## Observing the carbon cycle in the Southern Ocean from biogeochemical floats with pH sensors





Nancy L. Williams<sup>1</sup>, Laurie Juranek<sup>1</sup>, Richard Feely<sup>2</sup>, Ken Johnson<sup>3</sup>, Jorge Sarmiento<sup>4</sup>, Lynne Talley<sup>5</sup>, Andrew Dickson<sup>5</sup>, Alison Gray<sup>4</sup>, Rik Wanninkhof<sup>6</sup>, Joellen Russell<sup>7</sup>, Steve Riser<sup>8</sup>, and Yui Takeshita<sup>3</sup>

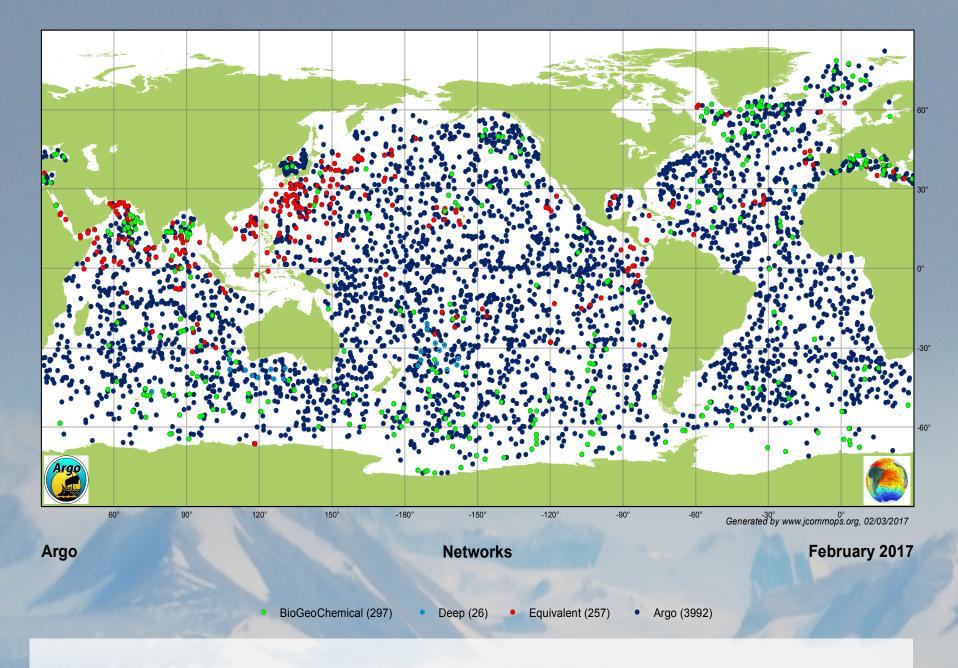
<sup>1</sup>College of Earth, Ocean and Atmospheric Sciences, Oregon State University, OR, USA <sup>2</sup>Pacific Marine Environmental Laboratory, NOAA, Seattle, WA, USA <sup>3</sup>Monterey Bay Aquarium Research Institute, Moss Landing, CA, USA <sup>4</sup>Princeton University, Princeton, NJ, USA

<sup>5</sup>Scripps Institution of Oceanography, University of San Diego, La Jolla, CA, USA <sup>6</sup>Atlantic Oceanographic and Meteorological Laboratory, NOAA, Miami, FL, USA <sup>7</sup>Department of Geosciences, University of Arizona, Tucson, AZ, USA <sup>8</sup>University of Washington Oceanography, Seattle, WA, USA



#### **Overview of SOCCOM**

The Southern Ocean plays a major role in the global carbon cycle by accounting for around half of the overall ocean carbon sink yet it is relatively undersampled and not wellrepresented in climate models. The Southern Ocean Carbon and Climate Observations and Modeling (SOCCOM) project aims to fill this observational gap by deploying 200 autonomous biogeochemical profiling floats in the Southern Ocean over 5 years. Now in year 3, there are over 80 floats in the water and reporting data back every 10 days (green dots in the Southern Ocean in the map to the left). These data are publicly available and are quality controlled in near-real time.

