 45°N and of 4.2 Pg C north of 50°N in the year 1982. By linear interpolation we obtain 4.6 Pg C for the region north of 48°N. *Gruber* [1998] estimates the error of the inventory, including systematic errors, to be in the order of 20%; this is consistent with the finding by *Wanninkhof et al.* [1999] that different methodologies to estimate the C_{ant} inventory within the North Atlantic agree to within 20% and that the estimate by *Gruber* [1998] may be biased to low values. In the box model, the inventory of C_{ant} in the NH and ND boxes in the year 1982 increases with increasing overturning and mixing.

[31] The gray shaded region in Figures 5a and 5b indicates the values of overturning and mixing that are con-

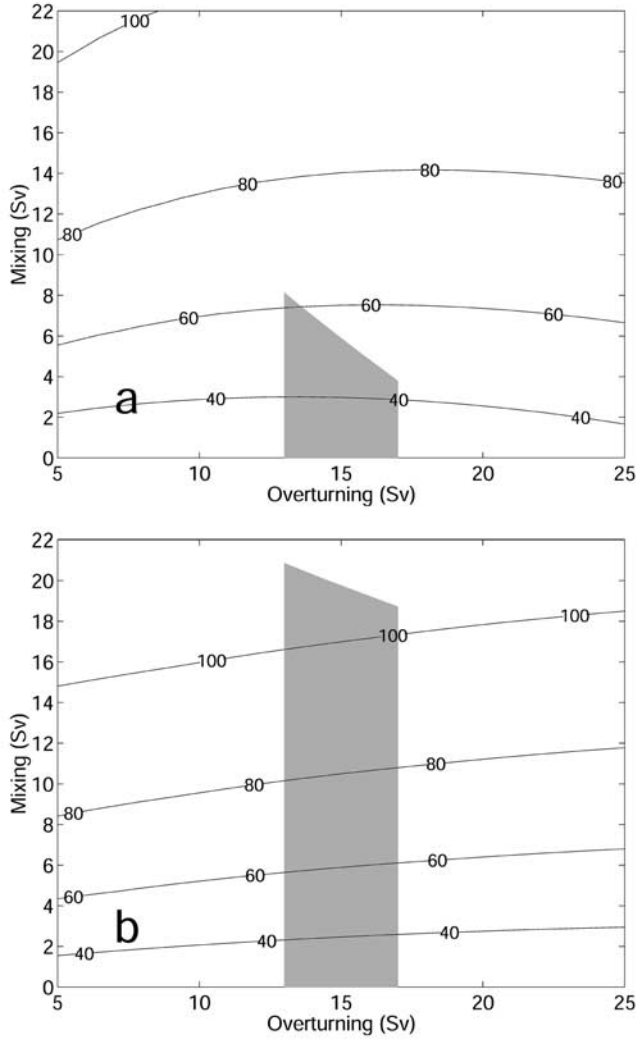

Figure 5. Atmosphere-ocean flux of anthropogenic carbon in the NH box in 1990 (in Tg C a^{-1}) over a range of overturning and mixing strengths, assuming a gas transfer velocity of 0.2 m h^{-1}. For the meaning of the shaded area, see the text.

sistent both with the overturning estimate of 15 ± 2 Sv by *Ganachaud and Wunsch* [2000] and with the requirement that the model inventory of C_{ant} in the year 1982 in the NH and ND boxes does not deviate more than 20% from 4.6 Pg C. For scenario A this constrains the high latitude vertical mixing to values below about 10 Sv, for scenario B to values below about 20 Sv. Within the range of mixing and overturning strengths indicated by the shading in Figure 5, the air-sea flux of C_{ant} (in the year 1990) varies between 20 and 60 Tg C a^{-1} for scenario A and between 20 and 110 Tg C a^{-1} for scenario B. Given the simplicity of the box model the absolute values of these flux estimates should be taken with a grain of salt. Their range, however, and also the dependency of the estimate on the circulation structure and the strength of mixing, indicates that model agreement with data-based inventory estimates (to within their present uncertainty) alone does not constrain air-sea flux of C_{ant} in the North Atlantic very well.

