

Comment on "The Ocean Sink for Anthropogenic CO₂"

Using data from recently completed hydrographic surveys of dissolved inorganic carbon (DIC) and related tracers in the world's oceans, Sabine *et al.* (1) arrived at an estimate of 118 ± 19 Pg C for the uptake of anthropogenic CO₂ by the oceans through 1994. This estimate uses the "ΔC* method" pioneered by Gruber (2) and now widely applied to estimating ocean carbon changes. Here, I highlight several complications associated with the ΔC* method that have not been previously discussed. Consideration of these factors suggests that estimates of ocean uptake of anthropogenic CO₂ may need revising.

One complication is that the ocean inventory of anthropogenic CO₂ is an incomplete measure of the change in the ocean carbon content. The term "anthropogenic CO₂," as used by Sabine *et al.*, refers to the excess carbon dioxide that has accumulated in the ocean as a direct response to rising CO₂ levels since preindustrial times. Changes in carbon accumulation driven by processes within the ocean, such as warming (whether anthropogenic or otherwise), or changes in ocean stratification are not counted as "anthropogenic" CO₂. These contributions are certainly much smaller than the component driven by rising atmospheric CO₂ levels, but they are not necessarily negligible. A complete global carbon budget must therefore also include a term for these ocean-driven exchanges of CO₂.

It is relatively straightforward to estimate the direct effect of long-term warming on air-sea carbon exchanges (3, 4). For example, using the box-diffusion model (5) tuned for consistency to match the Sabine *et al.* estimate of 118 petagrams of carbon in the absence of warming, the net uptake in the presence of warming is found to be 105 Pg C. This is consistent with a warming correction of -13 Pg C (6-8). Warming releases CO₂ from the ocean primarily because CO₂ is less soluble in warmer water.

It is likely that warming over the past century has also influenced CO₂ exchange indirectly through increases in the density stratification of the upper ocean, thereby decreasing vertical mixing and increasing the trapping of nutrients and metabolic CO₂ in subsurface waters. There is no simple way to estimate this stratification effect, but based on the results of general circulation models (3, 4), the effect through 1994 is most likely on the order of +6 Pg C, offsetting the warming effect. Combining the warming and stratification effects thus leads to an estimate of -7 Pg C for the ocean-driven term, with an

uncertainty that is not well constrained but probably is about ±10 Pg C.

Another complication is that the ocean inventory of anthropogenic CO₂ may not be determined reliably using the ΔC* method in the presence of warming or other ocean variability. The ΔC* method is a hybrid of two methods, the first applied in the upper ocean where the isopycnal layers are contaminated everywhere with anthropogenic CO₂ and the second applied in the deeper waters where the isopycnal layers are partially uncontaminated. In the upper ocean, the ΔC* method principally relies on chlorofluorocarbon ventilation ages in combination with the known history of atmospheric CO₂. If a different atmospheric history were used, the estimate of anthropogenic CO₂ uptake in these waters would change proportionally, which illustrates that the method is not a direct observation of carbon accumulation but effectively a model-dependent estimate, albeit a highly constrained one. This model assumes that the ocean circulation has remained steady with time and is therefore subject to error if circulation rates have changed. For example, the box-diffusion model indicates that if the vertical diffusion rates were 20% higher before 1980, the Sabine *et al.* estimate (1), which effectively projects modern diffusion rates over the entire period, would underestimate the actual uptake by 7 Pg C.

In the deeper waters, the ΔC* method depends on the spatial gradients in the tracer ΔC*, which is a mathematical function of total carbon, oxygen, nitrate, phosphate, silica, alkalinity, temperature, and salinity. The assumption is made that the gradient in ΔC*, along a given isopycnal surface from the older uncontaminated waters to the younger contaminated waters, is a measure of anthropogenic CO₂. However, the gradient in ΔC* can be produced not only by uptake of CO₂ but also by other processes, particularly air-sea exchanges of heat and O₂ (9). Based on the ΔC* sensitivity to heat and O₂ (10) and plausible estimates of changes in heat and O₂ content of the deeper waters (11-16), corrections on the order of 3 to 5 Pg C are implied, with the heat and O₂ effects partly canceling. More work is needed to assess these corrections as well as the impact on variable circulation, which are complicated by our limited knowledge of global hydrographic changes before the late 20th century. Until these corrections are properly assessed, it seems appropriate to revise upward the uncertainty in the estimate of anthropo-

genic CO₂ uptake. A reasonable revision might be from ±19 to ±23 Pg C/year.

