Recommendation for Oxygen Measurements from Argo Floats: Implementation of In-Air-Measurement Routine to Assure Highest Long-term Accuracy

Situation

As Argo has entered its second decade and chemical/biological sensor technology is improving constantly, the marine biogeochemistry community is starting to embrace the successful Argo float program. An augmentation of the global float observatory, however, has to follow rather stringent constraints regarding sensor characteristics as well as data processing and quality control routines. Owing to the fairly advanced state of oxygen sensor technology and the high scientific value of oceanic oxygen measurements (Gruber *et al*., 2010), an expansion of the Argo core mission to routine oxygen measurements is perhaps the most mature and promising candidate (Freeland *et al*., 2010).

In this context, SCOR Working Group 142 "Quality Control Procedures for Oxygen and Other Biogeochemical Sensors on Floats and Gliders" (www.scor-int.org/SCOR_WGs_WG142.htm) set out in 2014 to assess the current status of biogeochemical sensor technology with particular emphasis on float-readiness, develop pre- and post-deployment quality control metrics and procedures for oxygen sensors, and to disseminate procedures widely to ensure rapid adoption in the community.

Progress in Characterization of Oxygen Optode Sensors

The optode-based oxygen sensor technology has reached what is probably the highest maturity among all biogeochemical sensors. During recent years nearly all relevant characteristics of oxygen optodes have been studied intensively in view of their readiness for float applications. Examples of this are individual sensor calibration protocols (e.g., Bittig *et al*., 2012), the optodes' pressure sensitivity (Bittig *et al*., 2015), their time response as a function of the flow regime (Bittig *et al*., 2014), and their *ex situ* drift characteristics (Bittig *et al*.; 2012; D'Asaro and McNeil, 2013; Bittig and Körtzinger, 2015). All these studies provided the insight into the possibilities and limitations to achieve highest data quality that is needed to develop protocols and best practices recommendations.

Long-term Stability of Oxygen Optode Sensors

The ultimate accuracy goal for float-based oxygen measurements (1 µmol kg^{-1}; Gruber *et al*., 2010) cannot be met unless both initial calibration and long-term drift are extremely tightly constrained. It has been shown that oxygen optodes are prone to significant *ex situ* drift (Bittig *et al*.; 2012; D'Asaro and McNeil, 2013) which results in the need for an *in situ* calibration routine to be carried at the float deployment. Contrary to earlier findings (e.g., Tengberg *et al*., 2008), there is increasing (as of now unpublished) evidence which indicates that oxygen optodes can also exhibit a small but significant *in situ* drift which exceeds the stringent accuracy goal over the lifetime of a float. It has thus become obvious that for achieving this highest accuracy goal an *in situ* calibration routine that is available throughout the float's lifetime needs to be developed and implemented.

Proposal of In-Air-Measurement Routine on O_2 Floats

Addressing the long-term drift issue, Körtzinger *et al*. (2005) already proposed to mount the optode on the float's top cap to use the sensor's capability of in-air oxygen measurement as a means of drift correction. More recent evidence (Fiedler *et al*., 2013; Emerson and Bushinsky, 2014) provided further support to this idea. It has not been until very recently, however, that through dedicated studies (Bittig and Körtzinger, 2015; Johnson *et al*., 2015) we were able to confirm the functioning and utility of in-air oxygen measurements as a means of *in situ* calibration and drift correction of oxygen optodes on Argo floats. Based on this sound evidence, SCOR WG 142 is now proposing to implement an in-air oxygen measurements routine on all future Argo oxygen floats. To our knowledge such a routine is the only means of providing the necessary tight constraint on oxygen data accuracy over the entire lifetime of a float. The achievable accuracy is very close to the accuracy goal of 1 µmol kg^{-1}.