[32] Nevertheless, we may draw some semiquantitative conclusions from the model results presented: Firstly, the temperature-related (see above) gradient of C_{ant} acts to drive loss of C_{ant} to the atmosphere within the North Atlantic. The loss in the year 1990 can be calculated to be on the order of 50 or 16 Tg C a^{-1} (scenario A or B) north of 48°N, assuming 15 Sv of overturning, and a C_{ant} gradient of about 13 μmol kg^{-1}. However, at least for our chosen model circulation scheme, box temperatures, etc., this heat-transport driven outgassing is smaller than the uptake caused by the accumulation within the surface (25 Tg C a^{-1}) and deep (0 to 90 Tg C a^{-1}, depending on the strength of the mixing) North Atlantic. The heat-transport related flux is further counteracted by the distribution of undersaturation and supersaturation of CO_2 within the Atlantic basin, that, by the nonlinearity of the buffer factor, acts to reduce the surface C_{ant} concentration gradient to between 0 and 10 μmol kg^{-1}, depending mainly on the strength of the undersaturation within the NH box. In our model, presently the heat-flux related outgassing of C_{ant} within the North Atlantic is only a minor contribution to the total air-sea flux, that is dominated by the uptake caused by the net accumulation of anthropogenic carbon in the ocean.

[33] The relative role of these two different processes contributing to the air-sea flux, however, is likely to change in the future. This can be illustrated by integrating the model into the future, using the IPCC stabilization scenario S650 [*Houghton et al.*, 1995] for prescribing atmospheric pCO_2 after the year 1990. In this scenario, the increase rate of atmospheric pCO_2 peaks in the year 2050, and pCO_2 reaches a constant value of 650 μatm in the year 2200. Figure 6 shows time series of the different terms in the balance of C_{ant} in the NH box (equation (2)) from an integration of the box model. The flux out of the surface box due to vertical mixing (dotted line, second term on the right hand side of equation (2)) reaches a maximum in the middle of this century and then decreases due to accumulation of C_{ant} in the ND box. The net advective gain of C_{ant} (dashed line, first term on the right hand side of equation (2)) caused by the Revelle factor difference in surface waters, however, is negative and increases continuously in size with increasing pCO_2, reaching a constant value of little less than 0.1 Pg C a^{-1} in 2200. As a consequence, the air sea gas flux of C_{ant} (thick solid line, left hand side of equation (2)) begins to decrease in the first half of this century, and changes sign around 2100, making the North Atlantic a source of C_{ant} to the atmosphere at this time. While thus presently the air-sea flux is balanced primarily by the disequilibrium terms (dotted and thin solid lines), the heat-flux related term becomes dominant in the future. Needless to say, the exact time-evolution depends on details of the model, but clearly the result indicates that the regional distribution of C_{ant} uptake can vary significantly with time.

4. Summary and Discussion

[34] We have used a box model of the circulation within the Atlantic basin to study the fluxes and inventories of

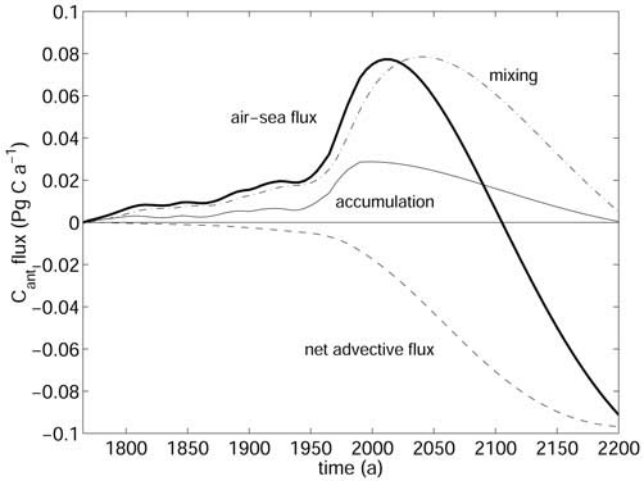

Figure 6. Terms in the mass balance of C_{ant} in the NH box (equation (2)) over the time period 1765 to 2200, using the IPCC stabilization scenario S650 for prescribing atmospheric pCO_2 after 1990. Overturning and high latitude vertical mixing have been held at 15 and 10 Sv, respectively, the partitioning of the northward return flow between the TR and IW boxes is according to scenario A, i.e., $\alpha = 7/14$, $\beta = 2/14$. The air-sea flux of C_{ant} in the NH box (thick solid line) is the sum of the other three terms.

