Oxygen corrections applied to delayed mode data

- deployment: dfo-bb046-20220707
- glider: dfo-bb046
- sensor: oxygen_0054
- calibration date: November 1st, 2021
- description: Calvert Island Line

1.0 Preamble

This document describes dissolved oxygen data processing steps applied to delayed mode data collected using a Rinko ARO-FT-CE dissolved oxygen optode mounted on an Alseamar SeaExplorer autonomous ocean glider. This sensor is mounted in the nose cone of the glider, adjacent to the CTD, and measures oxygen concentration. It has a response time of less than 1 s. Corrections applied use data collected by the CTD on the glider. Note that when converting between oxygen units, potential density is used.

1.1 Set up the processing

The processing steps below are applied to delayed mode data stored in a single netcdf timeseries file created using the Pyglider data processing package (<https://github.com/c-proof/pyglider>). This data has already undergone CTD sensor corrections. The metadata and a detailed report describing the corrections being applied will be made available via the deployment page on the C-PROOF website: <https://cproof.uvic.ca/gliderdata/deployments/dfo-bb046/dfo-bb046-20220707/>.

```
Out[5]: xarray.Dataset
```


```
Out<sup>[6]:</sup> xarray.DataArray 'oxygen_concentration' (time: 1759051)
```

```
[1759051 values with dtype=float64]
▼ Coordinates:
  time (time) datetime64[ns] 2022-07-07T16:45:19.204999936 .....
                                                                            \mathbf{r}latitude (time) float64 ...
                                                                            \Boxlongitude (time) float64 ...
                                                                            \mathbf{r}depth (time) float64 ...
                                                                            \Boxpind (time) float64 ...
                                                                            \mathbf{r}► Indexes: (1)
► Attributes: (10)
```

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Loading coefficients for Rinko sensor
```
2.0 Corrections applied to delayed mode data for this mission

This document covers the following steps:

- 1. Compensate for pressure and salinity effects
- 2. Convert from concentration in μ mol/L to phase
- 3. Determine the sensor response time lag correction
- 4. Apply the sensor response time lag correction
- 5. Convert from phase to concentration in μ mol/L
- 6. Determine the optode drift correction
- 7. Apply the optode drift correction

2.1 Compensate for pressure and salinity effects

The Rinko FT User's manual states that corrections must be applied for pressure and salinity effects to the dissolved oxygen concentration in μ mol/L (oxygen_concentration).

The pressure compensation factor is estimated as: p _factor = (|P| / 100) \cdot Cp + 1; where P is the pressure from the CTD in dbars, and Cp is the calibration coefficient for pressure correction, listed on the calibration certificate for each sensor.

The salinity compensation factor is estimated as: s _factor = exp[S \cdot (B0 + B1 \cdot Ts + B2 \cdot Ts² + B3 \cdot Ts³) + C0 \cdot S2]; where S is the fully corrected salinity from the CTD in PSU, B0 to B3 and C0 are coefficients specified in the Rinko manual, Ts is the scaled temperature: Ts = $ln[(298.15 - T) / (273.15 + T)]$; and T is the temperature from the CTD in degrees Celsius.

Unlike the Aanderaa sensors, the Rinko optodes apparently do not have an internal reference salinity. The manual states "Note that the physical value output of the instrument does not consider salinity and/or pressure." This is equivalent to sal_ref = 0 for the purposes of the salinity compensation correction above.

Then compensated oxygen concentration is calculated: oxygen_comp = oxygen_uncomp ⋅ s_factor ⋅ p_factor;

The units of oxygen_comp are μ mol/L.

2.2 Convert oxygen concentration in μ molL $^{-1}$ to phase

The uncalibrated phase (Phase) is the difference between the phase obtained when the foil is excited by Blue light and by Red light. These hexadecimal values are referred to as 'AD values', as opposed to calculated temperature and dissolved oxygen concentration, which are referred to as 'Physical values'.

The time response correction (5.1) is applied to the AD value of dissolved oxygen (AD value of DO), which is functionally equivalent to the calibrated phase. Then the dissolved oxygen concentration in μ mol/L is calculated using the Stern-Volmer relationship proposed by Uchida et al., 2010:

 $DO[\mu \text{mol/L}] = \{((1 + d0 \cdot T)/(d1 + d2 \cdot N + d3 \cdot t + d4 \cdot t \cdot N))^{e0} - 1\} \cdot \{1/(c0 + c1 \cdot T + c2 \cdot T^2)\},$

where calibration coefficients c0, d0, e0 etc. are printed on the calibration certificate for that sensor, T is temperature, and N is the AD value of DO/10000. Typically $e0 = 1$ and $d3 = d4 = 0$, so that we do not require values of t, the LED accumulation time [s].

Our sensors are normally set to output dissolved oxygen concentration in μ mol/L (oxygen_concentration), which is then converted to calibrated phase (AD value of DO) using the temperature measurement from the oxygen sensor, the time response correction is applied, and then the resulting field is converted back to $DQ[\mu$ mol/L] using the fully corrected temperature measurement from the CTD.

2.3 Determine the sensor reponse time lag correction

The time response correction is applied to the calibrated optode phase (AD value of DO for Rinko sensors) to account for the slow sensor response time relative to the diving rate of the glider.

Following Nicholson et al., 2008 and Howatt et al., 2018, a response time constant τ is determined by minimizing the error between all measured upcast values vs. all measured downcast values. A first-order lag correction is determined by calculating τ as in Fofonoff et al., 1974 based on the equation:

 $Phase_{true} = Phase_{measured} + \tau \cdot d/dt \cdot Phase_{measured}$ where $Phase$ is the calibrated optode phase, 'true' is the true value and 'measured' is the measured value, and d/dt indicates a first derivative w.r.t. time during a given upcast or downcast. Derivatives are calculated using a centered finite difference scheme after successive upcasts and downcasts are interpolated onto the same depth grid. To avoid large derivatives caused by points at the start and end of individual profiles, any dt value greater than one standard deviation from the mean is excluded from the calculation.

Then a least squares linear regression is performed on the following equation: $Phase_{measured}^{upcast} - Phase_{measured}^{downcast} = -\tau \cdot (d/dt \cdot Phase_{measured}^{upcast} - d/dt \cdot Phase_{measured}^{downcast}$ $\frac{downcast}{measured})$

which assumes that successive upcasts and downcasts are identical.

Expected ranges for the response time constant for each type of sensor are provided in Bittig et al., 2014. For our Rinko sensors, the calculated value of τ is expected to fall in the range 1 to 3 seconds. If the calculated

response time constant falls outside of these ranges, manual inspection of the mission data is required to determine the cause.

Given the rapid response time of Rinko sensors, it is expected that τ may be too small to necessitate applying a time lag correction. We verify this below.

Grouping upcasts and downcasts, stand by. Grouping upcasts and downcasts complete.

Interpolating fields.

Now we use the upcasts and downcasts that have been interpolated to a regular depth grid to estimate τ using least-squares regression applied to the entire time series.

