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Natural and anthropogenic air-sea disequilibrium of CO_2 in the Indian Ocean

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Abstract. We estimate the preindustrial and anthropogenic components of the air-sea disequilibrium in CO_2 on various water-density classes in the Indian Ocean. In general, the rapid increase in atmospheric CO_2 has caused the disequilibrium, $\Delta p\mathrm{CO}_2$, to increase significantly over the industrial era. For example, at the potential density $\sigma_0 = 26.7$, which outcrops in mid-latitudes and whose waters contain the most anthropogenic carbon per density interval, $\Delta p\mathrm{CO}_2$ has increased from 13ppm in 1780 to 20ppm in 2000. The impact of this tendency on the disequilibrium of dissolved inorganic carbon (DIC) in surface waters is largely offset, however, by the CO_2-buffering effect. For $\sigma_0 = 26.7$, the DIC disequilibrium has only increased from 8.7μmol/kg in 1780 to 9.5μmol/kg in 2000. For some waters, in fact, the DIC disequilibrium has decreased.

1. Introduction

The ocean plays a major role in the perturbed carbon cycle, but quantifying the uptake and ocean inventory of anthropogenic carbon is difficult, and considerable uncertainties remain. The flux of carbon into the ocean is driven by the difference ("disequilibrium") between the atmospheric CO_2 partial pressure ($p\mathrm{CO}_{2,atm}$) and the oceanic partial pressure ($p\mathrm{CO}_{2,ocn}$) that would be in equilibrium with the dissolved inorganic carbon (DIC) concentration of surface waters. Measurements of surface-water DIC have allowed estimates of the air-sea disequilibrium, $\Delta p\mathrm{CO}_2 = p\mathrm{CO}_{2,atm} - p\mathrm{CO}_{2,ocn}$, in the present day [*Takahashi et al.*, 1997]. This total disequilibrium is comprised of both anthropogenic and preindustrial components. Globally-averaged, the preindustrial ocean was in approximate equilibrium with the ocean, but locally, the air-sea disequilibrium was likely significant in many places. Local disequilibrium existed because the oceanic entry and exit regions of carbon do not coincide, partly due to regionally-varying transport to and from the surface and partly due to regionally-varying biota, which consume DIC. Superposed on this background preindustrial disequilibrium is the oceanic signal of increasing atmospheric $p\mathrm{CO}_{2,atm}$ due to human activity. Rising $p\mathrm{CO}_{2,atm}$ in the presence of a finite air-sea equilibration time causes $\Delta p\mathrm{CO}_2$ to become more positive.

Here we separate the natural and anthropogenic components of $\Delta p\mathrm{CO}_2$ in the Indian Ocean. We extend the method of *Hall et al.* [2004] with an additional feature: we do not assume that the DIC perturbation is independent of the preindustrial state. The relaxation of this assumption results in a small increase ($\sim$3%) to the anthropogenic Indian Ocean carbon mass and uptake estimated by *Hall et al.* [2004]. More significantly, it allows us to estimate the change in preindustrial air-sea disequilibrium due to anthropogenic CO_2.

2. Methodology

The flux, F, of carbon across the air-sea interface is driven by the air-sea disequilibrium in $p\mathrm{CO}_2$, and is comprised of preindustrial and anthropogenic components. The anthropogenic component is

$$F'(t) = k\Delta p\mathrm{CO}_2'(t) = k(p\mathrm{CO}'_{2,atm} - p\mathrm{CO}'_{2,ocn}) \tag{1}$$

where primes indicate anthropogenic quantities and k is the exchange coefficient, dependent on wind-speed and solubility. The industrial era is assumed to begin in 1780 ($p\mathrm{CO}_{2,atm}(1780) \approx$ 280ppm), so that $F'(1780) = 0$.

