Air calibration of an oxygen optode on an underwater glider

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Running head: Glider oxygen air calibration
Abstract

An Aanderaa Data Instruments 4831 Oxygen optode was configured on an underwater glider such that the optode extended into the atmosphere during each glider surface interval enabling in situ calibration of the sensor by directly measuring the known partial pressure of the atmosphere. The approach, which has previously been implemented on profiling floats but not on gliders, was tested during a 15-day deployment at the New England shelf break in June 2016, a productive period during which surface O\textsubscript{2} saturation averaged 110%. Results were validated by shipboard Winkler O\textsubscript{2} calibration casts, which were used to determine a sensor gain factor of 1.055 ± 0.004. Consistent with profiling float observations, air measurements contain contamination from splashing water and/or residual seawater on the sensor face. Glider surface measurements were determined to be a linear combination of 36% of surface water and 64% atmospheric air. When correcting air measurements for this effect, a sensor gain correction of 1.055 ± 0.005 was calculated based on comparing glider air measurements to the expected atmospheric pO\textsubscript{2} calculated from atmospheric pressure and humidity data from a nearby NOAA buoy. Thus, the two approaches were in agreement and were both demonstrated to be accurate to within ±0.5%. We expect uncertainty in the air-calibration could be further reduced by increasing the vertical positioning of the optode, lengthening deployment time, or operating in waters with surface O\textsubscript{2} saturation closer to equilibrium.

Introduction

Oxygen is a central element in marine biogeochemistry as it is produced by photosynthesis and consumed by respiration. In the surface ocean, marine cycling of O\textsubscript{2} is coupled to the atmosphere via air-sea exchange processes. Measurements of dissolved oxygen are commonly used to infer rates of biogeochemical processes, including net community production (NCP),
which is the whole-ecosystem balance between photosynthesis and respiration (Emerson and Bushinsky 2014). The net oxygen produced by NCP is stoichiometrically linked to excess production of organic carbon that subsequently is available for export. $O_2$-based NCP estimates thus are a critical means to quantify carbon export and the biological carbon pump.

Dissolved oxygen sensors are perhaps the most mature biogeochemical sensors used by the oceanographic community. Over recent years, oxygen optodes have come to predominate in oceanographic applications displacing polarographic Clark electrode type sensors. These sensors are robust and reliable, yet, they are not perfect and are still subject to issues including drift after factory calibration which can vary from undetectable rates to several percent per year.

Oxygen optodes operate on the underlying principle of quantifying the luminescence of a metalloporphyrin (most commonly, platinum or rhuthenium) complex, the lifetime of which is a function of quenching by molecular oxygen (Klimant et al. 1995; Tengberg et al. 2006; Quaranta et al. 2012). Kinetics of quenching is described by the Stern-Volmer equation:

$$\frac{\tau}{\tau_0} = 1 + pO_2 K_{sv}$$  \hspace{1cm} (1)

where $\tau$ and $\tau_0$ are the lifetime of the luminophore in the presence and absence of $O_2$, $pO_2$ is the partial pressure of molecular oxygen and $K_{sv}$ is the Stern-Volmer constant. A useful characteristic of $O_2$ optodes is their ability to measure $pO_2$ in a range of media, including in seawater and in air.

One of the most promising techniques to address shortcomings in $O_2$ sensor accuracy is the ‘air calibration’ method that has recently been developed for application on Argo-style profiling floats (Bittig and Körtzinger 2015; Johnson et al. 2015; Bushinsky et al. 2016). The approach takes advantage of the fact that **$O_2$ optodes are capable of measuring $O_2$ partial pressure both in fluid and in air.** Periodic measurements of lower tropospheric air can serve as a reference
**standard to track sensor accuracy and drift.** Dry atmosphere has a known and constant O$_2$ content, the air O$_2$ partial pressure ($p_{O_2,a}$) can be precisely estimated knowing sea level pressure ($p_{atm}$):

$$p_{O_2,a} = (p_{atm} - p_{H_2O})\chi_{O_2} \text{ where } p_{H_2O} = \phi p_{H_2O}$$

where $\chi_{O_2}$ is 0.20946, the dry air mixing ratio of O$_2$ (Glueckauf 1951), $\phi$ is relative humidity and $p_{H_2O}^*$ is the saturated vapor pressure, a function of temperature and salinity (Wagner and Prüß 2002; Dickson et al. 2007).