```
Sensor response lag coefficient [in seconds] tau = 0.3900298432008188
99th percentile significance = 0.17794354502764664
R-value for the linear regression = -0.048271998224472305
```
2.4 Apply the sensor response time lag correction

The value of τ = 0.4 \pm 0.2s is small as expected, given the 1s response time of the sensor. We note that the least squares fit had a relatively low R-value, suggesting that the upcasts and downcasts were not offset by a consistent amount throughout the time series. Given this, and the small offset, we elect not to apply a sensor reponse time lag correction. This choice additionally avoids applying the smoothing and filter required for this correction, better preserving the signals in the data.

2.5 Convert from phase to oxygen concentration in μ **mol/L**

Given that we are not applying a time response correction, we use 'oxygen_comp' (oxygen concentration in μ mol/L) for the next step in the processing.

2.6 Determine the optode drift correction

The sensor drift correction is applied to the time-response corrected, compensated dissolved oxygen concentration data 'DO' to account for the tendency of oxygen optodes to drift over time as the sensor ages. Although drift increases as a function of the number of samples collected, sensors tend to drift more quickly during storage than while in the field by about a factor of 10.

The sensor drift correction attempts to correct for the drift that does occur by comparing the oxygen optode data to a trustworth profile of dissolved oxygen concentration measurements collected nearby in space and time. Ideally, this comparison would be with Winkler titrated bottle samples collected at the same time and location as one of the glider's dives. In practice, a hierarchy of 'trustworthy' data sources is used, within some chosen tolerance for distance and time from the glider's sampling locations.

The drift correction itself is a linear adjustment applied to DO[μ mol/kg] with slope p1 and intercept p2:

