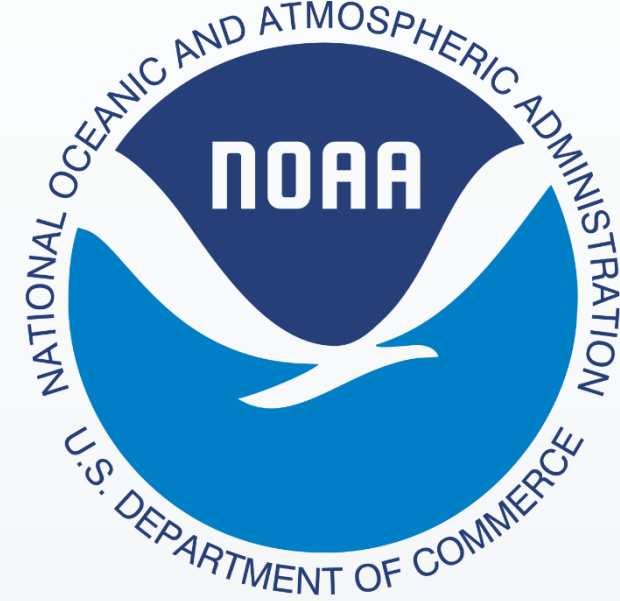
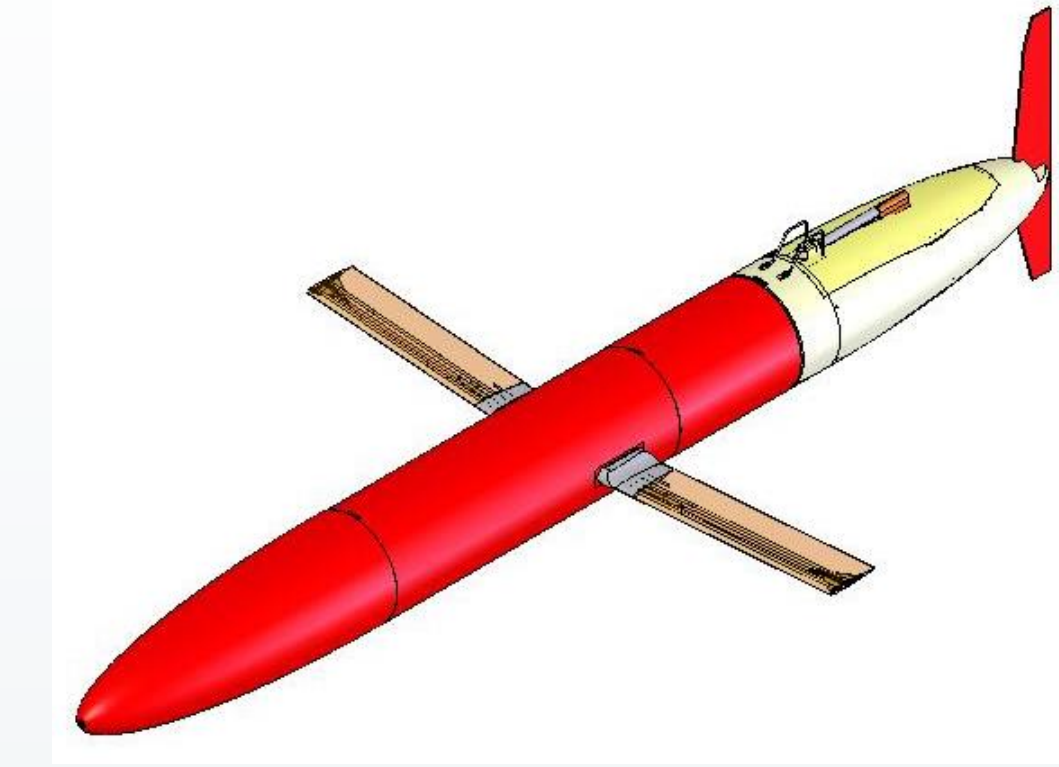


Calibrations for Long-Term Dissolved Oxygen Measurements on CUGN Gliders



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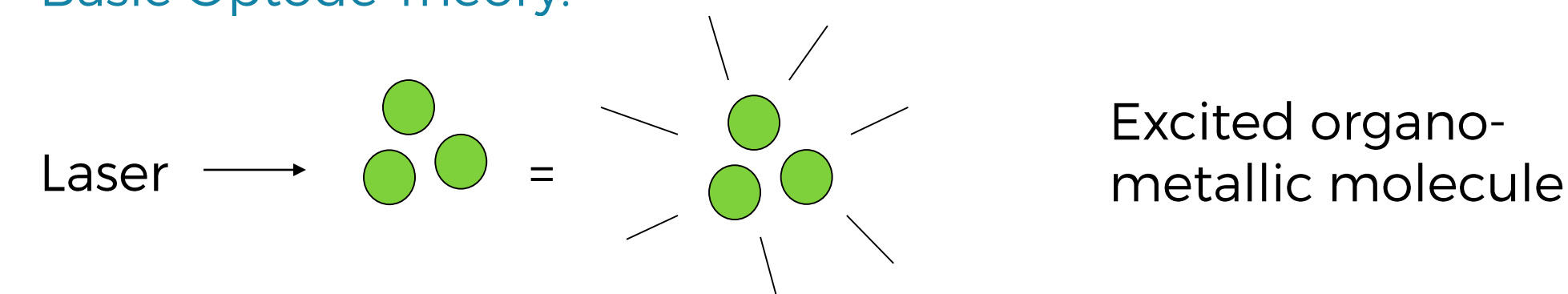
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Abstract