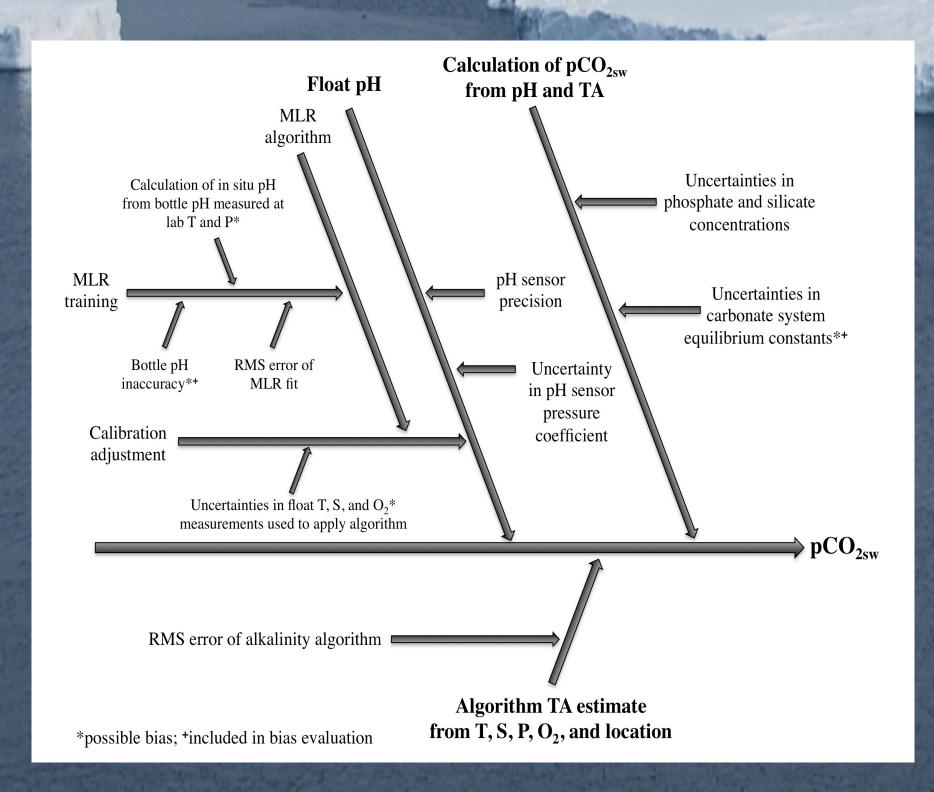


### How well can we calculate pCO<sub>2seawater</sub> from float pH?

To calculate the flux of carbon dioxide between the atmosphere and the ocean we need to calculate the  $\Delta pCO_2$ :

$$\Delta pCO_2 = pCO_{2seawater} - pCO_{2atmosphere}$$

A positive  $\Delta pCO_2$  implies that the ocean will release carbon to the atmosphere. A float-based estimate of pCO<sub>2seawater</sub> can be calculated using the float pH measurements and an estimate for total alkalinity (Carter et al., 2016). The uncertainty in float pCO<sub>2</sub> is 2.7% as compared to a 1% uncertainty in a traditional ship-based underway measurement. This uncertainty was estimated using a careful analysis of uncertainties from three main sources: the float pH measurement, the alkalinity estimate, and the calculation of pCO<sub>2</sub> from pH and TA, as summarized in the fishbone diagram below.



### References

CO<sub>2</sub> Atlas (SOCAT), Earth Syst. Sci. Data Discuss., 8, 297–323, doi:10.5194/essd-2016-15. Boss, E., D. Swift, L. Taylor, P. Brickley, R. Zaneveld, S. Riser, M. J. Perry, and P. G. Strutton (2008), Observations of pigment and particle distributions in the western North Atlantic from an autonomous float and ocean color satellite, Limnol. Oceanogr., 53(5\_part\_2), 2112–2122, doi:10.4319/lo.2008.53.5\_part\_2.2112. Carter, B. R., N. L. Williams, A. R. Gray, and R. A. Feely (2016), Locally interpolated alkalinity regression for global alkalinity estimation, Limnol. Oceanogr. Methods, 14(4), 268–277, doi:10.1002/lom3.10087. Johnson, K. S., L. J. Coletti, H. W. Jannasch, C. M. Sakamoto, D. D. Swift, and S. C. Riser (2013), Long-term nitrate measurements in the ocean using the in situ ultraviolet spectrophotometer: Sensor integration into the APEX profiling float, J. Atmos. Ocean. Technol., 30(8), 1854–1866, doi:10.1175/JTECH-D-12-00221.1.