By mounting optodes in a position such that the sensor is exposed to the air when a float is at the surface, $p_{O_2,a}$ can be measured during each surface interval. Any changes in apparent $p_{O_2,a}$ over time can be attributed to sensor drift. The intercept of $d(p_{O_2,a})/dt$ with the deployment time represents the initial sensor bias (Bushinsky et al. 2016). Here, we present the first application of an air calibrating optode on a mobile platform, a Teledyne Webb Research G1 200m Slocum Glider. The system was demonstrated during a 15-day deployment at the New England shelf break.

**Materials and procedures**

**Air-calibration mounting**

An Aanderaa Data Instruments model 4831 oxygen optode (serial number 289, foil batch 1206EM) was re-configured on a Teledyne Webb Research 200m G1 Slocum glider such that the optode was mounted fore of the glider tail (Fig 1A). When new, the optode was multipoint factory calibrated by Aanderaa (calibration date 15 December, 2013) and all calculations were performed using the modified Stern-Volmer equation (Uchida et al. 2008). When the glider is at the surface,
the modified mount holds the optode approximately 15 cm above the water line (Fig 1B). The optode was positioned with the sensor foil facing in the forward direction. This orientation has a number of potential benefits. The vertical orientation reduces potential exposure to ambient light compared to an upwards facing foil. Also, optode response time has been observed to depend on sensor orientation relative to the direction of flow because when the sensor foil is facing directly into the flow, diffusive boundary layer thickness is minimized and response time is optimized (Bittig et al. 2014).

Figure 1: The prototype air-calibration mount is shown in the lab with glider rear fairing removed (left) and at sea at the New England Shelf Break (right). The sensing foil is located on the angled face of the sensor, facing into the direction of flow. This orientation both reduces interference from incident light and improves sensor response time.

Glider operations

The Slocum glider was deployed on 02 June, 2016 from the R/V Tioga at 40.5°N 71°W and was recovered on 18 June, 2016. In addition to the optode, the glider was equipped with a Seabird CTD, WET Labs optical puck and Satlantic SUNA nitrate sensor. The glider conducted three initial longer cross-shelf transects before rendezvousing with the R/V Endeavour which arrived on site on 14 June, 2016. During the final four days, the glider conducted shorter sections
following a drifting Wire Walker as well as conducting calibration casts in coordination with the ship on 15 and 17 June 2016 (Fig 2).

Figure 2: Map of glider deployment. The colorbar indicates day in June, 2016. Location of the two calibration casts are shown in red and blue.

When water depth permitted, the glider repeatedly dove to its maximum rated depth of 200m. A paired 200 m dive and ascent lasted about 50 minutes. The glider does not breach the surface on every ascent, instead inflecting downward just below the surface. The glider surfaces about every third ascent. During surface intervals, the oxygen sensor was programmed to continue to measure at a frequency of 1/4 Hz. The duration of each surface interval was about 10-15 minutes.
during which $O_2$ measurement was interrupted for several minutes while the glider transmitted
data to shore. On average, 209 $O_2$ measurements were acquired during each surface interval.

**Mooring Data**

The expected $pO_{2,air}$ was calculated based on meteorological data collected from nearby
NOAA National Data Buoy Center Station 44008 located at 40.503°N 69.248°W and Eq. 2.
Hourly sea level pressure, air temperature and dewpoint data were used to calculate $p_{atm}$, $\phi$ and
$p_{H_2O}$. Measurement height for sensors on buoy 44008 were located at a height of 4 m. Values for
$p_{H_2O}$ where corrected to a glider sensor height of 0.1 m using the method of Bittig et al. (2015).
The deployment spanned a range of low to moderate sea-states with windspeed varying from 0 –
12 m s$^{-1}$ and significant wave height varying from 0.4 to 2.8 m.

**Winkler calibrations**

Prior to recovery, the glider rendezvoused with the R/V Endeavor. Two calibration casts
were conducted using the CTD on the R/V Endeavor on the mornings of 15 June 2016 and 17 June
2016. For each calibration cast, the glider was held at the surface in the vicinity of the Endeavor
(within ~500 m) and commanded to dive at the time when the CTD was lowered. Water was
collected in Niskin bottles at nominal depths of 200 m, 150 m, 100 m 50 m, the depth of chlorophyll
a maximum (44 m and 38 m, respectively), 30 m, 20 m, 5 m and 1 m. Dissolved Oxygen samples
for Winkler titration were collected in 125 m iodine titration flasks following standard operating
procedures (Langdon 2010). 1 m and 5 m samples were collected in triplicate while all other
depths were collected in duplicate.