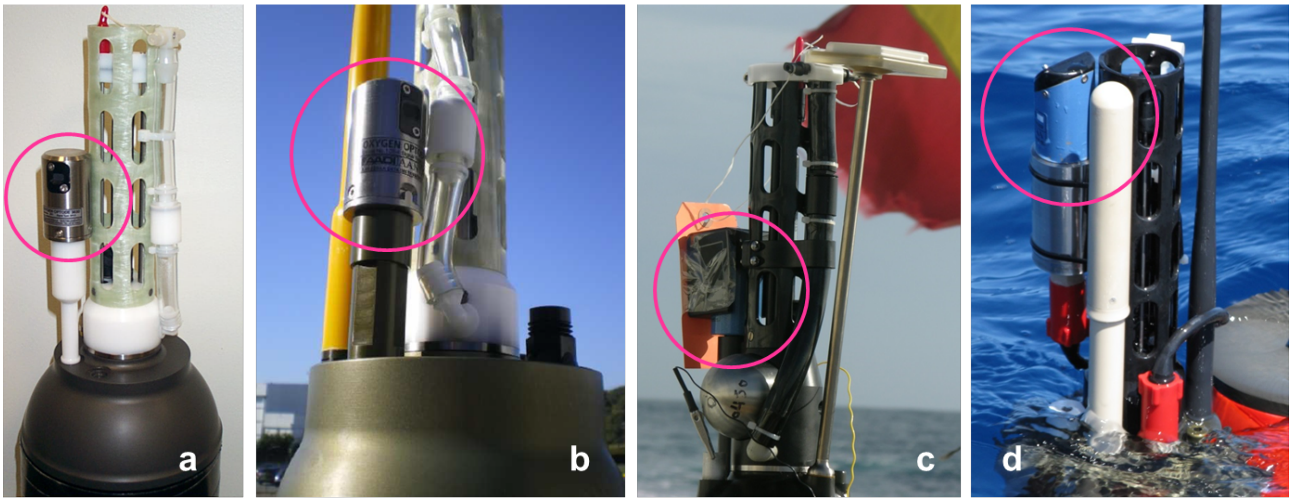


Figure. Oxygen optodes mounted on the top caps of floats: (a) APEX float with pole-mounted Aanderaa optode 3830, (b) PROVOR CTS3 DO float with pole-mounted Aanderaa optode 3830, (c) NAVIS float with pole-mounted Aanderaa optode 4330, and NEMO float with cable-mounted Aanderaa optode 4330.

Prior to the implementation of the proposed in-air measurement routine, a significantly improved initial data accuracy can be achieved by performing a single in-air measurement sequence (> 10 min) shortly before deployment of the float. Both the atmospheric pressure and the water vapor pressure must be determined to 1 mbar accuracy at the same time as the oxygen measurement. This will require that the operator pre-wets the sensor membrane to ensure that it has similar response to the in water values.

Requirements for Implementation of In-Air-Measurement Routine

For the implementation of an in-air oxygen measurement routine the following requirements have to be met:

- Prerequisite for the implementation of an in-air measurement routine is an oxygen optode which has been shown to measure reliably in air (e.g., Aanderaa optodes 3830 and 4330).
- The optode's sensing foil has to be exposed to air which is currently not possible with the Sea-Bird optode SBE-63. While the pumped-mode of the SBE-63 has significant beneficial effects on the sensor time constant (Bittig *et al*., 2014), results from dual-optode floats show that the positive effect of the shorter time constant is only significant at very steep vertical gradients. We are therefore convinced that the in-air measurement option is more important to assure highest data quality. We therefore encourage Sea-Bird and other optode manufacturers to explore the possibility of an in-air measurement option for their optodes.
- The oxygen optode has to be mounted in an elevated position on the top cap of the float (see figure). Both a pole and a cable mount have been shown to work. The optode should be attached to the CTD cage, ideally near to top end of the cage. A minimal elevation of 20 cm above the water line is recommended.
- The measurement routine should contain a short measurement sequence with the optode in air. For this in-air cycle, 5-10 measurements over a few minutes (optode sample interval ≥15 s) are required. It is further recommended to perform a short measurement sequence with the optode still submerged in seawater as this will significantly reduce the uncertainty of

the sub-surface term and hence improve the correction. On floats featuring an air-bladder system (APEX, NEMO, NAVIS) the two measurement sequences can be easily accomplished before and after the filling of the air bladder, respectively.

