Uptake of natural and anthropogenic carbon by the Labrador Sea

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[1] We apply to Classical Labrador Sea Water (CLSW) the transit-time distribution (TTD) method to estimate the inventory and uptake of anthropogenic carbon dioxide (C_{ant}). A model of TTDs representing bulk-advection and diffusive mixing is constrained with CFC11 data. The constrained TTDs are used to propagate C_{ant} into CLSW, allowing the air-sea disequilibrium to evolve consistently. C_{ant} in the Labrador Sea (LS) surface waters cannot keep pace with increasing atmospheric CO_2 and is highly undersaturated. Our best estimate for 2001 is an anthropogenic inventory of 1.0 Gt C and an uptake of 0.02 Gt C/year. By additionally using the constraint of present-day CO_2 measurements, we estimate that the preindustrial LS was neutral or a weak source of CO_2 to the atmosphere. Our estimates are subject to possible error due to the assumption of steady-state transport and carbon biochemistry. **Citation:** Terenzi, F., T. M. Hall, S. Khatiwala, C. B. Rodehacke, and D. A. LeBel (2007), Uptake of natural and anthropogenic carbon by the Labrador Sea, *Geophys. Res. Lett.*, *34*, L06608, doi:10.1029/2006GL028543.

1. Introduction

[2] The North Atlantic (NA) is considered the ocean region with the largest storage of anthropogenic dissolved inorganic carbon (C_{ant}). Large concentrations of C_{ant} may be present at depths below 1.5 km [e.g., *Sabine et al.*, 2004], the result of the formation and spreading of North Atlantic Deep Water, of which Classical Labrador Sea Water (CLSW) is a major component. However, considerable uncertainties remain in the NA and globally, in part due to approximations built into the methods of inference. Here we focus on the uptake of C_{ant} by LS, where CLSW is formed in winter by deep convection in the cyclonic gyre of the LS [e.g., *Khatiwala et al.*, 2002]. This weakly stratified water mass can reach depths greater than 2 km. To estimate LS uptake and inventory of C_{ant} we apply the TTD technique [*Hall et al.*, 2004], which avoids commonly made assumptions of weak-mixing and constant disequilibrium.

2. Methodology

[3] The concentration of any passive inert tracer χ, averaged over an isopycnal volume V, can be expressed as a weighted sum over all its past outcrop values:

$$\chi^V(t) = \int_0^\infty \chi^A(t - \tau) \cdot \mathcal{G}_V(\tau)\, d\tau \qquad (1)$$

where $\mathcal{G}_V(\tau)$ is the V-averaged TTD since water in V was last in contact with a formation region of sea-surface area A, and $\chi^A(t)$ is the concentration history averaged over the formation-region. By applying (1) to anthropogenic dissolved inorganic carbon, C_{ant}, we exploit the widely-made assumptions that C_{ant} penetrates the ocean as a passive and inert tracer along isopycnals, and the ocean circulation is in steady state [e.g., *Sabine et al.*, 2004]. Although the error incurred by this assumption is of considerable interest, we do not address it here. Our analysis should be viewed as a steady-state projection of the transport information gleaned from modern-day tracers to C_{ant} uptake over the industrial era.