Equation (1) has two unknowns, F' and $p\mathrm{CO}'_{2,ocn}$. To close the system *Hall et al.* [2004] employ a second, independent relationship: $F'(t) = dM'/dt$, where M' is the mass of anthropogenic carbon in the water density class. M' is expressed in terms of the history of DIC' in surface waters and the volume transit-time distribution, $\mathcal{G}_V(t)$, that relates the mean concentration of any tracer over a volume V to the tracer's concentration history on surface waters. Combining, one has

$$F'(t) = V\frac{d}{dt}\int_0^t \mathrm{DIC}'(t-t')\mathcal{G}_V(t')\, dt'. \tag{2}$$

Equating (1) and (2) provides an integral equation for $\mathrm{DIC}'(t)$, if a relationship between $p\mathrm{CO}'_{2,ocn}$ and DIC' can be obtained and an estimate of $\mathcal{G}_V(t)$ is available. Now, by definition, DIC and $p\mathrm{CO}_{2,ocn}$ are related by the equilibrium inorganic carbon system. Given one (and knowledge of T, S, and alkalinity) the other can be computed. Were this equilibrium relationship, DIC $= f(p\mathrm{CO}_{2,ocn})$, linear, then one would have DIC$' =$ constant$\times p\mathrm{CO}'_{2,ocn}$, independent of $p\mathrm{CO}_{2,ocn}(1780)$. In this case one would not need the preindustrial ocean DIC state. Such an assumption was made by *Thomas et al.* [2001] and *Thomas and Ittekkot* [2001]. Alternatively, *Hall et al.* [2004] used the full nonlinear relationship, but assumed that the preindustrial ocean was locally in equilibrium with the atmosphere; i.e., that $p\mathrm{CO}_{2,ocn}(1780) = 280$ppm. The DIC $= f(p\mathrm{CO}_{2,ocn})$ relationship, however, is nonlinear (Fig. 1), and the preindustrial DIC in surface waters was generally not in equilibrium with the atmosphere. The value of the preindustrial state affects the magnitude of the DIC perturbation in response to a given $p\mathrm{CO}_{2,atm}$ perturbation. For example, on the $\sigma_0 = 26.7$ isopycnal, a 90ppm increase in $p\mathrm{CO}_{2,atm}$ starting at 200ppm results in an equilibrium DIC increase of 70μmol/kg, while the same $p\mathrm{CO}_{2,atm}$ increase starting at 280ppm results in a DIC increase of only 46μmol/kg (Fig. 1). To include these effects, when equating (1) and (2), we now write

$$
\begin{aligned}
& k \ \Big(p\mathrm{CO}'_{2,atm}(t) - (\ p\mathrm{CO}_{2,ocn}(t) - p\mathrm{CO}_{2,ocn}(1780)\ )\Big) \\
&= V \frac{d}{dt} \int_0^t \Big(f(p\mathrm{CO}_{2,ocn}(t-t')) - f(p\mathrm{CO}_{2,ocn}(1780)) \Big)\ \mathcal{G}_V(t')dt', \qquad (3)
\end{aligned}
$$

which makes explicit the fact that a preindustrial state must be specified.

Unfortunately, the preindustrial disequilibrium is not known. *Takahashi et al.* [1997], however, provided observationally-based estimates of the geographic distribution of the total disequilibrium in 1995. We have averaged the Takahashi values in September (to capture late-winter subduction) onto the outcrops of the Indian Ocean isopycnals (Fig. 2). We separate the present-day and preindustrial disequilibrium components by solving (2) iteratively for

$p\mathrm{CO}_{2,ocn}(1780)$ until $\Delta p\mathrm{CO}_2(1995)$ matches the Takahashi value within a small tolerance. At each step of the iteration (2) is solved numerically for $p\mathrm{CO}_{2,ocn}(t)$, using $\mathcal{G}_V(t)$ as described below. For k we use the estimates of *Carr et al.* [2002], based on QuickScat and SSMI scatterometer data.