```
oxygen_concentration_adjusted [\mumol/kg] = p1 DO[\mumol/kg] + p2
```
Following Bittig et al., 2018, the drift is characterized by a reduced sensor response plus a small offset in the opposite direction. The slope should be positive, and within about 10\% of unity. The intercept should be within a few [μ mol/kg] of zero and negative. In practice, the correction is determined with the intercept set to zero a priori. We have found that an intercept of zero typically produces better agreement in the near-surface mixed layer and in deep water, the most appropriate segments of the water column for comparison.

If the slope is too large, the comparison may be rejected. It is expected that the drift for an individual sensor will increase with time (though not linearly). If this is not the case, or if a sudden large increase in drift is detected, the comparison should be re-evaluated and/or the sensor should be examined.

To determine the drift correction, a least-squares fit is performed in density space between all of the suitable comparison profiles and the associated glider optode measurements. The glider profiles to be used are binaveraged to the densities associated with the oxygen measurements from the comparison profile, with a bin size of +/-0.1 kg/m³ (which can be adjusted higher if needed). The linear least-squares fit is applied to the binned oxygen optode measurements from the glider vs. the measurements from the comparison profile. The associated correlation coefficient for the fit is expected to be above r² = 0.95, and in practice is often above r² $= 0.99.$

Note that potential density is used, not in-situ density, since a given volume of water may move vertically by a significant amount due to isopycnal heaving, and we wish to remove this effect from the comparison. The portion of the profiles that is within the pycnocline is excluded from the comparison by visually identifying a depth at the base of the pycnocline and retaining only data below it, as well as data in the very near surface that will be close to the saturation value.

The goodness of fit is evaluated by examining the agreement between the deep and shallow drift-corrected glider oxygen measurements with those from the comparison profile. For the shallowest measurements, the saturation value of oxygen at the comparison profile location is calculated and used to provide context for the expected near-surface oxygen concentration values.

Finally, the linear sensor drift correction is applied to the DO measurements (not to the data binned by density).

For this mission, two comparison profiles are available: 1) A profile of Winkler-titrated bottle samples collected by the Hakai Institute at the time of glider recovery in Hakai Pass and 2) A profile using an oxygen sensor on a lowered CTD, also collected by the Hakai Institute at the time of glider recovery. We examine both these profiles compared to the available glider data.

We see good agreement between the comparison profile from the oxygen sensor used during the CTD cast and the Winkler bottle samples, with the exception of the densest, deepest water. For the deepest Winkler sample, it appears that the bottle salinity is quite different from that measured by the CTD, which affects the oxygen agreement in potential density space as well. We now compare to the available glider data.

Number of glider profiles available for comparison 2 Profile indices of profile(s) available for comparison [893. nan]

The comparison profile was collected at the time of glider recovery, during the final glider profile, and includes high-quality Winkler-titrated bottle samples as well as the profile collected by the oxygen sensor attached to the CTD. Given the agreement between the Winkler samples and the oxygen from the CTD profile, and given the small number of Winkler samples available for comparison, we determine the correction to the glider using the oxygen sensor data.

We compare to the last full-depth glider profile collected, and determine the comparison using all available data, not restricting the densities. There is a slight offset from the glider oxygen profile visible in density space, which is what we expect to correct.

We now apply a least-squares fit between the two profiles in isopycnal space. We force the intercept to pass through zero, as this has been demonstrated to result in more accurate corrections. As oxygen optodes drift, they tend to read lower values of oxygen [Bittig et al., 2015], so we expect the correction to produce a slight increase in oxygen concentration.

```
slope m = [1.1] and R2 = 0.97
```
<matplotlib.legend.Legend at 0x20f66cdde90> Out[27]:

2.6 Applying the optode drift correction

Sanity checks We now apply our drift correction and confirm that the drift correction has had the intended effect. We check the following:

- 1. Do we see better agreement with the full comparison profile, particularly in the deep water and at the surface?
- 2. Are values at the surface consistent with saturated (or over-satured) water?
- 3. Are values at 1000 m consistent with other deep oxygen samples or at least reasonable?

<matplotlib.legend.Legend at 0x20f0de853d0> Out[29]:

Agreement with comparison profile: The agreement with the comparison profile has improved significantly, except near the surface where there is high variability.

Surface values: Both the glider profile and comparison profile appear over-saturated right at the surface. Before the drift correction, the glider is in decent agreement with the comparison profile below 5 m but less saturated above 5 m. After the correction, agreement below 5 m is not quite as good, but the glider profile is closer to 100% saturation above 5 m and matches to the comparison profile more closely. This type of surface comparison provides information, but is not conclusive, particularly in a dynamic environment such as Hakai Pass.

The minimum oxygen value before the drift correction is 5.0 umol/kg The minimum oxygen value after the drift correction is 5.5 umol/kg

Comparison of deep oxygen: There are no good DFO profiles from beyond the shelf break to compare with during the glider mission. However, we see that the drift correction has increased the deep oxygen values slightly. This is a good sanity check, since oxygen optode sensor drift tends to cause lower values. Furthermore, the change caused by the drift correction is smallest for the deep oxygen data, as expected.

Conclusion on drift correction

Given the high-quality comparison profile, and the supporting evidence suggesting the estimated drift correction produces reasonable results, we choose to apply the drift correction. However, note that the optode on this glider was calibrated only 8 months before the mission, and the drift correction estimated is large.

The change in oxygen concentration after applying the drift correction is between 0 and 10 μ mol/kg below 400m, and up to nearly 40 μ mol/kg at the surface.

Corrected data saved to file: ./dfo-bb046-20220707/dfo-bb046-20220707_corrected_v2.nc

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Out[36]: xarray.Dataset
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'./dfo-bb046-20220707//dfo-bb046-20220707_grid.nc' Out[38]:

jupyter nbconvert Oxygen_dfo-bb046-20220707_v2.ipynb --to=webpdf -- TemplateExporter.exclude_input=True