[4] To estimate $\mathcal{G}_V$ we first apply (1) to CFC11, a passive, inert transient tracer with no natural background. Both $CFC11^V(t)$ and $CFC11^A(t)$ can be estimated from observations, allowing us to invert (1) for $\mathcal{G}_V(t)$. Because we assume steady state circulation, once $\mathcal{G}_V$ is estimated, it can be applied to $C_{ant}(t)$ at any time. We assume $\mathcal{G}_V(t)$ to have a domain-averaged "inverse Gaussian" functional form [*Hall et al.*, 2004], where the two parameters are the mean residence time, τ_M, and Peclet number, Pe. The high Pe limit corresponds to bulk-advective transport (weak mixing), while the low Pe limit corresponds to diffusive transport (strong mixing). Pe and τ_M are allowed to range freely, subject to the CFC11 constraint applied via (1). No assumptions are made about the relative importance of bulk advective and diffusive transport, in contrast to other studies that assume mixing to be weak [e.g., *Gruber*, 1998; *Sabine et al.*, 2004]. Since the single datum, $CFC11^V$, cannot simultaneously constrain Pe and τ_M, a family of $\mathcal{G}_V$ is obtained. The $\mathcal{G}_V$ are applied to $C_{ant}^A(t)$, giving a range of values, from a minimum for strong mixing (low Pe) to a maximum for weak mixing (high Pe). However, the multiple-tracer analysis of *Waugh et al.* [2004] showed the weak-mixing limit to be unrealistic. Here, results are quoted in the weak-mixing limit, and otherwise noted. In the figures the weak- and strong-mixing estimates are both shown, along with their individual uncertainties. As it turns out, LSW parameters are such that the difference between our carbon inferences in the weak- and strong- mixing limits is smaller than other uncertainties.

[5] We use chlorofluorocarbons data from the WOCE Campaign that have been objectively mapped onto the CLSW density range $\sigma_\theta = 27.897 - 27.985$ (D. A. LeBel et al., The Distribution of CFC-11 in the North Atlantic During WOCE: Inventories and calculated water mass formation rates, submitted to *Deep-Sea Research, Part I*, hereinafter referred to as LeBel et al., submitted manuscript, 2006). CLSW CFC11 concentrations are shown in Figure 1.

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CLSW CFC-11 Concentration [pmol kg^{-1}]
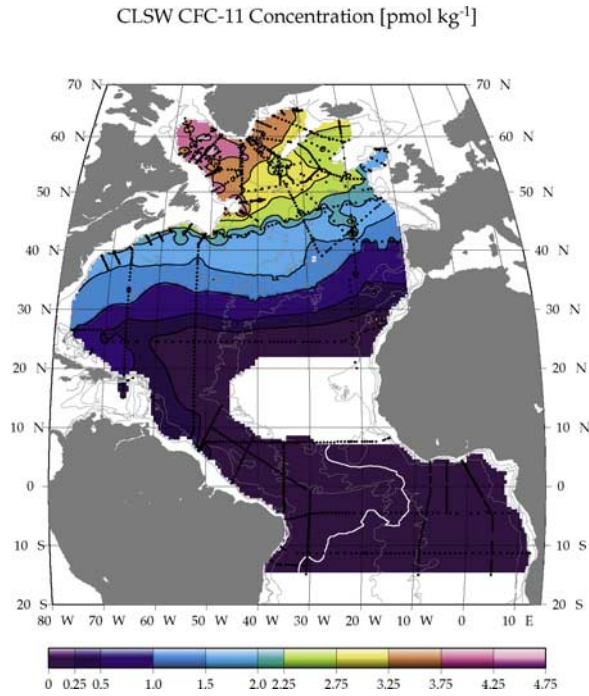
Figure 1. WOCE CFC11 concentrations objectively mapped on CLSW as described by LeBel et al. (submitted manuscript, 2006).

A time-averaged convective column in the LS (the formation region) is assumed to be the sole source for this water. To obtain the CFC11 inventory, I_{CFC}, we integrate the gridded concentrations over the CLSW volume V from the northern edge of the formation region to 42°N. South of 42°N CLSW signal is weak, and there may be contamination of Mediterranean Outflow Water. We find $V = 9 \cdot 10^{15}$ m^3 and $I_{CFC} = 22 \cdot 10^6$ moles.

[6] We estimate the CFC11 formation-region history by scaling the atmospheric history [*Walker et al.*, 2000] to match the observed LS values, a procedure which implicitly allows for subsaturation of CFC11^A(t). This is equivalent to applying a solubility function to atmospheric CFC11(t) and multiplying the resulting time series by a single saturation fraction. The CFC11 saturation implied by our scaling is 66%, consistent with 60% of *Smethie and Fine* [2001].