The $\mathcal{G}_V(t)$ required for the calculation are derived from CFC data, as described in detail by *Hall et al.* [2004]. Briefly, CFC12 data measured in the Indian Ocean during WOCE are used to constrain a two-parameter model of $\mathcal{G}_V(t)$ for isopycnal volumes V. $\mathcal{G}_V$ propagates tracer signals on the outcrop into the interior, as in (2), and has the interpretation as the distribution of transit times since water in V made last contact with the surface [e.g., *Haine and Hall*, 2002; *Primeau*, 2004]. The two parameters are a V-averaged Peclet number, Pe, and a mean transit time, Γ. A single observation (e.g., CFC12 concentration averaged over V) cannot simultaneously constrain the two parameters. Instead, a family of $\mathcal{G}_V$ is obtained, all of which are consistent with the CFC12 value. The high Pe limit, representing weak diffusive mixing, is equivalent to using an average CFC concentration age, τ_{CFC}, as a lag time in the surface-water DIC$'$ history, i.e., $\mathrm{DIC}'_{interior} = \mathrm{DIC}'_{surface}(t - \tau_{CFC})$. Such use introduces a positive bias to $\mathrm{DIC}'_{interior}$ estimates [e.g., *Gruber et al.*, 1996; *Hall et al.*, 2002]. In fact, *Hall et al.* [2004] in the Indian Ocean and *Waugh et al.* [2004] for the North Atlantic find that the low Pe limit (strong mixing) is most consistent with multiple tracers analyzed in combination, and we use this limit here. The low Pe limit results in about 30% less anthropogenic carbon mass in the Indian Ocean than the high Pe limit [*Hall et al.*, 2004].

3. Results

Fig. 4 shows the change in disequilibrium over the industrial era at the outcrop of the $\sigma_0 = 26.7$ surface. We estimate $\Delta p\mathrm{CO}_2(1780) \approx 13$ppm for this water. The disequilibrium has increased rapidly since the 1950s, reaching about 20ppm in 2000. The disequilibrium can also be expressed in terms of DIC: $\Delta\mathrm{DIC} = \mathrm{DIC}_{eq}(t) - \mathrm{DIC}(t)$, where $\mathrm{DIC}_{eq}(t)$ is the DIC that would be in equilibrium with $p\mathrm{CO}_{2,atm}(t)$. For $\sigma_0 = 26.7$ we estimate that $\Delta\mathrm{DIC}(1780) \approx 8.7\mu$mol/kg, reaching 9.5μmol/kg in 2000. The fractional increase in ΔDIC over the industrial era (9%) is considerably smaller than the fractional change in $\Delta p\mathrm{CO}_2$ (54%). This is due to the nonlinearity in the equilibrium DIC $= f(p\mathrm{CO}_{2,ocn})$ relationship (Fig. 1). Atmospheric CO_2 rises at an increasingly rapid rate, leading to an increasingly large lag of $p\mathrm{CO}_{2,ocn}$ (i.e., increasing $\Delta p\mathrm{CO}_2$). However, the rate of increase of DIC_{eq} with $p\mathrm{CO}_{2,atm}$ is progressively slower at higher $p\mathrm{CO}_{2,atm}$, and this partially offsets the tendency for increased disequilibrium in DIC. This well-known reduction in the rate of increase of DIC_{eq} with $p\mathrm{CO}_{2,atm}$ is called the CO_2 buffering factor. As CO_2 dissolves in sea water the pH decreases, so that the change in DIC is not proportional to the change in CO_2. The Revelle factor, the ratio of the relative changes, $(d\mathrm{CO}_2/\mathrm{CO}_2)/(d\mathrm{DIC}/\mathrm{DIC})$, is typically in the range of 8–15.

Fig. 5 shows the preindustrial and year-2000 disequilibrium as a function of equivalent latitude of the isopycnal outcrops. (Equivalent latitude is the latitude that encompasses the same Indian Ocean area as the outcrop contours, and is close to true latitude because the outcrops are oriented approximately zonally.) The total disequilibrium is largest around $-30°$, although the anthropogenic is largest in the range -40° to -50°. (The volume defined by $\sigma_0 = 26$ to 27 has the most anthropogenic carbon per density interval [*Hall et al.*, 2004].)