Due to logistical limitations on the R/V Endeavor cruise, Winkler $O_2$ samples could not be
analyzed on the ship, but instead stored for the duration of the cruise in dark conditions with water
sealing flask necks until they were analyzed at WHOI on 21-22 June, 2016. While immediate
analysis is preferred, studies have demonstrated successful sample storage without biasing $O_2$ determinations for many days and even many months (Zhang et al. 2002; Langdon 2010). Samples were titrated in the Nicholson Lab at WHOI using custom-designed Winkler titrator with automated potentiometric endpoint detection. Standard deviation of replicates averaged $\pm 0.28 \mu\text{mol kg}^{-1}$ or $\pm 0.12\%$.

**Assessment**

*Winkler $O_2$ evaluation*

Cross-calibration against discrete Winkler $O_2$ observations has been, to-date, the preferred method for calibration of glider oxygen sensors (Nicholson et al. 2008). The approach requires close coordination of ship and autonomous operations to ensure a close match in time and space between shipboard samples and the glider profile. Two calibration casts were conducted from the R/V Endeavor, the first cast began at 11:52 UTC on 15 June 2016 was coordinated such that the glider was located 200 m to the south of the ship’s location. The second cast was at 11:05 UTC on 17 June 2016. The glider was located 950 m to the east of the ship at the time of the cast. For each calibration cast, the glider dive was initiated within five minutes of the start of the CTD cast.

Bottle samples were matched to their corresponding glider profiles by identifying the glider data point nearest in density ($\sigma_0$) space to avoid any noise introduced by vertical motions of internal waves. Sensor lag time can introduce a historesis effect. Bottle values were matched to both the descent and ascent profiles and the two values were averaged. A linear for paired values was calculated both assuming (1) a linear fit; and (2) a linear fit with forced zero intercept (Table 1). The latter method is equivalent to a gain correction. The raw glider $O_2$ measurements ($[O_2]^{raw}_w$) were corrected ($[O_2]^{meas}_w$) using simple gain factor ($G$):

$$[O_2]^{meas}_w = G[O_2]^{raw}_w$$  \hspace{1cm} (3)
Table 1: Winkler Calibration fit parameters. Best fit parameters are shown for each of two calibration casts. Each fit is evaluated at 100% saturation. Sensor gain, used to correct the glider optode, is the inverse of the zero-intercept fit. Despite differences in best-fit slope and intercept, each fit evaluated at atmospheric equilibrium resulted in a similar value.

<table>
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<th>Linear fit</th>
<th>Zero intercept</th>
<th>Linear fit</th>
<th>Zero intercept</th>
<th>Gain</th>
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<tr>
<td>m</td>
<td>b</td>
<td>M</td>
<td>$\Delta O_{2w}^{raw} @100%$</td>
<td>$\Delta O_{2w}^{raw} @100%$</td>
</tr>
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<td>15 June</td>
<td>0.924</td>
<td>2.3%</td>
<td>0.949</td>
<td>94.7 ±0.6%</td>
</tr>
<tr>
<td>17 June</td>
<td>0.897</td>
<td>4.8%</td>
<td>0.947</td>
<td>94.5 ±0.4%</td>
</tr>
<tr>
<td>Combined</td>
<td>0.913</td>
<td>3.3%</td>
<td>0.948</td>
<td>94.6 ±0.3%</td>
</tr>
</tbody>
</table>

The gain factor, $G$, needed to correct glider O$_2$ observations is calculated as the inverse of the slope of the fit line of Winkler O$_2$ versus raw glider O$_2$ with zero intercept (Figure 3). For both casts combined, we calculate a gain of $G_{all} = 1.055 \pm 0.004$. The gain factor calculated independently from the first and second cast were $G_1 = 1.054 \pm 0.006$ and $G_2 = 1.056 \pm 0.005$, respectively. $R^2$ was 0.994, 0.995 and 0.995 for combined data, calibration cast 1 and calibration cast 2, respectively. When not forced to a zero intercept, the best linear fit had zero intercepts of 2.3 ± 2.5%, 4.8 ±1.6% and 3.3 ±1.4% for cast 1, cast 2 and combined data, respectively. The above regressions were calculated for O$_2$ percent saturation, but almost identical results were calculated when concentration was used (data not shown). In summary, the calibration casts showed a linear relationship between optode O$_2$ with the optode consistently measuring low, correctable by multiplying by a gain factor of 1.055 ±0.004. Uncertainty ranges in each case are based on standard error of the slope of the Type 1 Regression fit.
Figure 3: Glider $\Delta O_2$ from calibration casts on 15 June (a) and 17 June (b) prior to calibration (blue) and post calibration (orange). Solid lines show average of dives and climbs (light traces). Black symbols indicate Winkler bottle samples. Panel c. shows best least squared linear fits with (blue) and without (red) assuming a zero intercept. Two sigma uncertainty ranges are shown in blue and red shading. Sensor gain (the inverse of the slope of the linear least square fit) was 1.055 ±0.004.
Winkler $O_2$ results provide a ground-truth for air calibration measurements. In the following section we compare Winkler-calibrated glider $O_2$ observations to air $O_2$ measured by the glider and inferred from buoy atmospheric measurements.

