The oceanic sink for anthropogenic CO₂


Methods and Materials

Brewer (S1) and Chen and Millero (S2) made the first attempts to separate the relatively small anthropogenic CO₂ signal from measured DIC values nearly 25 years ago. They assumed that anthropogenic CO₂ could be estimated by correcting measured sub-surface DIC concentrations for the contributions of organic matter decomposition and dissolution of carbonate minerals and taking into account the DIC concentration the water had in the preindustrial ocean when it was last in contact with the atmosphere, referred to as preformed DIC. Since the preindustrial ocean DIC concentrations were not measured, the large preformed DIC component was estimated from empirical relationships with nutrients and temperature and an assumption that the deep ocean contains no anthropogenic CO₂. Gruber et al. (S3) improved the separation method by defining a quasi-conservative tracer, C*, that separates the preformed DIC into an equilibrium component that can be calculated from thermodynamics, and a substantially smaller disequilibrium component. Another strength of this approach is that it is not as strongly affected by mixing as the former methods. The separation can be summarized by:

\[
\text{DIC}^{\text{anth}} (\mu\text{mol kg}^{-1}) = \text{DIC}^{\text{meas}} - \Delta \text{DIC}^{\text{bio}} - \text{DIC}^{\text{eq}} - \Delta \text{DIC}^{\text{diseq}}
\]  

(1)

Where \(\text{DIC}^{\text{anth}}\) is the anthropogenic CO₂ concentration of a sub-surface water sample; \(\text{DIC}^{\text{meas}}\) is the measured DIC concentration; \(\Delta \text{DIC}^{\text{bio}}\) is the change in DIC as a result of
biological activity (both organic carbon and CaCO₃ cycling); $DIC^{(eq)}$ is the DIC of seawater (at the temperature, salinity, and preformed alkalinity of the sample) in equilibrium with a pre-industrial CO₂ partial pressure of 280 µatm; and $\Delta DIC^{(diseq)}$ is the air-sea CO₂ disequilibrium a water parcel had when it was last in contact with the atmosphere, expressed in µmol kg⁻¹ of DIC.

The first three terms on the right side of the equation can be calculated explicitly for each water sample and are called $\Delta C^*$:

$$\Delta C^* = DIC^{(meas)} - DIC^{(eq)} + \frac{117}{170}(O_2 - O_2^{(sat)}) - \frac{1}{2}(TA - Alk0 - 16/170(O_2 - O_2^{(sat)}) + 106/104N^*_{anom})$$

(2)

where $DIC^{(meas)}$, $TA$ and $O_2$ are the measured concentrations for a given water sample in µmol kg⁻¹; Alk0 is the preformed alkalinity value; $O_2^{(sat)}$ is the calculated oxygen saturation value that the waters would have if they were adiabatically raised to the surface; and $N^*_{anom}$ is the net denitrification signal in the waters. Alk0 was estimated for each basin using a multiple linear regression of the surface alkalinity values to conservative tracers.

For any given water parcel in the interior of the ocean, the net air-sea disequilibrium value represents the weighted average of individual air-sea disequilibria from various source waters. We adopted an optimum multiparameter (OMP) analysis to evaluate the relative contributions of the different water sources on individual isopycnal surfaces. Two methods were then used to estimate the disequilibrium correction, $\Delta DIC^{(diseq)}$, for the different water sources (Eq. 1). For shallow or ventilated isopycnal surfaces that contain measurable levels of chlorofluorocarbons (CFC), the $\Delta DIC^{(diseq)}$ terms for the water sources were derived from the CFC-12 corrected $\Delta C^*$ calculation,
\[ \Delta C_{t12} \text{, } \Delta C_{t12} \] is derived in the same manner as \[ \Delta C^* \], but rather than evaluating the carbon concentration the waters would have in equilibrium with a preindustrial atmosphere, they were evaluated with respect to the CO\textsubscript{2} concentration the atmosphere had when the waters were last at the surface based on the concentration ages determined from CFC-12 measurements. For isopycnal surfaces located in the interior of the ocean where CFC-12 is absent and where one can reasonably assume that there is no anthropogenic CO\textsubscript{2}, the \[ \Delta C^* \] values in these waters are equal to \[ \Delta DIC^{\text{diseq}} \]. To ensure that the \[ \Delta DIC^{\text{diseq}} \] values for deep density surfaces were not contaminated with anthropogenic CO\textsubscript{2}, we only used \[ \Delta C^* \] values showing no obvious trend along the isopycnal surface.

