

TECHNICAL NOTE 1.4: Measurement of Air-Sea Carbon Fluxes using the CO₂-Pro Atmosphere Instrument

Measurement of the magnitude of ocean CO₂ flux both spatially and temporally in the World's oceans is important to understanding carbon cycling and predicting future changes in ocean chemistry and global climate. It is well known that the oceans play a major role in sequestering CO₂ from the atmosphere, leading to a decrease in the pH of ocean waters and depletion of the carbonate ion. The magnitude and direction of CO₂ flux varies in time and space due to biological, physical, and chemical processes,

The air-sea CO₂ flux can be estimated from:

$$F = kS\Delta p\text{CO}_2$$

where F is the flux, $\Delta p\text{CO}_2$ is the difference in water and air CO₂ ($p\text{CO}_2$ SW – $p\text{CO}_2$ air), S is the solubility of CO₂ in the water at the in situ temperature and salinity (see Wanninkhof and McGillis, 1999), and k is the CO₂ gas transfer velocity.

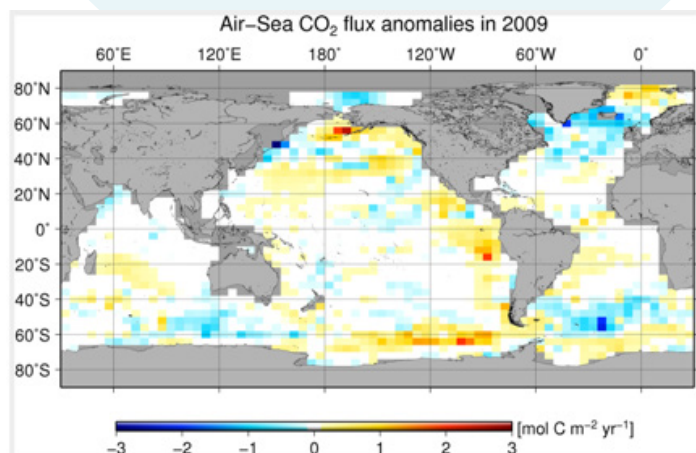
Boutin et al (2009) describe in detail air-sea CO₂ transfer velocity calculations and estimates. The gas transfer velocity is strongly related to wind speed, however, uncertainties exist in this relationship across the full spectrum of wind speeds.

Variability in surface water $p\text{CO}_2$ occurs both spatially and temporally over a range of scales, and so estimates of $p\text{CO}_2$ SW from other parameters indirectly remains challenging. This limits accurate CO₂ fluxes to space and time where direct measurements of both surface water

$p\text{CO}_2$ and air CO₂, in combination with surface water temperature and salinity and air wind speed have been made in unison.

In the open ocean, surface water movement is dominated by wind stress and allows for flux to be calculated accurately based on the gas transfer velocity determined from wind speed. In riverine and estuarine systems, turbulence in the water can be generated from topography and changes in runoff dynamics, leading to uncertainty in the gas transfer velocity across the oceans. Other complicating factors include wind, fetch and whether the sea state is fully developed.

Currently, global maps of air-sea CO₂ flux through time with limited resolution and substantial uncertainty are created from computer models with limited data. These maps provide limited predictions or information for coastal waters where CO₂ dynamics are exponentially more complex than the open ocean. How coastal waters affect the global carbon budget is still poorly known and not well quantified. More long-term data collection will be needed to assess the role coastal waters play



<https://www.pmel.noaa.gov/co2/story/Surface+CO2+Flux+maps>

TECHNICAL NOTE 1.3: Accuracy of CO₂-Pro Series Sensors

More measurements in time and space are required to not only quantify air-sea CO₂ fluxes, but also to understand future changes.