During each surface interval, the optode records measurements of the near-surface atmosphere. We consider several factors that could contaminate this record such as (1) a response-time adjustment period immediately after surfacing and (2) the influence of splashing water or residual water on the sensor surface. Because the optode has a nominal response time around 30 seconds, it is likely that some time is needed after surfacing for measurements to stabilize. Air measurements, binned by time since surfacing, indicate that this adjustment period lasted roughly 60 seconds before measurements stabilized (Fig 4). During this period, apparent air $O_2$ decreased by about 4% on average.

Figure 4: Change in measured air $O_2$ saturation (%) as a function of time since surfacing. The mean air $O_2$ for each surface interval is subtracted. Error bars indicate the standard deviation for each 10 second time bin. Each bin contains, on average, 722 measurements.
Over the full deployment the glider recorded 35,177 total air $O_2$ measurements during 168 surface intervals. Compared to profiling floats, which surface infrequently and usually only make a few measurements at the surface, the glider dataset provides a large amount information to characterize $O_2$ optode sensor response at the surface. For each surface interval, we calculated the measured value relative to standard air $O_2$ such that:

$$\Delta O_{2,a}^{\text{meas}} = \frac{pO_{2,a}^{\text{meas}}}{pO_{2,ref}^{\text{ref}}} - 1 \quad \text{where} \quad pO_{2}^{\text{ref}} = \chi_{O_2}p_{\text{sat}} \tag{4}$$

where $pO_{2}^{\text{ref}}$ is the partial pressure of $O_2$ at 1 atm and 100% saturated water vapor pressure ($p_{\text{sat}}$). Note that $pO_{2,a}^{\text{meas}} / pO_{2}^{\text{ref}}$ is equal to $[O_2]_a^{\text{meas}} / [O_2]_{eq}$ where $[O_2]_{eq}$ is the equilibrium solubility (Garcia and Gordon 1992). The expected $O_2$ anomaly for air ($\Delta O_{2,a}$) is defined analogously, using NOAA buoy data and Eq. (2) such that deviations in $\Delta O_{2,a}$ from zero are due to changes in atmospheric pressure and relative humidity.

Figure 5: Histograms of $\Delta O_{2,a}^{\text{meas}}$ for all surface measurements ($n = 35,711$) and for surface measurements excluding the first 90 seconds of each surface interval ($n = 24,199$). The vertical dashed line indicates the mode value of $\Delta O_{2,a}^{\text{meas}} = 3.6\%$. 
The distribution of air $\Delta O_{2,a}^{meas}$ measurements is skewed towards positive values (i.e., towards the observed positive surface water saturation) with a long tail on the upper end of the distribution (Figure 5). Removing data from the first 90 seconds of each surface interval significantly reduces the long tail, yet the distribution remains skewed. In both cases, the distribution has the same mode (peak) bin at $\Delta O_{2,a}^{meas} = 3.6\%$ which corresponds to the 28th and 32nd percentile for all measurements and for cutoff measurements, respectively. For comparison to surface seawater measurements, we assign a single value for $\Delta O_{2,a}^{meas}$ for each surface interval by taking the 32nd percentile of measurements from a surface interval after excluding the first 90 seconds of observations. Corresponding surface seawater $O_2$ was calculated by taking the average of observations from 1 - 2.5 m depth during the ascent immediately prior to the surface interval. A descent value was calculated by linearly interpolating in time the surface (1 - 2.5m) averages from non-surfacing periods to the average time of each surface interval. Descents immediately after surface intervals were not used because a time-lag effect, reverse of that observed immediately after surfacing, was observed during these dives, biasing surface values low over the upper several meters. Similar to what has been observed on profiling floats (Bittig and Körtzinger 2015; Johnson et al. 2015), we found a correlation between $\Delta O_{2,a}^{meas}$ and the surface water $O_2$ saturation, $\Delta O_{2,w}^{meas}$ with a slope of $0.36 \pm 0.03$ and $R^2$ of 0.44 (Fig 6). The slope of 0.36 is comparable, but somewhat higher than published values for profiling floats of 0.22 (Bittig and Körtzinger 2015) and 0.29 (Johnson et al. 2015). Following Bittig and Körtzinger (2015) we corrected measured $O_2$ such that:

$$\Delta O_{2,a}^{corr} = \frac{\Delta O_{2,a}^{meas} - m(\Delta O_{2,w}^{meas})}{1-m}$$

(5)
where $\Delta O_{2,a}^{corr}$ is the corrected air measurement and $m$ is the slope of 0.36. After completing the above correction, the difference between glider measured air and the expected $O_2$ of air based on buoy atmospheric pressure measurements ($\Delta O_{2,a}^{corr} - \Delta O_{2,a}^{buoy}$) was with error of zero ($\Delta O_{2,a}^{corr} - \Delta O_{2,a}^{buoy} = -0.01 \pm 1.18\%$), where the uncertainty range is based on one standard deviation (Fig 7).

Put in other terms, when $\Delta O_{2,a}^{corr}$ is calculated from raw $\Delta O_{2,a}^{raw}$ instead of $\Delta O_{2,a}^{corr}$, the gain calculated from air $O_2$ is $(\Delta O_{2,a}^{buoy} - 1)/(\Delta O_{2,a}^{raw} - 1)$ and equal to 1.055, within rounding error of the $G$ calculated from Winkler calibration.

If each surface interval is considered an independent estimate of $\Delta O_{2,a}^{corr}$, then the calculated standard error of the mean is 0.09%. $\Delta O_{2,a}^{corr}$ was weakly, but significantly correlated with $\Delta O_{2,a}^{buoy}$ ($R^2 = 0.035$, $p = 0.02$) indicating that the glider air calibration may be able to track small variations in atmospheric pressure. The low correlation is not unexpected, as $\Delta O_{2,a}^{buoy}$ has a very small dynamic range ($-0.6 \pm 0.6\%$).

Figure 6: Surface oxygen saturation anomaly versus measured air anomaly showed a linear relationship with a slope of 0.36 and $R^2$ of 0.44.
Figure 7: Initial glider air $O_2$ measurements ($\Delta O_{2,a}^{\text{meas}}$; yellow) were corrected ($\Delta O_{2,a}^{\text{corr}}$; purple) for influence from surface water $O_2$ saturation ($\Delta O_{2,w}^{\text{meas}}$; blue). Corrected ($\Delta O_{2,a}^{\text{corr}}$) values, when using a gain of 1.055, were within error of the expected atmospheric $O_2$ content as determined from buoy sea level pressure measurements ($\Delta O_{2,a}^{\text{buoy}}$; orange).

Discussion

In this study, we demonstrated that a newly developed air calibration method for dissolved oxygen optodes produced results in good agreement with ship-based calibration casts with Winkler bottle $O_2$ titrations. Each method determined that a gain factor of 1.055 was necessary to correctly calibrate the glider optode. Accurate air-calibration assessment must take into account the influence of surface ocean saturation, likely due to splashing waves and spray, that cause the optode to measure a combination of atmosphere and surface ocean during surface intervals. Following Bittig et al. (2015) we determined a relative contribution of 64% air ($\Delta O_{2,a}^{\text{meas}}$) and 36% for surface water ($\Delta O_{2,w}^{\text{meas}}$). Given the high biologically driven supersaturation of 7-15% observed during the glider deployment, the above correction resulted in the corrected air $O_2$ measurement being about a 4% lower than raw measurements.
Uncertainty in the absolute accuracy of the air calibration method stems from several potential sources, including the scatter in $\Delta O_{2,a}^{corr}$, uncertainty in the sea level pressure and humidity data used to calculate $\Delta O_{2,a}^{buoy}$ and uncertainty in magnitude of surface water influence. Here, we assess the contribution of these sources of uncertainty to overall uncertainty in the air calibration method. In the section above, we determined a standard error of the mean of $\pm 0.09\%$ for $\Delta O_{2,corr}$, but additional potential sources of bias increase the true uncertainty. The accuracy in quantifying $\Delta O_{2,a}^{buoy}$ is calculated from propagating a $\pm 1$ hPa typical uncertainty for $p_{atm}$ and a $\pm 5\%$ uncertainty for $p_{H_2O}$ in Eq. (2) resulting in an uncertainty of $\pm 0.11\%$ in $\Delta O_{2,a}^{buoy}$. The greatest source of uncertainty stems from uncertainty in $m$ (Eq. 5). Propagating the $\pm 0.03$ uncertainty in $m$ through Eq. (5) results in a $\pm 0.5\%$ uncertainty in $\Delta O_{2,a}^{corr}$. Thus, we consider $\pm 0.5\%$ to the best measure of overall uncertainty for the accuracy of the air O$_2$ glider calibration. Applied to the gain factor, the uncertainty equates to $1.055 \pm 0.005$, similar in magnitude to the $\pm 0.004$ uncertainty determined from Winkler calibration.