To generate a global anthropogenic CO\textsubscript{2} inventory, the individual sample estimates from the Indian (S4), Pacific (S5), and Atlantic (S6) oceans were objectively gridded (S7) onto 33 depth surfaces with one degree resolution. These three sets of maps where merged with a fourth set of maps that was separately generated for the Southern Ocean. An error weighted mean was calculated for grid cells with more than one estimated value. Since the global survey had limited data coverage in the marginal basins (the South China Sea/Indonesian region, Yellow Sea, Japan/East Sea, Sea of Okhotsk, Gulf of Mexico, North Sea, Mediterranean Sea, and the Red Sea) and the Arctic Ocean (north of 65°N), these areas were excluded from the mapped regions.

The uncertainty in the total inventory is estimated to be approximately 16% based on uncertainties in the anthropogenic CO\textsubscript{2} estimates and mapping errors. Uncertainties in the former arise from both random errors and potential biases. The random errors, including the precision of the original measurements, have been estimated to be about ±8
μmol kg\(^{-1}\) \((S3-6, S8)\). This estimate is about twice as large as the standard deviation of the \(\Delta C^*\) values below the deepest anthropogenic CO\(_2\) penetration depth suggesting that the propagated errors may be a maximum estimate of the random variability. Based on these estimates, the limit of detection for this technique is assumed to be approximately 5 μmol kg\(^{-1}\). The impact of these random errors on the uncertainty of the inventory is negligible, as a large number of samples were averaged to estimate the inventory.

The potential biases in the technique are much more difficult to evaluate and could include errors in the 1) biological correction resulting from the assumed stoichiometric relationships, 2) water mass age estimates based on CFCs, 3) assumption of minimal diapycnal mixing, 4) assumption that oxygen was in equilibrium in surface waters and 5) that the air-sea disequilibrium term is constant over time. Biases in the technique have been primarily evaluated with sensitivity studies and comparisons with other approaches (e.g. S3-6, S8-12). These studies estimated the potential biases to be about 10-15%. The mapping errors can be estimated from the objective mapping calculations \((S7)\), but are also difficult to assess quantitatively since the mapping errors are highly correlated both vertically and horizontally \((S13)\). We assume that their contribution is smaller than 15%.

To arrive at a full global ocean inventory, we assume that the inventory in the unmapped regions south of 65°N (the marginal basins) scales with ocean surface area. This adds about 6 Pg C to the total. Including the Arctic Ocean (defined here as all ocean north of 65°N) using an area scaling approach would increase the total by about 3-4% to 116.5 Pg C. Willey et al. \((S14)\) found that the Arctic Ocean accounted for approximately 5% of the global ocean CFC inventory in 1994. Given the correlation between CFC and
anthropogenic CO₂ inventories (S15), we adopt the scaling based on CFC inventories for the Arctic Ocean, and arrive at our final global anthropogenic CO₂ inventory estimate of 118±19 Pg C. This inventory pertains to a nominal year of 1994, approximately the median year of our oceanographic measurements.

**References**


Figure S1. Zonal total inventory (A) determined by vertically integrating the anthropogenic CO₂ in each one degree grid then summing up for each degree of latitude, and zonal mean inventory (B) determined by taking the vertically integrated values and dividing by the area of each grid box and averaging for each degree of latitude. Zonal mean inventory shows that the Atlantic generally has the highest average inventories on a per square meter basis, but when the total area is taken into consideration, the Pacific has the highest total inventories everywhere except north of 20°N.

Table S1. Distribution of Anthropogenic CO₂ inventories in Pg C by basin and latitude band for 1994.

<table>
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<th>Atlantic</th>
<th>Pacific</th>
<th>Indian</th>
<th>World</th>
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<td>4</td>
<td>1</td>
<td>-</td>
<td>5 (5%)</td>
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<tr>
<td>14-50°N</td>
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<td>11</td>
<td>1</td>
<td>28 (26%)</td>
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<td>8</td>
<td>6</td>
<td>21 (20%)</td>
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<tr>
<td>14-50°S</td>
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<td>18</td>
<td>13</td>
<td>42 (40%)</td>
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<tr>
<td>&gt;50°S</td>
<td>2</td>
<td>6</td>
<td>2</td>
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<tr>
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<td>40 (38%)</td>
<td>44 (41%)</td>
<td>22 (21%)</td>
<td>106</td>
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