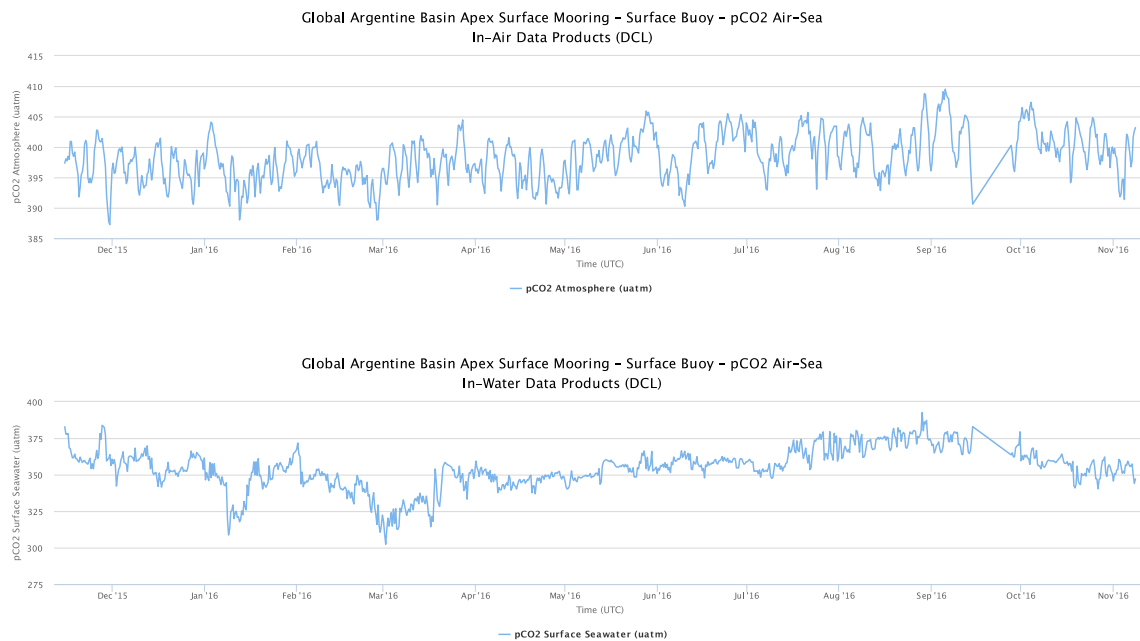
The CO₂-Pro Atmosphere™ submersible pCO₂ sensor is designed for use by scientists for applications where long-term, stable measurements of surface CO₂ are required. It's compact size and ease of use allow for simple integration into most stationary and mobile monitoring platforms, from buoys to VOS, to ASVs.

The CO₂-Pro Atmosphere™ measures the partial pressure of CO₂ gas in both the surface water and air above the surface. An internal zeroing feature provides drift correction for stable and accurate long-term measurements. Designed for use on buoys, the rugged unit is comprised of a CO₂-Pro™ that mounts under the buoy for water measurement connected to a weatherproof box that is used to sample air from above the sea surface. Alternating measurements of pCO₂ in

air and water using one detector provide accurate data for reliable surface flux calculations. The instrument is well-suited for integration into shipboard flow-through systems.

The CO₂-Pro Atmosphere operates through permeation of gases dissolved in liquids through a patented supported semi-permeable tubular membrane to a non-dispersive infrared detector (NDIR). The NDIR sensor is factory calibrated using trace gases from the NOAA ESRL GMD Central Calibration Laboratory (<http://www.esrl.noaa.gov/gmd/ccl/>).

The CO₂-Pro Atmosphere was chosen as the air-sea pCO₂ instrument for the Coastal and Global Scale Nodes component of the US OOI, Ocean Observatories Initiative. An example of some of the data collected from one of the measurement nodes is shown below for the Argentine Basin, a sink for CO₂ during most of the year. Daily air CO₂ levels fluctuate between 390 and 405 μatm, and surface waters range from 300 to 395 μatm.



References:

Boutin, J., Quilfen, Y., Merlivat, L., Piolle, J. F. 2009. Global average of air-sea CO₂, transfer velocity from QuikSCAT scatterometer wind speeds. *Journal of Geophysical Research*, v.114, C04007, doi: 10.1029/2007JC004168.

Wanninkhof, R., McGillis, W.R. 1999. A cubic relationship between air-sea CO₂ exchange and wind speed. *Geophys Res Lett.*, 26: 1889-1892. <https://doi.org/10.1029/1999gl900363>