[7] To evaluate C_{ant}^A(t), it is often assumed that the anthropogenic contribution to the air-sea disequilibrium is small compared to the natural background [e.g., *Gruber et al.*, 1996; *Sabine et al.*, 2004]. This "constant disequilibrium" assumption allows for the use of equilibrium inorganic carbon chemistry to estimate C_{ant}^A(t) from the partial pressure of anthropogenic CO$_2$ in the atmosphere, given temperature, salinity, and alkalinity of the water mass under consideration [*Thomas et al.*, 2001]. However, at least on a global scale the disequilibrium must have evolved over the industrial era, because preindustrially the atmosphere and the ocean were in approximate equilibrium, while in the present day the atmosphere leads the ocean in pCO$_2$, due to anthropogenic emissions. To avoid the assumption of constant disequilibrium we follow the

procedure of *Hall et al.* [2004], who solve the following equation for C_{ant}^A(t):

$$K_{ex}A\left(p\text{CO}_{2,ant}^a(t) - p\text{CO}_{2,ant}^o(t)\right)$$
$$= \frac{d}{dt}\left(\rho V \int_0^\infty C_{ant}^A(t-\tau) \cdot \mathcal{G}_V(\tau)\, d\tau\right) \quad (2)$$

where $p\text{CO}_{2,ant}^a$(t) is the partial pressure of CO$_2$ in the LS that would be in equilibrium with the atmospheric CO$_2$ and is calculated using CO$_2$ solubility [*Weiss and Price*, 1980], $p\text{CO}_{2,ant}^o$(t) is the actual anthropogenic CO$_2$ partial pressure in the LS mixed layer, and K_{ex} is the annual-mean air-sea exchange coefficient. (We use annual-mean values for K_{ex} and A to be consistent with our calculation of $\mathcal{G}_V$, which has no seasonality.) Equation (2) is the statement that the air-sea flux into the LS must equal the rate of change of the inventory within CLSW, expressed as $\frac{d}{dt}(\rho V \cdot \overline{C_{ant}^V})$, with $\overline{C_{ant}^V}$ from equation (1). To solve expression (2) a relationship between $p\text{CO}_{2,ant}^o$ and C_{ant}^A is required. The total quantities (preindustrial plus anthropogenic) $p\text{CO}_2^o$ and C^A are related by definition by the equilibrium inorganic carbon system, $p\text{CO}_2^o = f(\text{C}^A)$, and so the anthropogenic quantities are related as $p\text{CO}_{2,ant}^o(t) = f(\text{C}^A(t)) - f(\text{C}^A(1780))$. (We use the equilibrium carbon chemistry coefficients of *Dickson and Millero* [1987] and the empirical relationship for alkalinity, A$_T$, in terms of salinity, S, described by *Millero et al.* [1998], A$_T$=51.24·S +520.1.) Apparently, the unknown preindustrial state must be specified. However, given a modern-day observations of C^A at a date t_{obs} (e.g., the 1995 climatology of *Takahashi et al.* [2002]), we have C^A(1780) = C^A(t_{obs}) − C$_{ant}^A$(t_{obs}). Therefore,

$$p\text{CO}_{2,ant}^o(t) = f\left(\text{C}^A(t_{obs}) - \text{C}_{ant}^A(t_{obs}) + \text{C}_{ant}^A(t)\right) - f(\text{C}^A(t_{obs})$$
$$- \text{C}_{ant}^A(t_{obs})) \quad (3)$$