Everywhere $\Delta p\mathrm{CO}_2 > 0$, and $\Delta\mathrm{DIC} > 0$. By contrast, while the anthropogenic signal $\Delta p\mathrm{CO}_2'$ is everywhere positive, $\Delta\mathrm{DIC}' \equiv \Delta\mathrm{DIC}(t) - \Delta\mathrm{DIC}(1780)$ switches sign around -45°. $\Delta\mathrm{DIC}'$ is influenced by two opposing effects, as noted above. On the one hand, the increasing lag of $p\mathrm{CO}_{2,ocn}(t)$ behind the nonlinear growth in $p\mathrm{CO}_{2,atm}(t)$ drives an increasing corresponding lag in DIC behind DIC_{eq} (growth in $\Delta\mathrm{DIC}'$). On the other hand, at higher $p\mathrm{CO}_{2,atm}$, the CO_2-buffering effect causes DIC_{eq} to increase more slowly with $p\mathrm{CO}_{2,atm}$ (decline in $\Delta\mathrm{DIC}'$). For $\sigma_0 = 26.7$ these effects roughly cancel, and $\Delta\mathrm{DIC}'$ is near zero (Figs. 4 and 5). At higher σ_0 (south of -45°), $\Delta\mathrm{DIC}' > 0$, while at lower σ_0 (north of -45°) $\Delta\mathrm{DIC}' < 0$.

4. Impact on Inventory Estimates

Although it is $\Delta p\mathrm{CO}_2$ that drives the air-sea flux of carbon, the behavior of $\Delta\mathrm{DIC}'$ has consequences for the estimation anthropogenic carbon inventories in many studies [e.g., *Gruber et al.*, 1996; *Sabine et al.*, 1999; *Thomas et al.*, 2001; *McNeil et al.*, 2003; *Hall et al.*, 2004]. Many of these studies have made the assumption that the air-sea disequilibrium has changed little over the industrial era. *Hall et al.* [2004] partially relaxed this assumption and estimated that changes in disequilibrium reduced the inventory and uptake of anthropogenic carbon in the Indian Ocean by 6%–9% compared to constant disequilibrium. (*Hall et al.* [2004] also estimated that allowing for strong isopycnal mixing reduces inventory estimates by 30% compared to estimates assuming weak mixing—this reduction stands, and is not subject to revision here.) However, *Hall et al.* [2004] assumed that the anthropogenic perturbation was independent of the preindustrial state and took $p\mathrm{CO}_{2,ocn}(1780) = p\mathrm{CO}_{2,atm}(1780) = 280$ppm. Allowing for $\mathrm{DIC} = f(p\mathrm{CO}_{2,ocn})$ nonlinearity and a nonzero preindustrial disequilibrium increases the DIC$'(t)$ in surfaces waters. The increased DIC$'(t)$ is carried into the interior by the CFC-constrained $\mathcal{G}_V$, resulting in higher inventories.

Three estimates for the DIC$'(t)$ surface-water history are shown in Fig. 6 on the 26.7 and 25.5 isopycnals. The solid line represents the best estimate from our present calculation; the dot-dash line is the *Hall et al.* [2004] result, which allows change in the disequilibrium over the industrial era, but assumes zero preindustrial disequilibrium; and the dash line is the result assuming air-sea equilibrium for all times. The *Hall et al.* [2004] curve is lower than the equilibrium curve because their calculation allows for the increased disequilibrium consistent with the increasing carbon uptake. However, when preindustrial DIC is allowed to be lower than equilibrium, as in this present calculation, the DIC$'(t)$ curve is raised compared to the *Hall et al.* curve. For some isopycnals (e.g., 26.7) there is approximate cancellation between the effect of time-varying disequilibrium and the effect of preindustrial disequilibrium, and the resulting DIC$'(t)$ is close to equilibrium. The cancellation is not exact, as the magnitudes of the competing effects depend on the particular domain.

Summed over all the isopycnals of the Indian thermocline, the effect of including the preindustrial state on the inventory and uptake of anthropogenic carbon is only 3%, although it is as large as 11% on individual isopycnals. Assuming preindustrial equilibrium results in a year-2000 inventory of 14.8 Gt C and uptake of 0.26 Gt/yr, in the strong-mixing limit for $\mathcal{G}_V(t)$. (These values are marginally higher than those reported by *Hall et al.* [2004] due to the use of different T and S data in computing the isopycnal outcrop positions.) Allowing for preindustrial disequilibrium in the present calculation we obtain for the inventory 15.3 Gt and for the uptake 0.27 Gt/yr. This nominal increase is well within the $\pm 20\%$ uncertainty estimated by *Hall et al.* [2004]. Moreover, we have introduced additional uncertainty through the reliance on the Takahashi estimate of 1995 total disequilibrium. As in *Hall et al.* [2004], these inventory and uptake estimates are smaller than those of *Sabine et al.* [1999] and *McNeil et al.* [2003] primarily due to the allowance for mixing in the form of $\mathcal{G}_V(t)$.