anthropogenic carbon in the North Atlantic ocean. It was shown that the temperature dependency of the Revelle factor can lead to the somewhat counterintuitive result that the cooling of the northward flow of warm water throughout the Atlantic drives outgassing of anthropogenic carbon. Superimposed on this heat-flux driven loss is an uptake of anthropogenic carbon caused by the ocean responding to the increase of atmospheric pCO_2. The size of the disequilibrium flux primarily depends on the rate of exchange of water between the deep ocean interior and the surface. The size and even the sign of the air-sea flux of anthropogenic carbon within the northern North Atlantic therefore results from balance between two counteracting processes; this balance is sensitive to the vertical structure of the northward flowing limb of the overturning circulation, to the overturning strength, and to the strength of the exchange between high-latitude surface and deep waters. A further sensitivity of this balance arises due to the nonlinearity of the buffering of the carbonate system in seawater: The amount of anthropogenic carbon in surface seawater depends not only on temperature and salinity, but also on the pCO_2 undersaturation or supersaturation. The distribution of pCO_2 in the Atlantic with under-saturation in high latitudes further reduces the heat-flux related outgassing of anthropogenic carbon.

[35] These sensitivities should be taken into account when interpreting fluxes of anthropogenic carbon obtained from numerical carbon cycle models. It may not be surprising that the overturning strength and vertical structure, and therefore northward heat flux matter for the air-sea flux of C_{ant} in the North Atlantic; models with a weak northward heat transport are likely to overestimate local C_{ant} uptake slightly. The dependency of the uptake on the distribution of surface pCO_2, however, came as a surprise to us. It has two further implications: The first is that the biological pump, by influencing the sea surface pCO_2 has an indirect effect on the regional pattern of uptake of anthropogenic carbon by the ocean. The second is that perturbation carbon models such as *Sarmiento et al.* [1992], that implicitly imply that the preindustrial ocean was locally in equilibrium with the atmospheric pCO_2 at constant TA, probably overestimate the latitudinal gradient of surface C_{ant} and therefore underestimate the uptake of anthropogenic carbon in the North Atlantic.

[36] The direct exchange between surface and deep waters in the North Atlantic is one of the key processes determining the local uptake of anthropogenic carbon, but is also exceedingly difficult to quantify both from measurements and general circulation models. We attempted to constrain this exchange in the box model by demanding that the C_{ant} inventory in the two North Atlantic boxes be consistent with the data-based estimate by *Gruber* [1998]. It turned out, however, that this requirement does not put a strong constraint on the vertical exchange and, consequently, on the local air-to-sea flux of C_{ant}. We conjecture that a similar statement holds true also for numerical carbon cycle models.

[37] Due to the inherent limitations of the presented simple box model, we cannot claim to resolve the apparent contradiction between estimates of northward anthropogenic carbon transport within the Atlantic [*Holfort et al.*, 1998; Rosón et al., submitted manuscript, 2001; Macdonald et al., submitted manuscript, 2002] and the calculated air-sea flux of anthropogenic carbon from numerical carbon cycle models [*Sarmiento et al.*, 1992, 1995; *Orr et al.*, 2001]. Nevertheless, it seems at present to be difficult to reconcile the model results with a net outgassing of anthropogenic carbon within the North Atlantic, proposed by Rosón et al. (submitted manuscript, 2001). In the model, the disequilibrium-driven uptake seems to dominate over the heat-flux related outgassing, and the air sea flux of C_{ant}, while smaller than in most numerical carbon cycle models, is directed into the ocean.

