

Annotated Bibliography: Air-sea Carbon Dioxide Exchange

- 1) In order to predict future changes in the global carbon cycle, it is imperative to understand how the carbon cycle operates today. The ocean is presently a large carbon reservoir, storing nearly 38,000 petagrams of *natural* carbon, the component of carbon that is in equilibrium with the pre-industrial carbon dioxide (CO₂) concentration in the atmosphere; and more than 100 petagrams of anthropogenic carbon, the component of carbon that is driven by the human-induced increase in atmospheric CO₂ concentrations. While it is believed that the net air-sea flux of natural CO₂ is near zero, for the decade of the 1990's, the ocean absorbed anthropogenic CO₂ from the atmosphere at a rate of 2.2 petagrams of carbon per year. Chapter 7.3 of Solomon et al. (2007) describes the size of the ocean reservoir and details the air-sea fluxes of natural and anthropogenic CO₂ based on observational constraints. This chapter provides the most recent estimates of carbon inventory & fluxes on the global scale.

References:

Solomon, S., et al., eds., 2007: Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

- 2) When CO₂ enters the ocean, it reacts with seawater to produce carbonic acid, bicarbonate ions, and carbonate ions in a series of equilibrium reactions. The total concentration of inorganic carbon in seawater, dissolved inorganic carbon (DIC), is therefore the sum of the concentrations of all the species of inorganic carbon. More than 88% of the inorganic carbon in the ocean is in the form of bicarbonate ions, with carbonate ions making up another 10%, and aqueous CO₂ comprising less than 1%. This is a key reason for the large oceanic carbon reservoir (see (1)). Other important variables for oceanic carbonate chemistry include: pH, a measure of the hydrogen ion concentration; pCO₂, the partial pressure of CO₂; and alkalinity (Alk), a measure of the excess in proton acceptors over proton donors in the seawater solution. By measuring any two of the variables (DIC, Alk, pCO₂, pH), one can solve for the complete seawater carbonate system. Chapter 4.1 of Emerson and Hedges (2008) describes the carbonate system in seawater.

References:

Emerson, S. and J. Hedges, 2008: Chemical Oceanography and the Marine Carbon Cycle. Cambridge University Press, Cambridge, United Kingdom, 453pp.

- 3) The flux of CO₂ across the air-sea interface depends on the partial pressure of CO₂ in the atmosphere, the partial pressure of CO₂ in the surface ocean, and the magnitude of the gas transfer coefficient. Taro Takahashi, a scientist at Lamont-Doherty Earth Observatory, has spent the last five decades measuring this process. Takahashi (2002) and Takahashi (2009) describe the methodology for measuring surface ocean pCO₂ in the global ocean and calculating the air-sea flux of CO₂ based on oceanic pCO₂ measurements.

References:

Takahashi, T., et al., 2002: Global sea-air CO₂ flux based on climatological surface ocean pCO₂, and seasonal biological and temperature effects. Deep-Sea Research II, 49, 1601-1622.

Takahashi, T., et al., 2009: Climatological mean and decadal change in surface ocean pCO₂ and net sea-air CO₂ flux over the global oceans. Deep-Sea Research II, 56, 554-577.

Surface ocean pCO₂ database:

<http://cdiac.ornl.gov/oceans/LDEO_Underway_Database/>

- 4) According to Henry's law, the partial pressure of a gas above the ocean is directly proportional to the concentration of the gas in the ocean, provided that the ocean and atmosphere are in thermodynamic equilibrium with respect to the gas. If the ocean is not in equilibrium with the atmosphere, as is commonly the case for CO₂, then there will be a net flux of CO₂ across the air-sea interface. If the pCO₂ of the surface ocean exceeds that of the atmosphere, then the ocean is *supersaturated* with respect to CO₂, and the ocean will tend to flux CO₂ into the atmosphere. Likewise, if the pCO₂ of the atmosphere is lower than that of the ocean, the ocean is *undersaturated* with respect to CO₂, and the ocean will tend to absorb CO₂ from the atmosphere. Chapter 3.1 of Sarmiento and Gruber (2006) uses Henry's law to describe the partial pressure and flux of gas across the air-sea interface.

References:

Sarmiento, J.L. and N. Gruber, 2006: Ocean Biogeochemical Dynamics. Princeton University Press, Princeton, NJ, USA, 503pp.

- 5) Surface ocean pCO₂ is sensitive to variations in sea surface temperature: higher temperatures correspond to higher pCO₂ values. This is because the solubility of CO₂ strongly varies with temperature: cold water can hold more CO₂ than warm water. As the surface ocean warms with climate change, the oceanic sink for anthropogenic carbon will be somewhat diminished by this 'solubility' effect. Takahashi et al. (1993) describe the relationship between surface ocean pCO₂ and surface T in various oceanic regions, assuming that DIC and Alk remain constant. They note that pCO₂ is only slightly sensitive to variations in surface salinity.

References:

Takahashi, T., J. Olafsson, J.G. Goodard, D.W. Chipman, and S.C. Sutherland, 1993: Seasonal variation of CO₂ and nutrients in the high-latitude surface oceans: A comparative study. *Global Biogeochemical Cycles*, 7, 843-878.

Satellite sea surface temperature database:

< <http://www.nodc.noaa.gov/SatelliteData/pathfinder4km/>>

World Ocean Atlas (global ocean temperature and salinity observations):

< http://www.nodc.noaa.gov/OC5/WOA05/pr_woa05.html>

- 6) Surface ocean pCO₂ is extremely sensitive to changes in the surface concentrations of DIC and alkalinity: higher DIC and lower Alk correspond to higher pCO₂ values. Chapter 8.3 of Sarmiento and Gruber (2006) explores the processes that control surface ocean pCO₂ and its seasonal variability. Ocean sampling expeditions carried out during the 1970's, 1990's, and 2000's collected measurements of total carbon dioxide (DIC) and total alkalinity from more than 9,000 hydrographic stations across the globe. These data are made publicly available on the Carbon Dioxide Information Analysis Center (CDIAC) webpage, and calibration/interpolation details can be found in Key et al. (2004).