In summary, the Sabine *et al.* (1) estimate of anthropogenic CO₂ uptake should be combined with an additional term of about -7 ± 10 Pg C to account for air-sea CO₂ exchanges driven by warming and stratification. The error estimate on the anthropogenic contribution should furthermore be increased to about ±23 Pg C to reflect uncertainties associated with changes in ocean circulation, heat content, and O₂ content on the ΔC* method. Combining these corrections yields an estimate of 111 ± 25 Pg C for the net oceanic uptake of CO₂ from 1800 to 1994. I hope that this comment will initiate a process to examine these corrections more closely.

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References and Notes

1. C. L. Sabine *et al.*, *Science* **305**, 367 (2004).
2. N. Gruber, J. L. Sarmiento, T. F. Stocker, *Global Biogeochem. Cycles* **10**, 809 (1996).
3. J. L. Sarmiento, T. M. C. Hughes, R. J. Stouffer, S. Manabe, *Nature* **393**, 245 (1998).
4. G. K. Plattner, F. Joos, T. F. Stocker, O. Marchal, *Tellus Ser. B Chem. Phys. Meteorol.* **53**, 564 (2001).
5. H. Oeschger, U. Siegenthaler, U. Schotterer, A. Gugelmann, *Tellus* **27**, 168 (1975).
6. This estimate is based on driving the box-diffusion model with the global average sea surface temperature (SST) from 1860 to 1994, as computed from the 5° by 5° global data set (7), and accounts for the effects of warming on CO₂ solubility and carbon-system chemistry. The calculation neglects changes in temperature from 1800 to 1860, under the assumption that these changes were small (8).
7. P. D. Jones, A. Moberg, *J. Clim.* **16**, 206 (2003).
8. P. D. Jones, T. J. Osborn, K. R. Briffa, *Science* **292**, 662 (2001).
9. ΔC* is sensitive to air-sea O₂ exchange despite the tendency for O₂ to remain close to atmospheric equilibrium in surface waters. During photosynthesis in surface waters, for example, the tracer ΔC* would be conserved were it not for air-sea exchange of CO₂ and O₂. These exchanges typically do not cancel because O₂ equilibrates more rapidly than CO₂. Rapid O₂ equilibration thus actually drives changes in ΔC*.
10. The specific sensitivity of ΔC* to heat and O₂ are ~13 μmol kg⁻¹ °C⁻¹ and ~0.8 mol mol⁻¹, as can be derived by formally differentiating the expression for ΔC* with respect to O₂ and potential temperature.
11. S. Levitus, J. I. Antonov, T. P. Boyer, C. Stephens, *Science* **287**, 2225 (2000).
12. L. Bopp, C. Le Quéré, M. Heimann, A. C. Manning, P. Monfray, *Global Biogeochem. Cycles* **16**, 1022 (2002); 10.1029/2001GB001445.
13. R. F. Keeling, H. Garcia, *Proc. Natl. Acad. Sci. U.S.A.* **99**, 7848 (2002).
14. T. J. Crowley, S. K. Baum, K. Y. Kim, G. C. Hegerl, W. T. Hyde, *Geophys. Res. Lett.* **30**, 1932 (2003).
15. R. J. Matear, A. C. Hirst, *Global Biogeochem. Cycles* **17**, 1125 (2003); 10.1029/2002GB001997.
16. G. K. Plattner, F. Joos, T. F. Stocker, *Global Biogeochem. Cycles* **16**, 1096 (2002).
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