Substitution of (3) into (2) results in a nonlinear integral equation in the single unknown C_{ant}^A(t), which we discretize and write in matrix form. The resulting nonlinear system of equations is solved using Newton's method.
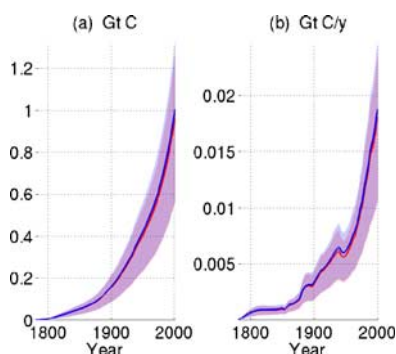
3. Results

3.1. Anthropogenic Carbon

[8] Figure 2 shows $p\text{CO}_{2,ant}^a$(t) and our best estimates of $p\text{CO}_{2,ant}^o$(t) in the weak- and strong-mixing limits. Also shown is the impact of uncertainty in K_{ex} and A (see below). The anthropogenic signal in the LS mixed layer is 17−38% and 15−35% the concurrent atmospheric value in the strong- and weak-mixing limits. Once $p\text{CO}_{2,ant}^o$ is obtained we can evaluate the anthropogenic inventory, I_{ant}, using equation (1) and the flux (uptake) $F_{ant} = d\, I_{ant}/dt$. Figure 3 shows our best estimates of I_{ant} and F_{ant} in the weak- and strong-mixing limits. The inventory and uptake have increased steadily over the industrial era, driven in our analysis solely by changes in $p\text{CO}_{2,ant}^a$. (In reality, other factors likely play a role, such as variation in ocean transport and carbon biochemistry.) In 2001 we estimate in the low Peclet limit an inventory $1.0_{-0.4}^{+0.3}$ Gt and an uptake $1.8_{-0.8}^{+0.5} \times 10^{-2}$ Gt/yr, where the
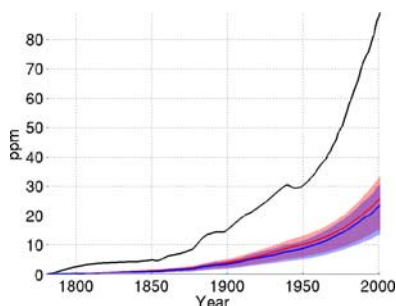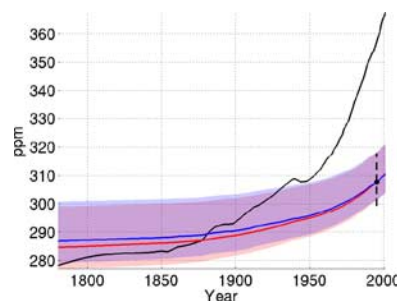
Figure 2. LS formation region best estimate $pCO_{2,ant}^o$ in the strong (red line) and weak mixing (blue line) limits. Shaded regions represent the uncertainty estimates applied separately to each mixing limit (see text for details.) Also shown is $pCO_{2,ant}^a$ (black line.)


Figure 4. Total (natural + anthropogenic) LS outcrop pCO_2^o (colors as in Figure 2). The dot symbol represents the annual mean estimate for 1995 of *Takahashi et al.* [2002] over the LS outcrop region, and the vertical dotted bars represent its estimated uncertainty. For comparison, pCO_2^a is also shown (black line.)

ranges include uncertainties in K_{ex}, A, and $pCO_2(1995)$ (see below).