References:

Key, R.M., et al., 2004: A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP). *Global Biogeochemical Cycles*, 18, GB4031, doi:10.1029/2004GB002247.

Sarmiento, J.L. and N. Gruber, 2006: *Ocean Biogeochemical Dynamics*. Princeton University Press, Princeton, NJ, USA, 503pp.

Global Ocean Data Analysis Project (global, full depth DIC and Alk):

< <http://cdiac.ornl.gov/oceans/glodap/>>

- 7) Concentrations of DIC and Alk in the ocean vary from place to place, and are controlled by a variety of organic and inorganic processes. Generally speaking, the DIC concentration is higher at depth than at the surface. This vertical DIC gradient is maintained by (a) the solubility pump: the density structure of the ocean dictates that deep ocean water is only in contact with the atmosphere at the high latitudes, where surface temperatures are low and CO₂ solubility/uptake is high; (b) the biological 'soft tissue' pump: organic matter formation via phytoplankton photosynthesis at the surface consumes DIC and organic matter remineralization at depth produces DIC; and (c) the biological 'hard tissue' pump: calcium carbonate (CaCO₃) precipitation at the surface decreases DIC, and CaCO₃ dissolution at depth increases DIC. Ocean alkalinity is also affected by the biological pumps:

organic matter formation (dissolution) leads to a slight increase (decrease) in Alk; and CaCO_3 precipitation (dissolution) causes large decreases (increases) in Alk. Chapter 4.4 of Emerson and Hedges (2008) provides an excellent description of the processes that control the alkalinity and DIC of seawater.

References:

Emerson, S. and J. Hedges, 2008: Chemical Oceanography and the Marine Carbon Cycle. Cambridge University Press, Cambridge, United Kingdom, 453pp.

- 8) In order to determine the magnitude of air-sea CO_2 exchange, one must also have some measure of the gas transfer coefficient. The stagnant film model is a simple model of gas exchange that illustrates how turbulence in the atmosphere or ocean can impact the transfer coefficient. Imagine that the air-sea interface consists of 4 distinct layers (from top to bottom): a layer of turbulent gas transfer in the atmosphere, a thin film layer of molecular gas diffusion in the atmosphere, a thin film layer of molecular gas diffusion in the ocean, and a layer of turbulent gas transfer in the ocean. As the molecular diffusion of gas is slower than the turbulent transfer of gas, and molecular diffusion is slower in water than air, the rate-limiting process for air-sea gas exchange is the diffusion across the ocean thin film layer. Therefore, vertical turbulence in the ocean-atmosphere system reduces the thickness of the ocean thin film, and increases the transfer velocity of gas across the air-sea interface. Wanninkhof (1992) was among the first to discuss how variability in wind speed (and therefore, turbulence in the ocean-atmosphere system) can create variations in the gas transfer velocity and the flux of CO_2 across the air-sea interface. His parameterization for air-sea gas transfer is widely used in climate models.

References:

Wanninkhof, R., 1992: Relationship between wind speed and gas exchange over the ocean. *Journal of Geophysical Research*, 97, 7373-7383.

- 9) The net air-sea CO_2 flux at any location can be determined four different ways: (a) measuring surface ocean pCO_2 (e.g. Takahashi et al., 2009); (b) using output from atmospheric inversion models, where measurements of atmospheric CO_2 and estimates of atmospheric circulation are combined to infer sources and sinks of CO_2 over large terrestrial and oceanic regions; (c) using output from oceanic inversion models, where measurements of interior ocean carbon and estimates of interior ocean circulation are combined to infer air-sea CO_2 exchange, and (d) using output from ocean forward models, where ocean circulation is predicted in three dimensions based on atmospheric circulation patterns, and carbon concentrations vary with air-sea gas exchange, circulation, and biological processes. Gruber et al. (2009)

suggest that these estimates have recently started to converge in key oceanic regions for the global carbon cycle.

References:

Gruber, N., et al., 2009: Ocean sources, sinks, and transport of atmospheric CO₂. *Global Biogeochemical Cycles*, 23, GB1005, doi:10.1029/2008GB003349.

10) The oceanic sink for anthropogenic CO₂ is likely to change in the future. As atmospheric CO₂ concentrations rise, so too will the size of the oceanic carbon reservoir. On millennial timescales, nearly all of the anthropogenic emissions will be absorbed by the ocean, however on decadal and centennial timescales, the uptake is likely to be substantially smaller. This is because the ocean carbon sink is sensitive to changes in the climate system. For example, the oceanic uptake capacity is expected to decrease in the future as the ocean absorbs more anthropogenic CO₂, due to carbonate chemistry. Changes in circulation driven by climate change are also likely to alter the surface to deep mixing of waters in the ocean, altering the distribution of DIC and the magnitude of anthropogenic CO₂ uptake. Warming of the surface ocean will increase the oceanic pCO₂, slowing uptake of CO₂ from the atmosphere, and changes in the biological carbon pump may alter the distribution of DIC in the surface ocean and the uptake of CO₂ from the atmosphere. Chapter 3 of Field and Raupach (2004) describes these oceanic carbon cycle-climate 'feedbacks' in detail, and provides further reference material for the interested reader.

References:

Fields, C.B. and M.R. Raupach, 2004: *The Global Carbon Cycle: Integrating Humans, Climate, and the Natural World*. Island Press, Washington, D.C., USA, 526pp.