Bakker, D. C. E. et al. (2016), A multi-decade record of high-quality fCO<sub>2</sub> data in version 3 of the Surface Ocean

Johnson, K. S., H. W. Jannasch, L. J. Coletti, V. A. Elrod, T. R. Martz, Y. Takeshita, R. J. Carlson, and J. G. Connery (2016), Deep-Sea DuraFET: A pressure tolerant pH sensor designed for global sensor networks, Anal. Chem., 88(6), 3249–3256, doi:10.1021/acs.analchem.5b04653. Tengberg, A., J. Hovdenes, H. J. Andersson, O. Brocandel, R. Diaz, and D. Hebert (2006), Evaluation of a lifetime-

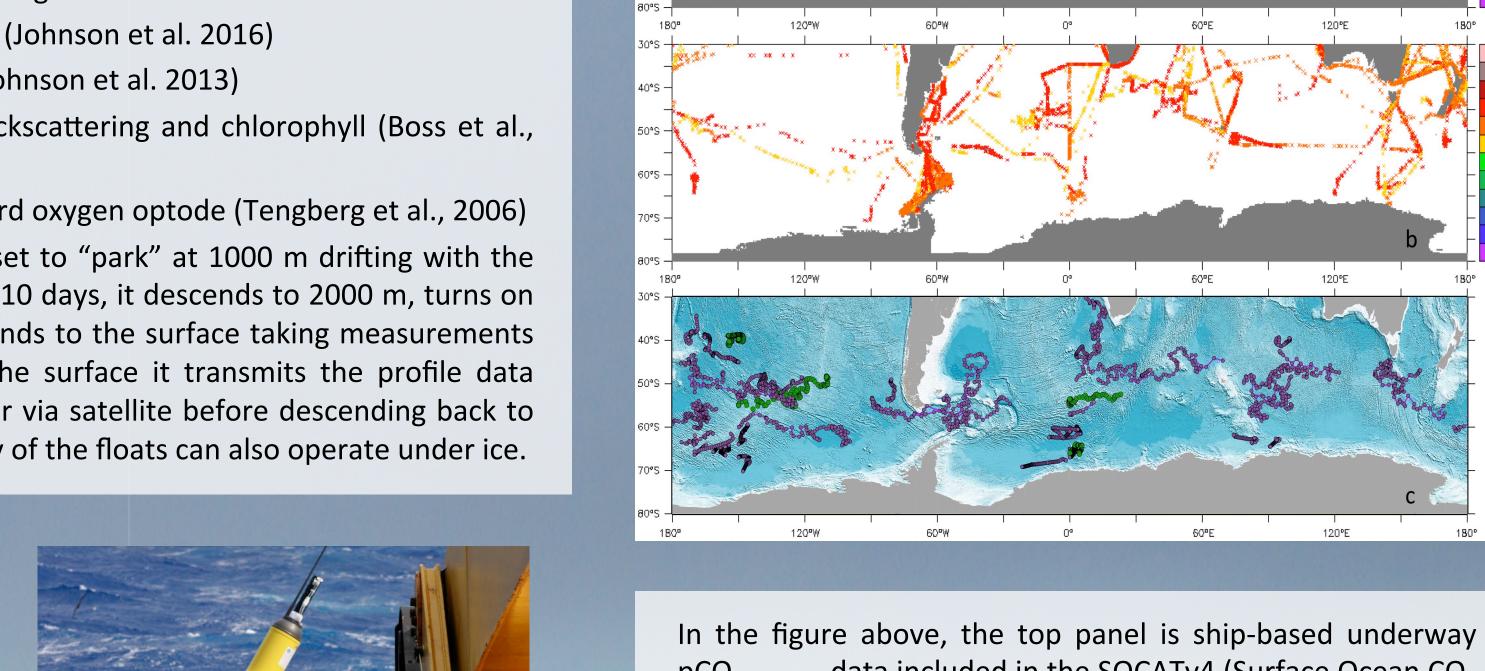
based optode to measure oxygen in aquatic systems, Limnol. Oceanogr. Methods, 4, 7–17. Williams, N. L. et al. (2017), Calculating surface ocean pCO 2 from biogeochemical Argo floats equipped with pH: an uncertainty analysis, Global Biogeochem. Cycles, 31(3), 591-604, doi:10.1002/2016GB005541.