[9] Uncertainty in K_{ex} and A significantly impact our anthropogenic carbon estimates. Our best estimate, K_{ex}^{best}, is the annual average of the North Atlantic values reported by *Carr et al.* [2002], based on QuickSCAT winds, assuming a velocity-squared dependence. *Carr et al.* [2002] report an 8% uncertainty in wind speed, but our effective error is larger, because we use only a fraction of one of their area-averaged K_{ex}. Moreover, because we use only annual averages, any covariance between K_{ex} and CLSW formation is neglected. Finally, there remains uncertainty as to the nature of the wind-speed dependence of K_{ex}. Our best estimate surface area, A^{best}, is a 500 km × 600 km region, centered in the LS (LeBel et al., submitted manuscript, 2006). However, CLSW formation is known to be episodic in intensity, location, and areal extent. To estimate the impact of these uncertainties we sample randomly from the uniform distributions K_{ex}: $0.5K_{ex}^{best} \rightarrow 1.5K_{ex}^{best}$ and A: $0.5A^{best} \rightarrow 2A^{best}$, for each pair computing $pCO_{2,ant}^o$ in the weak to strong mixing limits. For $pCO_2^o(1995)$ we use the work of *Takahashi et al.* [2002], and we assign an uncertainty range of ±10 ppm, from which we also sample randomly. We note that LS pCO_2 measurements reported by *DeGrandpre et al.* [2006] are in reasonable agreement with Takahashi's climatology. The value of $pCO_2^o(1995)$ has negligible impact on the anthropogenic estimates, because carbon chemistry is only weakly nonlinear in the range of anthropogenic CO_2 variation. (In the limit of strictly linear

chemistry, there is no dependence of the anthropogenic perturbation on the preindustrial state, and $pCO_2^o(1995)$ is not required.) The shaded region in Figure 2 represents one standard deviation above and below the mean computed over a number of such calculations, in the case of each the weak-mixing and strong-mixing limits.

3.2. Preindustrial Carbon

[10] Once $pCO_{2,ant}^o$ is known, we compute the total outcrop partial pressure as $pCO_2^o(t) = pCO_2^o(1780) + pCO_{2,ant}^o(t)$. As mentioned in Section 2, $pCO_2^o(1780)$ is determined by the requirement that $pCO_2^o(1995)$ matches the 1995 annually-averaged observationally-based estimate of *Takahashi et al.* [2002]. Figure 4 shows the resulting best estimate pCO_2^o. Our best estimate is $pCO_2^o(1780) = 285$ ppm, which is higher than the atmospheric value in 1780 of 278 ppm, suggesting that in 1780 the LS was a source of CO_2 to the atmosphere. It should be noted that zero flux is encompassed by the uncertainty around our best estimates. Moreover, we have not estimated the error of neglecting temporal variation in transport and biochemistry, which may be significant. We therefore do not assign a sign to the preindustrial flux. The uptake history is shown in Figure 5. Sometime between 1800 and 1960 pCO_2^o became signifi-

Figure 3. Anthropogenic (a) CLSW inventories and (b) LS uptake, with colors as in Figure 2.
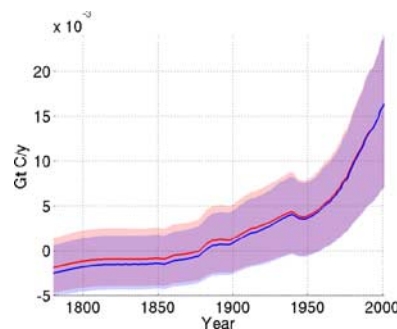
Figure 5. Total LS carbon uptake in the strong (red) and weak mixing limit (blue). Positive values indicate a net air-sea flux from the atmosphere to LS. Shaded regions represent uncertainty, applied separately to each mixing limit.

cantly larger than pCO_2^a, after which the LS became a clear sink of atmospheric CO_2.

4. Discussion

[11] We find that $pCO_{2,ant}^o$ in LS surface waters cannot keep pace with rapidly increasing atmospheric $pCO_{2,ant}^a$ and in 2001 was only 17%–38% of the concurrent atmospheric value in the strong-mixing limit. Constant air-sea disequilibrium is a poor approximation. The corresponding 2001 anthropogenic inventory in CLSW is $1.0_{-0.4}^{+0.3}$ Gt, and the uptake $1.8_{-0.8}^{+0.5} \times 10^{-2}$ Gt/yr. The small anthropogenic signal, when combined with present-day observations of total pCO_2^o, implies to a preindustrial pCO_2^o slightly higher than the preindustrial atmospheric value, suggesting that preindustrial LS was a weak source of carbon to the atmosphere, but this is not significantly different than zero, given uncertainties. Interestingly, in simulations by the MIT GCM with carbon biochemistry the preindustrial LS is also a source of CO_2 to the atmosphere, at least in winter (M. Follows, personal communication, 2005). The mechanisms for this outgassing are unclear and warrant further investigation. The convective plumes may entrain, then mix upward, deep water rich in dissolved inorganic carbon.