In practice, the magnitude of this uncertainty will depend both on the magnitude of $m$ (i.e., lower $m$ will reduce uncertainty) as well as on saturation anomaly of the surface ocean ($\Delta O_{2,w}^{meas}$) such that error will be smaller when surface water is closer to equilibrium (Fig 8). For conditions in most of the open ocean where $\Delta O_{2,w} - \Delta O_{2,a}$ is less than 5%, this source of error is significantly reduced. Further reduction in uncertainty could be achieved by reducing $m$ by increasing the mounting height of the air-calibration optode.

The accuracy we achieved with the glider deployment are comparable to recent results from profiling floats. Bittig et al. (2015) reported accuracy of $\pm 1\%$, Johnson et al. (2015) reported
<1% error. When comparing air calibration to Winkler calibration across eight floats Bushinsky et al. (2016) reported an $-0.5 \pm 0.7\%$ range. These float studies also investigated long term drift in optodes which was determined to generally be less than $0.5\% \text{ y}^{-1}$. Over the course of a 15-day deployment, this amounts to an undetectable change of $0.02\%$, so we are unable to evaluate sensor drift in this study. For longer glider deployments, such as year-long deployments at Ocean Observing Initiative (OOI) sites, quantifying drift likely is achievable.

Figure 8: Error associated with a 0.03 uncertainty in ($m$) the surface water contribution to $\Delta O_{2,\text{corr}}$ (see Eq. 5) as a function of the difference between air and surface water saturation. The white box indicates the range of observations from this study.

Comments and recommendations

The application of air calibration on underwater gliders opens up a range of exciting applications. Foremost, improved control on sensor accuracy will improve oxygen-based net community production estimates from gliders, which rely and precise characterization of air-sea
O$_2$ fluxes and thus are particularly sensitive to any biases in quantifying surface O$_2$ saturation (Emerson and Bushinsky 2014). Additionally, adding O$_2$ air calibration to a glider enables the possibility of autonomous cross-calibration of observing networks. For example, within an OOI Array, a glider equipped with an air calibrating optode could be piloted to dive at the location of moorings and other mobile assets that are equipped with oxygen sensors to create a cross-calibrated observing network.

We conclude that O$_2$ air calibration on gliders is a robust new tool for in situ calibration of dissolved oxygen sensors to 0.5% or better accuracy. Achieving this level of accuracy requires attention to two primary potential sources of bias including (1) A transient sensor response when the optode crosses the sea surface interface, which was observed to stabilize after about 50 seconds, and (2) the observed influenced of surface water saturation on air measurements, likely due to splashing waves. Air measurements must be corrected for this influence when surface saturation departs significantly from air pO$_2$ (i.e., using Eq. 5). We recommend that the correction factor, $m$, should preferably be determined directly for each given glider deployment, and literature values from this, or other sources should not be assumed applicable. An increased optode mount height, coupled with operating in open ocean conditions where surface O$_2$ saturation is typically within ±5% of equilibrium likely would reduce uncertainty in sensor accuracy to below 0.25%.

The air calibration method appears to be approaching the accuracy and precision achievable by traditional Winkler calibrations. For studies where surface oxygen saturation is of primary importance, air calibration can provide similar accuracy while avoiding the logistical constraints of conducting Winkler titrations and calibration casts. However, we feel there still is an important role for Winkler titrations for several reasons, including (1) Air calibration is still a
new approach and it should continue to be validated over a wider range of oceanographic conditions; and (2) Air calibration only provides a calibration point for surface $O_2$ saturation. Uncertainty about the accuracy and drift of optodes at lower oxygen concentrations remain, requiring further investigation.
References


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Table and Figure Captions

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