#### What is a SOCCOM float?

A SOCCOM float is an autonomous profiling float that measures temperature (T) and salinity (S) and carries the following additional biogeochemical sensors:

- Deep Sea DuraFET (Johnson et al. 2016)
- ISUS UV Nitrate (Johnson et al. 2013)
- WETLabs FLBB backscattering and chlorophyll (Boss et al., 2008)
- Aanderaa or Seabird oxygen optode (Tengberg et al., 2006) SOCCOM floats are set to "park" at 1000 m drifting with the

currents until, every 10 days, it descends to 2000 m, turns on its sensors, and ascends to the surface taking measurements along the way. At the surface it transmits the profile data back to a data center via satellite before descending back to its park depth. Many of the floats can also operate under ice.



pCO<sub>2seawater</sub> data included in the SOCATv4 (Surface Ocean CO<sub>2</sub> Atlas, Bakker et al., 2016) database south of 30°S from all years colored by month. The middle panel shows all SOCATv4 data south of 30°S from austral winter (July, August, September) and the bottom panel shows the locations of the SOCCOM floats as of January 2017.



#### Results

While float-based calculated pCO<sub>2seawater</sub> is inherently more uncertain than most ship- or mooring-based pCO<sub>2seawater</sub> measurements, a well-calibrated array of biogeochemical floats can complement the existing global dataset by providing a seasonal context to regions where wintertime measurements are sparse. The figure below shows ΔpCO<sub>2</sub> from four floats each representing one of four major Southern Ocean frontal zones. In the Polar Antarctic Zone (panel c) and in the Seasonal Sea Ice Zone (panel c) the floats (black dots) see significantly higher ΔpCO<sub>2</sub> (leading to more carbon flux out of the ocean) than either the Takahashi et al. (2014) or the Landschützer et al. (2014) climatology (blue and green lines, respectively).

- The floats agree with the climatologies during the austral summer when there are significantly more underway pCO<sub>2seawater</sub> data to create the climatologies
- Large disagreements arise when there are no suitable data to constrain the climatology, such as austral winter and in ice-covered waters
- This disagreement is not surprising, considering (1) the limited availability of austral winter and under ice observations to compute the climatologies and (2) the pCO<sub>2seawater</sub> climatologies are based on climatological sea ice cover, which may differ from ice cover during float observations
- Differences between the floats and the climatologies cannot be explained by temperature differences.