[38] An important finding is that the present dominance of disequilibrium fluxes over heat-flux driven fluxes in the model is not permanent: Slowing down the accumulation of anthropogenic carbon in the atmosphere such that its timescale approaches the timescale of the ventilation of the deep ocean leads to a decrease of disequilibrium fluxes and thereby to a dominance of heat-flux related fluxes of anthropogenic carbon. This was demonstrated in a model integration into the future, using the IPCC stabilization scenario S650 [*Houghton et al.*, 1995] to prescribe atmospheric pCO_2. At the end of the integration in the year 2200, anthropogenic carbon behaves like a gas with solubility that increases with temperature; that is, the physical pump for carbon is complemented by a physical counter-pump for anthropogenic carbon. Our calculations for the future carbon fluxes in the North Atlantic assume a constant circulation pattern. This assumption seems justified as there is no "clear observational evidence for greenhouse-induced circulation change up to the present" [*Rahmstorf*, 2000]. In fact, the present ocean observation system would likely not

detect a changing thermohaline circulation (THC) with high confidence even in the near future [*Santer et al.*, 1995; *Deutsch et al.*, 2002]. Many model simulations, however, predict a weakening of the future overturning circulation in response to global climate change. The predicted weakening of the THC in the future leads in the model simulations to a decrease in oceanic carbon uptake [*Sarmiento and Le Quéré*, 1996]. Our simulations neglect this hypothesized effect.

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References

Broecker, W., J. Ledwell, T. Takahashi, R. Weiss, L. Merlivat, L. Memery, T.-H. Peng, B. Jahne, and K. Munnich, Isotopic versus micrometeorologic ocean CO_2 fluxes: A serious conflict, *J. Geophys. Res.*, *91*, 10,517–10,527, 1986.

Ciais, P., et al., Partitioning of ocean and land uptake of CO_2 as inferred by $\delta^{13}C$ measurements from the NOAA Climate Monitoring and Diagnostics Laboratory Global Air Sampling Network, *J. Geophys. Res.*, *100*, 5051–5070, 1995.

Deutsch, C., M. Hall, D. Bradford, and K. Keller, Detecting a potential collapse of the North Atlantic thermohaline circulation before a point of no return: Implications for the design of an ocean observation system, paper presented at the EMF Summer Workshop: Climate Change Impacts and Integrated Assessment VIII, Energy Model, Forum, Snowmass, Colo., July 27–August 7, 2002. (Available at http:\\www.geosc.psu.edu\~kkeller).

Enting, I., T. Wigley, and M. Heimann, Future emissions and concentrations of carbon dioxide: Key ocean/atmosphere/land analyses, *Tech. Pap. 31*, CSIRO Div. of Atmos. Res., Melbourne, Victoria, Australia, 1994.

Fan, S., M. Gloor, J. Mahlman, S. Pacala, J. Sarmiento, T. Takahashi, and P. Tans, A large terrestrial carbon sink in North America implied by atmospheric and oceanic carbon dioxide data and models, *Science*, *282*, 442–446, 1998.

Ganachaud, A., and C. Wunsch, Improved estimates of global ocean circulation, heat transport and mixing from hydrographic data, *Nature*, *408*, 453–457, 2000.

Gouriou, Y., and G. Reverdin, Isopycnal and diapycnal circulation of the upper equatorial Atlantic Ocean in 1983–1984, *J. Geophys. Res.*, *97*, 3543–3572, 1992.

Gruber, N., Anthropogenic CO_2 in the Atlantic Ocean, *Global Biogeochem. Cycles*, *12*, 165–191, 1998.

Heimann, M., and E. Maier-Reimer, On the relations between the oceanic uptake of CO_2 and its carbon isotopes, *Global Biogeochem. Cycles*, *10*, 89–110, 1996.

Holfort, J., K. Johnson, A. Putzka, B. Schneider, G. Siedler, and D. Wallace, The meridional transport of inorganic carbon in the South Atlantic Ocean, *Global Biogeochem. Cycles*, *12*, 479–499, 1998.

Houghton, J., L. M. Filho, B. Callander, N. Harris, A. Kattenberg, and K. Maskell (Eds.), *Climate Change 1995, The Science of Climate Change: Contribution of Working Group I to the Second Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge Univ. Press, New York, 1995.

Keeling, R., and T.-H. Peng, Transport of heat, CO_2 and O_2 by the Atlantic's thermohaline circulation, *Philos. Trans. R. Soc. London, Ser. B*, *348*, 133–142, 1995.

Körtzinger, A., L. Mintrop, and J. Duinker, On the penetration of anthropogenic CO_2 into the North Atlantic Ocean, *J. Geophys. Res.*, *103*, 18,681–18,689, 1998.