[12] In contrast, *Hall et al.* [2004] found $pCO_{2,ant}^o$ in Indian Ocean surface waters to track closely $pCO_{2,ant}^a$. The major parameter difference between the two analyses is the length scale $d = V/A$ (the ratio of the domain volume to the outcrop area), which for the LS is roughly 100 times larger than for the Indian Ocean thermocline. Consider the weak-mixing limit. $\mathcal{G}_V$ takes the form $G_V(t) = \tau_{adv}^{-1}$ for $t < \tau_{adv}$, and zero thereafter, where τ_{adv} is τ_M in the weak-mixing limit. For simplicity, we assume linear carbon chemistry: $C_{ant} = \gamma pCO_{2,ant}^o$. (In fact, $F_{ant}(2001)$ inferred using full nonlinear carbon chemistry and chemistry linearized about an intermediate $pCO_{2,ant}^a$ differ by only 0.2%.) Equation (2) becomes:

$$\Delta pCO_{2,ant}(t) = \frac{U}{U_P} \left(pCO_{2,ant}^o(t) - pCO_{2,ant}^o(t - \tau_{adv}) \right) \quad (4)$$

(for $t - 1780 > \tau_{adv}$), where $U_P = K_{ex}/(\rho\gamma)$ is the "piston velocity" at which material crosses the air-sea interface, and $U = d/\tau_{adv}$ is the speed at which material gets transported into the interior. There are two limiting cases: For $U_P \gg U$ material builds up very quickly in surface waters compared to the rate at which it is transported away. In this limit the atmosphere and ocean are able to equilibrate, i.e., $pCO_{2,ant}^o \approx pCO_{2,ant}^a$. This turns out to be the relevant limit in the Indian Ocean. By contrast, the LS is closer to the other limit: $U_P \ll U$. The transport across the sea surface cannot keep pace with the transport away from the surface. Consequently $pCO_{2,ant}^o \ll pCO_{2,ant}^a$.

[13] We have assumed that the air-sea exchange relevant for CLSW occurs predominantly in the LS, although we have allowed for considerable uncertainty in sea-surface area. It is possible, however, that during the roughly one year required for CO_2 to equilibrate across the air-sea interface, C_{ant} from surface regions outside the LS is transported into the LS and supplies CLSW. The area, A, over which the relevant CLSW air-sea exchange occurs is then effectively larger. To estimate roughly the impact of this

effect assume that the CLSW formation rate is 5 Sv [e.g., *Smethie and Fine*, 2001], and that this formation is supplied by a slab 200 m thick converging on the LS. In one year continuity demands that the slab shrink by an area 7.8×10^5 km². This effective area of air-sea exchange is about 2.6 times larger than our best estimate, and it impacts our C_{ant} calculations as follows (in the low Pe limit): the present-day surface saturation is 40%, the uptake is 0.04 Gt C/y, the inventory is 1.9 Gt C, and the preindustrial LS is 278 ppm.

[14] Finally, recent estimates of trends in subpolar North Atlantic pCO_2 in surface waters based on direct measurements indicate a rate of increase greater than the atmospheric trend [*Omar and Olsen*, 2006; *Léfevre et al.*, 2004], opposite our CLSW result. This is not contradictory, because these studies have not focused on CLSW, which may behave differently. Indeed, *Tanhua et al.* [2007] find CLSW to be the one North Atlantic water mass whose C_{ant} uptake over the period 1981–2004 is significantly less than what would be expected if surface waters kept pace with the atmosphere.

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