5. Summary and Conclusions

We have estimated the preindustrial and anthropogenic components of the CO_2 air-sea disequilibrium of the Indian Ocean thermocline. For example, at the outcrop of the water-density class $\sigma_0 = 26.7 \pm 0.1$ (which contains the most anthropogenic carbon mass per density interval) the air-sea disequilibrium has increased from 13ppm in 1780 to 16ppm in 1960 to 20ppm in 2000, driven by the rapid increase in atmospheric CO_2. This increase would seem to invalidate the widely-made assumption that the disequilibrium has remained approximately constant in time. However, the impact on surface-water $\mathrm{DIC}'(t)$, and consequently on anthropogenic carbon inventory estimates, is largely offset by the CO_2-buffering effect. The disequilibrium expressed in terms of DIC for $\sigma_0 = 26.7 \pm 0.1$ has only increased from 8.7μmol/kg in 1780 to 9.5μmol/kg in 2000. In fact, for some densities ($\sigma_0 < 26.7$) the CO_2 buffering outweighs the effect of rapid $p\mathrm{CO}_{2,air}$ increase, and the DIC disequilibrium has actually decreased in time. These effects have the fortuitous consequence of causing canceling errors, were one to make the naive assumption of air-sea equilibrium at all times. However, it should not be expected that this approximate cancellation will hold in other domains and at other times.

The separation of the preindustrial and anthropogenic fractions of air-sea CO_2 disequilibrium provides a picture of the evolving spatial pattern of air-sea carbon flux. In the Indian

Ocean higher density waters (with more southerly outcrops) receive a larger fraction of the total flux than they did preindustrially (Fig. 5). We note, however, that to a good approximation the anthropogenic inventory and uptake can be estimated without recourse to the preindustrial state or temporal variation of air-sea disequilibrium. This study and *Hall et al.* [2004] show that, at least in the Indian Ocean, these effects are small corrections (∼10% or less) to anthropogenic carbon estimates made by simply assuming air-sea equilibrium to obtain $\mathrm{DIC}'(t)$. Larger corrections arise from the inclusion of mixing in the representation of the transit-time distribution, $\mathcal{G}_V(t)$, used to propagate $\mathrm{DIC}'(t)$ into the interior. The second-order sensitivity of this approach to the air-sea disequilibrium is in sharp contrast to the first-order sensitivity of approaches that estimate uptake directly from the measured air-sea disequilibrium.

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6. References

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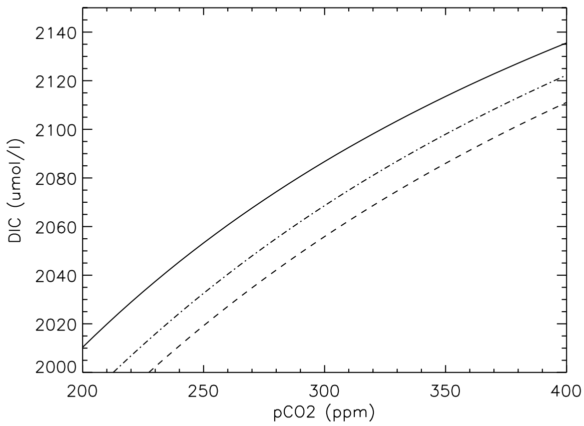

Figure 1. Equilibrium DIC-pCO_2 relationship for three sample densities: $\sigma_0 = 26.7$ (solid), $\sigma_0 = 26.1$ (dot-dash), and $\sigma_0 = 25.5$ (dash)

