

WebPanel 1. Atmosphere–ocean carbon dioxide (CO₂) fluxes and ocean acidification – terminology and basic equations

Explanations of how atmosphere–ocean gas fluxes and changes in ocean inorganic carbon (C) chemistry lead to ocean acidification are often complicated by different and inconsistent terminology, and approximations. The atmosphere–ocean carbon dioxide (CO₂) flux for regional to global scales is often expressed as a bulk flux formulation, where the flux, F_{CO_2} , is a function of the gas transfer velocity, k , and the atmosphere–ocean concentration difference that can be expressed in terms of concentration, $[\text{CO}_2]$, partial pressure, $p\text{CO}_2$, or fugacity, $f\text{CO}_2$. It is also sometimes expressed in terms of a dried mole fraction, $X\text{CO}_2$. Bulk flux formulations are expressed in terms of arbitrary reference levels, often defined by the position of the measurements used. For water measurements these range from ~0.2 m depth below the water for $p\text{CO}_2$ sensors located on buoys and down to 10 m depth for systems on ships. Air measurement heights range from 2 m above the water surface (for sensors located on buoys) up to 20 m above the water surface (for systems on ships). Near-surface concentration gradients between the point of measurement and the atmosphere–ocean interface, particularly within the water, can be substantial due to differences in temperature, salinity, and chemical composition. For accurate assessment, the near-surface concentrations need to be estimated, and the solubility coefficients that are a function of temperature and salinity need to be calculated for the surface conditions at the interface (see Panel 1 in main text). This is particularly pertinent when utilizing remote sensing, as the signals measured originate from the interface. The different expressions, along with their common approximations, shown as ~, are as follows:

$$F_{\text{CO}_2} = k ([\text{CO}_2]_{\text{w}} - \beta[\text{CO}_2]_{\text{a}}) = k (K_{0,\text{w}} f\text{CO}_{2\text{w}} - K_{0,\text{a}} f\text{CO}_{2\text{a}}) \sim k (K_{0,\text{w}} p\text{CO}_{2\text{w}} - K_{0,\text{a}} p\text{CO}_{2\text{a}})$$

(Equation 1),

$$F_{\text{CO}_2} \sim k K_0 (f\text{CO}_{2\text{w}} - f\text{CO}_{2\text{a}})$$

(Equation 2), and

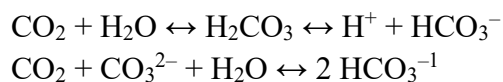
$$F_{\text{CO}_2} \sim k (K_{0,\text{w}} X\text{CO}_{2\text{w}} - K_{0,\text{a}} X\text{CO}_{2\text{a}})$$

(Equation 3).

The subscripts w and a refer to the surface-water mixed layer and air–marine boundary layer, respectively, both considered to be valid at the interface. The Ostwald solubility coefficient, β , is dimensionless. $K_{0,\text{w}}$ and $K_{0,\text{a}}$ are the solubility of CO₂ at the water side and air side of the interface, respectively, that are functions of temperature and salinity (Weiss 1974) and are expressed in mol atm⁻¹ L⁻¹. The $[\text{CO}_2]_{\text{w}}$ is the concentration of gaseous CO₂ in water (expressed in mol L⁻¹) and is also referred to as aqueous CO₂, or $[\text{CO}_2]_{\text{aq}}$. The fugacity of CO₂, $f\text{CO}_2$, is the partial pressure corrected for non-ideality of the gas, where the non-ideality corrections (Weiss 1974) are a function of temperature and pressure. For surface waters $f\text{CO}_{2\text{w,a}} \sim 0.994 p\text{CO}_{2\text{w,a}}$, such that consistently using either partial pressure or fugacity will yield essentially the same result. $p\text{CO}_2$ and $f\text{CO}_2$ are commonly reported in μatm . Whereas values for atmospheric CO₂

measurements are frequently reported as a mole fraction, X_{CO_2} (ppm or $\mu\text{mol mol}^{-1}$) in air without water vapor (dried air). Since $p_{CO_2} = (P - p_{H_2O}) X_{CO_2}$, the approximation listed above (Equation 3, ie F_{CO_2} calculated using X_{CO_2}) ignores the ambient pressure, P , leading to systematic biases and therefore is not recommended. As described above and in the main text, using the measured concentrations in air and water away from the interface can lead to appreciable biases, because mechanistically the transfer is retarded by the aqueous boundary layer of $\sim 100 \mu\text{m}$ thickness, such that the concentrations at the top and bottom of the aqueous boundary layer, which can be systematically different than those at depth, need to be determined. Using Equation 2 (ie ignoring these differences and the solubility K_0 is assumed independent of the position within the interface) can therefore lead to unknown biases and should be avoided if possible. The gas transfer velocity – also called the piston velocity or exchange coefficient – accounts for the kinetics of gas transfer (confusingly, the latter term “exchange coefficient” is also sometimes used when referring to the product $k K_0$). The gas transfer velocity is a strong function of the particular gas, temperature, and, to a lesser extent, salinity (Wanninkhof 2014). For regional and global CO_2 atmosphere–ocean gas fluxes, the gas transfer velocity is typically parameterized using wind speed, but, as explained in the main text, improved parameterizations are now being investigated using alternative proxies or measures of surface turbulence and energy dissipation, many of which can be observed using remote sensing.

Once CO_2 enters the water, it becomes part of the buffered aqueous inorganic C system that comprises the following species, with the approximate contribution in surface water in parentheses: aqueous CO_2 , CO_{2aq} (0.6%); carbonic acid, H_2CO_3 (0.01%); bicarbonate, HCO_3^- (90%); and carbonate, CO_3^{2-} (10%). The sum of these species is referred to as total (inorganic) C, and often abbreviated as TCO_2 , DIC, T_C , or C_T . Most of the CO_2 that enters the water reacts to become bicarbonate through the overall reactions:



The second reaction is the main buffering reaction that consumes carbonate, and the first reaction elevates H^+ . Both the increase of H^+ and CO_3^{2-} leads to ocean acidification. In seawater, the buffering reaction is efficient, and over 90% of the CO_2 entering seawater is transformed into bicarbonate.

WebReferences

- Wanninkhof R. 2014. Relationship between wind speed and gas exchange over the ocean revisited. *Limnol Oceanogr-Meth* **12**: 351–62.
- Weiss RF. 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar Chem* **2**: 203–15.