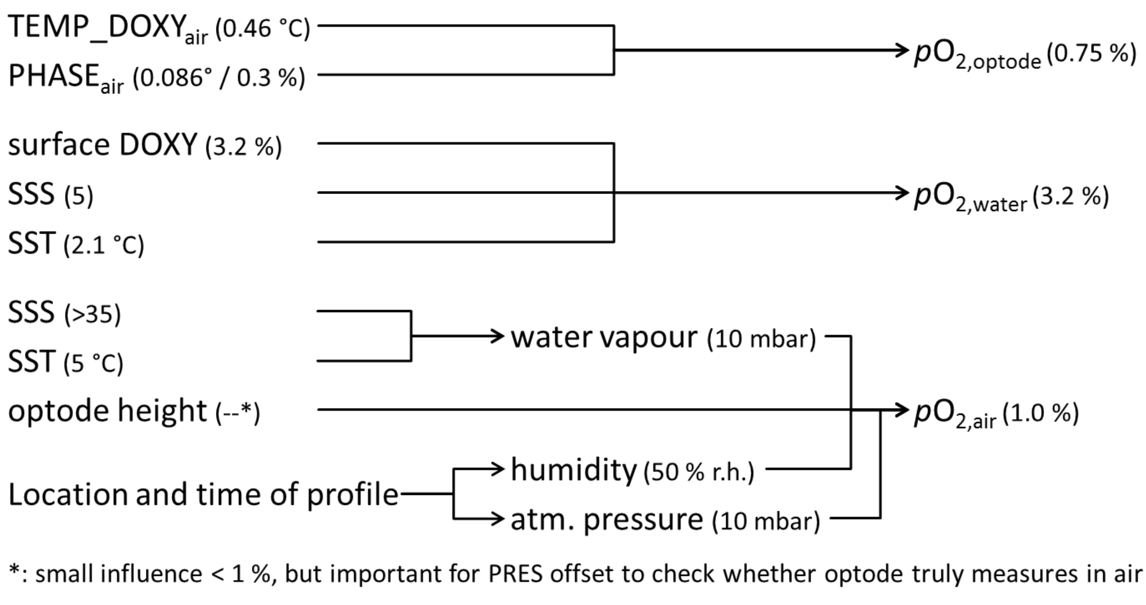
- It is proposed to perform the in-air measurement routine during each surfacing to ensure optimal statistics for the correction.
- To avoid the potential of warming of the dark sensor foil by direct sunlight, priority should be given to nighttime float surfacings.

Quantities Required for Oxygen Correction

In order to carry out an oxygen correction based on in-air-measurements the following quantities need to be known, either from direct observations or other sources:

- Optode in-air reading (TEMP_DOXY, PHASE)
- Optode in-water reading (TEMP_DOXY, PHASE or DOXY)
- Sea surface temperature (SST)
- Sea surface salinity (SSS)
- Optode height above water line (from metadata)
- Atmospheric pressure at 10 m height (from reanalysis product)
- Relative air humidity at 10 m height (from reanalysis product)

The following scheme illustrates an estimate of the sensitivity of the final correction to the uncertainty of the different input parameters. The numbers in brackets indicate the change of the respective input parameter that causes a 1 % change in the correction and hence the final accuracy of the oxygen measurement:



These results indicate the importance of a precise in-air measurement which cannot be met with a single data point but requires the proposed minimal sequence of 5-10 measurement points. Of somewhat small but still significant importance is a well constrained surface water oxygen reading which is improved with the proposed measurement sequence just below the surface (e.g., before filling of the air bladder). Fortunately, the accuracy of reanalysis products is usually much better than above values which makes their application less critical and should allow their use in all regions.