Lee, K., F. Millero, and R. Wanninkhof, The carbon dioxide system in the Atlantic Ocean, *J. Geophys. Res.*, *102*, 15,693–15,707, 1997.

Levitus, S., and T. Boyer, World Ocean Atlas 1994, technical report, Natl. Oceanic and Atmos. Admin., Silver Spring, Md., 1994.

Maier-Reimer, E., and K. Hasselmann, Transport and storage of CO_2 in the ocean-An inorganic ocean-circulation carbon cycle model, *Clim. Dyn.*, *2*, 63–90, 1987.

Orr, J., et al., Estimates of anthropogenic carbon uptake from four three-dimensional global ocean models, *Global Biogeochem. Cycles*, *15*, 43–60, 2001.

Qiu, B., and R. Huang, Ventilation of the North Atlantic and North Pacific: Subduction versus obduction, *J. Phys. Oceanogr.*, *25*, 2374–2390, 1995.

Rahmstorf, S., The thermohaline ocean circulation: A system with dangerous thresholds?, *Clim. Change*, *46*, 247–256, 2000.

Reynaud, T., P. LeGrand, H. Mercier, and B. Barnier, A new analysis of hydrographic data in the Atlantic and its application to an inverse modelling study, *Int. WOCE Newsl.*, *32*, 29–31, 1998.

Santer, B., U. Mikolajewicz, W. Brüggeman, U. Cubasch, K. Hasselman, H. Höck, E. Maier-Reimer, and T. Wigley, Ocean variability and its influence on the detectability of greenhouse warming signals, *J. Geophys. Res.*, *100*, 10,693–10,725, 1995.

Sarmiento, J., and C. Le Quéré, Oceanic carbon dioxide uptake in a model of century-scale global warming, *Science*, *274*, 1346–1350, 1996.

Sarmiento, J., and J. Toggweiler, A new model of the role of the oceans in determining atmospheric pCO_2, *Nature*, *308*, 621–624, 1984.

Sarmiento, J., J. Orr, and U. Siegenthaler, A perturbation simulation of CO_2 uptake in an ocean general circulation model, *J. Geophys. Res.*, *97*, 3621–3645, 1992.

Sarmiento, J., R. Murnane, and C. Le Quéré, Air-sea CO_2 transfer and the carbon budget of the North Atlantic, *Philos. Trans. R. Soc. London, Ser. A*, *348*, 211–219, 1995.

Schmitz, W., Jr., and M. McCartney, On the North Atlantic Circulation, *Rev. Geophys.*, *31*, 29–49, 1993.

Siegenthaler, U., and J. Sarmiento, Atmospheric carbon dioxide and the ocean, *Nature*, 365, 119, 125, 1993.

Takahashi, T., R. Feely, R. Weiss, R. Wanninkhof, D. Chipman, S. Sutherland, and T. Takahashi, Global air-sea flux of CO_2: An estimate based on measurements of sea-air pCO_2 difference, *Proc. Natl. Acad. Sci. USA*, *94*, 8292–8299, 1997.

Toggweiler, J., Variation of atmospheric CO_2 by ventilation of the ocean's deepest water, *Paleoceanography*, *14*, 571–588, 1999.

Wallace, D., Storage and transport of excess CO_2 in the oceans: The JGOFS/WOCE global CO_2 survey, in *Ocean Circulation and Climate: Observing and Modelling the Global Ocean*, edited by J. Siedler, J. Church, and J. Gould, pp. 489–521, Academic, San Diego, Calif., 2001.

Wanninkhof, R., S. Doney, T.-H. Peng, J. Bullister, K. Lee, and R. Feely, Comparison of methods to determine the anthropogenic CO_2 invasion into the Atlantic Ocean, *Tellus, Ser. B*, *51*, 511–530, 1999.

Watson, A., P. Nightingale, and D. Cooper, Modelling atmosphere-ocean CO_2 transfer, *Philos. Trans. R. Soc. London, Ser. B*, *348*, 125–132, 1995.

Wunsch, C., An estimate of the upwelling rate in the equatorial Atlantic based on the distribution of bomb radiocarbon and quasigeostrophic dynamics, *J. Geophys. Res.*, *89*, 7971–7978, 1984.

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