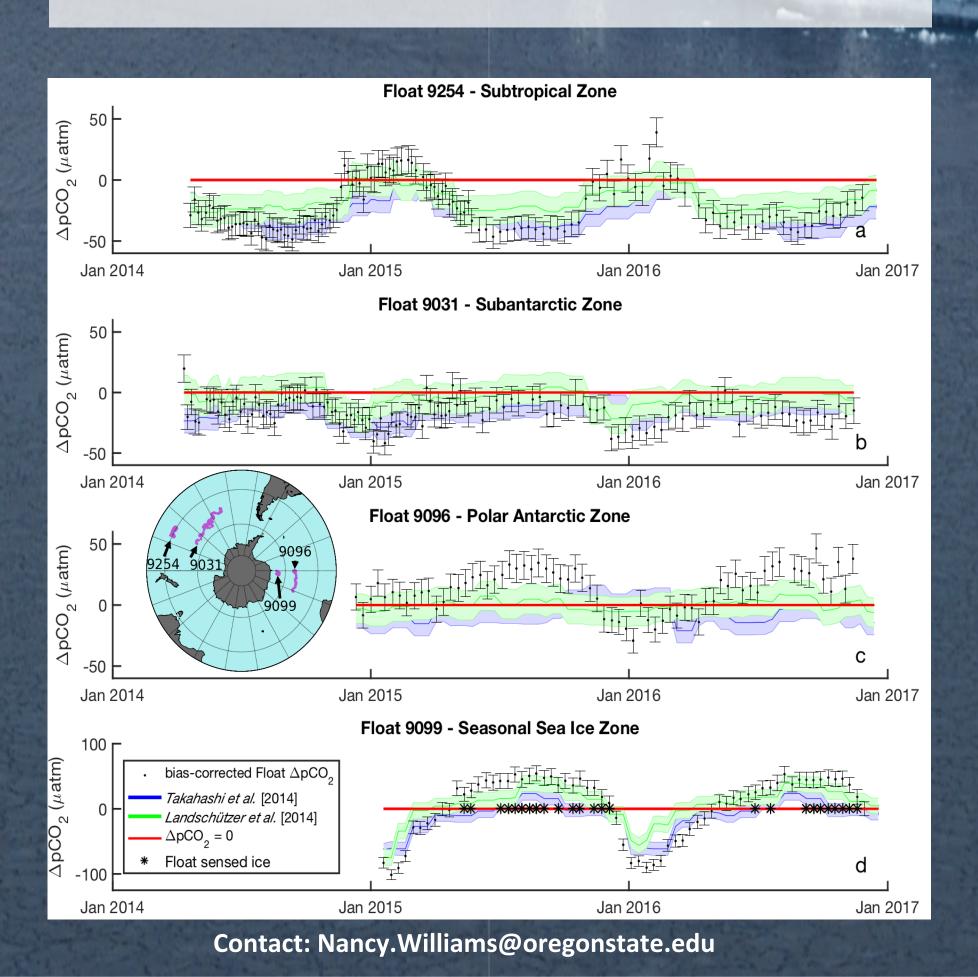
# Float 9099 pCO<sub>2</sub> - Seasonal Sea Ice Zone -65.5

The figure above shows a 3-D section plot of the upper water column pCO<sub>2</sub> for float 9099 along its 2.5-year lifetime from January 2015 through September 2017. This float is located in the South Atlantic in the Seasonal Sea Ice Zone. Float 9099 experiences ice coverage for up to half of the year (marked by gray boxes) and during this time the float location is interpolated between the last and first ice-free profiles. Each float pH measurement is plotted as a small black dot.

- In winter, ice traps the CO<sub>2</sub> from respiration and upwelled high-DIC waters
- The springtime ice-edge bloom draws down pCO<sub>2</sub>

### **Conclusions**

Ongoing shipboard and moored observation programs show that the pCO<sub>2seawater</sub> is increasing globally as a result of anthropogenic emissions. Nonetheless, our current understanding of the seasonal cycle and interannual variability, and thus the mechanisms controlling pCO<sub>2seawater</sub> and air-sea CO<sub>2</sub> flux, is lacking over many parts of the world ocean. Despite the estimated 2.7% relative standard uncertainty in current biogeochemical float-based pCO<sub>2seawater</sub> (pH, TA) estimates, it is clear from the differences between existing climatologies and new float pH-based pCO<sub>2seawater</sub> (pH, TA) estimates that incorporating information from these novel carbon observational platforms can improve climatologies, climate models, and future projections. While true space/time cross- overs between biogeochemical floats and shipboard pCO<sub>2</sub> systems are rare, and spatial and temporal heterogeneity make direct comparisons difficult, we have shown that a well-calibrated biogeochemical float provides meaningful data that strengthen the current body of pCO<sub>2seawater</sub> observations.



Acknowledgments This work was sponsored by US National Science Foundation's Southern Ocean Carbon and Climate Observations and Modeling (SOCCOM) Project under the NSF Award PLR-1425989. Logistical support for this project in Antarctica was provided by the U.S. National Science Foundation through the <u>U.S. Antarctic Program</u>. Nancy Williams is also supported by the ARCS Portland Chapter.