References

Bittig, H.C., B. Fiedler, T. Steinhoff, A. Körtzinger (2012). A Novel Electrochemical Calibration Setup for Oxygen Sensors. *Limnol. Oceanogr.: Methods* **10**, 921–933.

Bittig, H.C., B. Fiedler, R. Scholz, G. Krahmann, A. Körtzinger (2014). Time response of oxygen optodes on profiling platforms and its dependence on flow speed and temperature. *Limnol. Oceanogr.: Methods* **12**, 617–636.

Bittig, H.C., A. Körtzinger (2015). Tackling Oxygen Optode Drift: Near-Surface and In-Air Oxygen Optode Measurements on a Float Provide an Accurate in Situ Reference. *J. Atmos. Oceanic Technol.* **32**, 1536–1543.

Bittig, H.C., B. Fiedler, P. Fietzek, A. Körtzinger (2015). Pressure response of Aanderaa and Sea-Bird oxygen optodes. *J. Atmos. Oceanic Technol*., doi:10.1175/JTECH-D-15-0108.1, in pres.

Bushinsky, S.M., S. Emerson (2013). A method for in-situ calibration of Aanderaa oxygen sensors on surface moorings. *Mar. Chem.* **155**, 22–28, doi:10.1016/j.marchem.2013.05.001.

D'Asaro, E.A., C. McNeil (2013). Calibration and stability of oxygen sensors on autonomous floats. *J. Atmos. Oceanic Technol*. **30**, 1896–1906, doi:10.1175/JTECH-D-12-00222.1.

Emerson, S.R., S. Bushinsky (2014). Oxygen concentrations and biological fluxes in the open ocean. *Oceanography* **27**, 168–171, doi:10.5670/oceanog.2014.20.

Fiedler, B., P. Fietzek, N. Vieira, P. Silva, H.C. Bittig, A. Körtzinger (2013). In situ CO_2 and O_2 measurements on a profiling float. *J. Atm. Ocean. Techn.* **30**, 112-126, doi:10.1175/JTECH-D-12-00043.1.

Freeland, H. & Co-Authors (2010). "Argo - A Decade of Progress" in Proceedings of OceanObs'09: Sustained Ocean Observations and Information for Society (Vol. 2), Venice, Italy, 21-25 September 2009, Hall, J., D.E. Harrison & D. Stammer, Eds., ESA Publication WPP-306, doi:10.5270/ OceanObs09.cwp.32.

Gruber, N. & Co-Authors (2010). "Adding Oxygen to Argo: Developing a Global In Situ Observatory for Ocean Deoxygenation and Biogeochemistry" in Proceedings of OceanObs'09: Sustained Ocean Observations and Information for Society (Vol. 2), Venice, Italy, 21-25 September 2009, Hall, J., D.E. Harrison & D. Stammer, Eds., ESA Publication WPP-306, doi:10.5270/OceanObs09.cwp.39.

Johnson, K., J. Plant, S. Riser, D. Gilbert, 2015: Air oxygen calibration of oxygen optodes on a profiling float array. *J. Atmos. Oceanic Technol*., doi:10.1175/JTECH-D-15-0101.1, in press.

Körtzinger, A., J. Schimanski, U. Send (2005). High-quality oxygen measurements from profiling floats: A promising new technique. *J. Atm. Ocean. Techn*. **22**, 302-308.

Tengberg, A., J. Hovdenes, J.H. Andersson, O. Brocandel, R. Diaz, D. Hebert, T. Arnerich, C. Huber, A. Körtzinger, A. Khripounoff, F. Rey, C. Rönning, J. Schimanski, S. Sommer, A. Stangelmayer (2006). Evaluation of a life time based optode to measure oxygen in aquatic systems. *Limnol. Oceanogr.: Methods* **4**, 7-17.