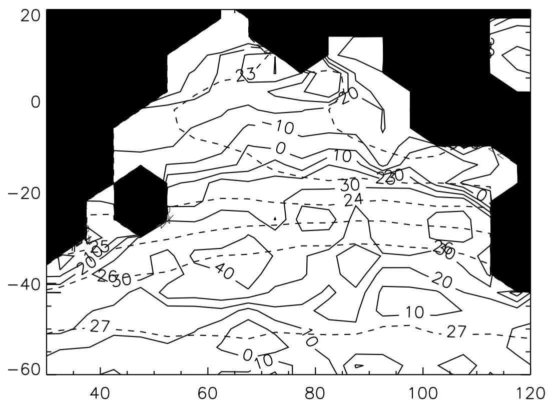

Figure 2. Distribution of total Indian Ocean disequilibrium (ppm, solid) for September, 1995 [*Takahashi et al.*, 1997]. Also shown are the outcrops of σ_0 isopycnals (dash).

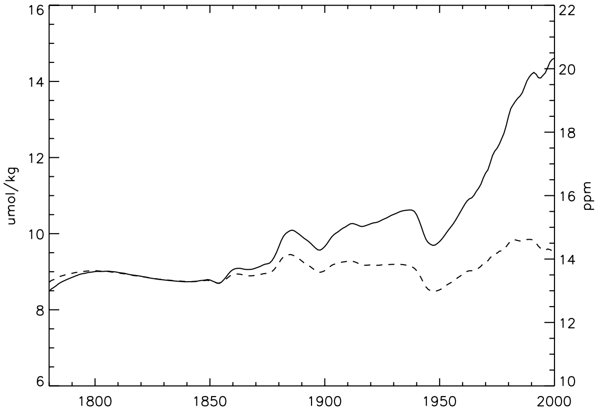

Figure 3. History of disequilibrium on $\sigma_0 = 26.7$ expressed pCO_2 (solid, right axis) and DIC (dash, left axis).

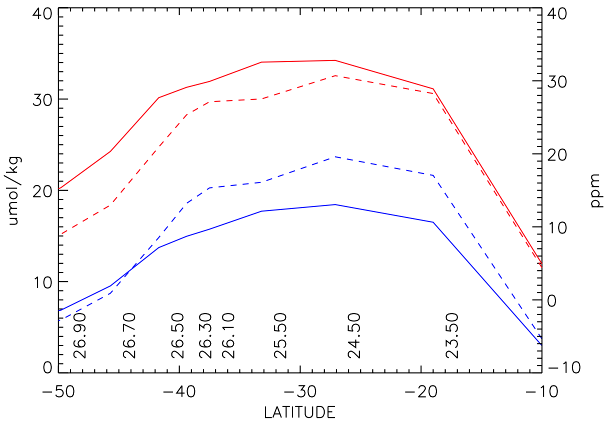

Figure 4. Disequilibrium as a function of equivalent latitude expressed as DIC (blue, right axis) and pCO_2 (red, left axis). Solid lines are for year 2000 and dashed lines for 1780. Isopycnals (σ_0) are labeled at their outcrop latitudes.

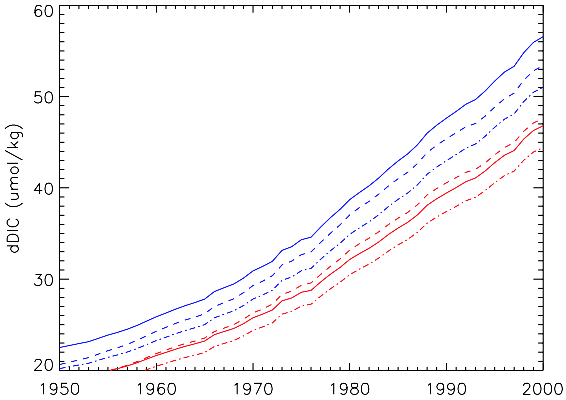

Figure 5. $DIC'(t)$ on the outcrops of the isopycnals $\sigma_0 = 25.5$ (red) and $\sigma_0 = 26.7$ (blue) as estimated in this study, with disequilibrium that is non-zero preindustrially and is allowed to vary subsequently (solid); as in *Hall et al.* [2004], with disequilibrium assumed to be zero preindustrially, but allowed to vary subsequently (dot-dash); and assuming air-sea equilibrium at all times (dash). Only the history since 1950 is shown to highlight differences. All curves start from zero in 1780.