The California Underwater Glider Network (CUGN) is a long-term monitoring glider network with currently over 10 years of temperature, salinity, and velocity data. Since 2017, gliders have carried a Seabird 63 dissolved oxygen sensor as part of their payload. Since dissolved oxygen sensors are known to drift after their factory calibration, it is desirable to have a correction or calibration procedure in place while collecting observations. CUGN glider missions are 3 months in duration, so the sensors can be calibrated directly before and after missions. We present our two-point calibration procedure and initial measurements of instrument drift over time. The calibration method should be applicable in general to repeatedly deployed and recovered oxygen sensors on autonomous platforms.

Introduction

The **SBE63** is an **optode sensor** for dissolved oxygen. Basic Optode Theory:



The molecule can fall back to its original energy state in one of three ways:

1. Emission of a photon – a radiative process, **fluorescence or phosphorescence**
2. Collides with other atoms or molecules and transfers energy – a non-radiative process, **dynamic quenching**
3. Other non-radiative means, **static quenching**.

Given $[A^*]$, the excited material, the following processes occur at rates k_1 , k_q , and k_2 , assumed to be constants:

- | | | |
|-------------------------------------|--------------------------|-------|
| 1. $[A^*] \rightarrow [A] + h\nu$; | fluorescence | k_1 |
| 2. $[A^*] + [Q] \rightarrow [A]$; | dynamic quenching | k_q |
| 3. $[A^*] \rightarrow [A]$; | static quenching | k_2 |

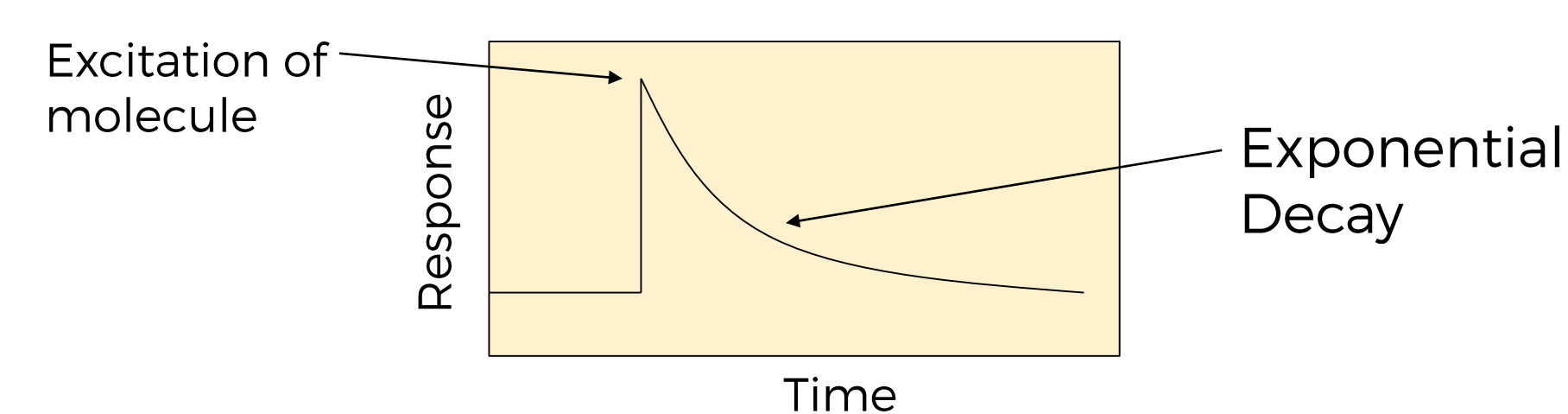
For natural rate of decay:

$$D[A^*]/Dt = -k_1[A^*] - k_2[A^*] = -(k_1 + k_2) [A^*].$$

With dynamic quenching:

$$D[A^*]/Dt = -(k_1 + k_2 + k_q[Q]) [A^*]$$

where k_q is the bimolecular quenching constant and $[Q]$ is the concentration of quenching substance (ex: $[O_2]$), assumed constant with time because its concentration is order of magnitude greater than that of the organo-metallic molecule.



We want to know the timescale of decay, or the fluorescence lifetime. For natural decay, $T_0 = 1/(k_1 + k_2)$. For dynamic quenching, $T = 1/(k_1 + k_2 + k_q)$. Thus, we get the Stern-Volmer equation

$$T_0/T = 1 + k_q T_0[Q] = 1 + k_{sv}[Q]$$

where k_{sv} is the Stern-Volmer quenching constant.

From Theory to Practice

$[O_2]$ causes decreased fluorescence lifetime of the platinum porphyrin molecule in the SBE 63 optode theoretically at the rate k_{sv} . Given the bimolecular quenching constant for a given temperature, the Stern Volmer equation should be linear. However, in optodes K_{sv} changes its value for high $[O_2]$, which suggests that part of the luminophore is inaccessible to oxygen in high $[O_2]$ environments (Johnson et al., 2015), so the real sensor model is empirical with a higher-order polynomial model. Seabird uses the model from Uchida et al. (2008).

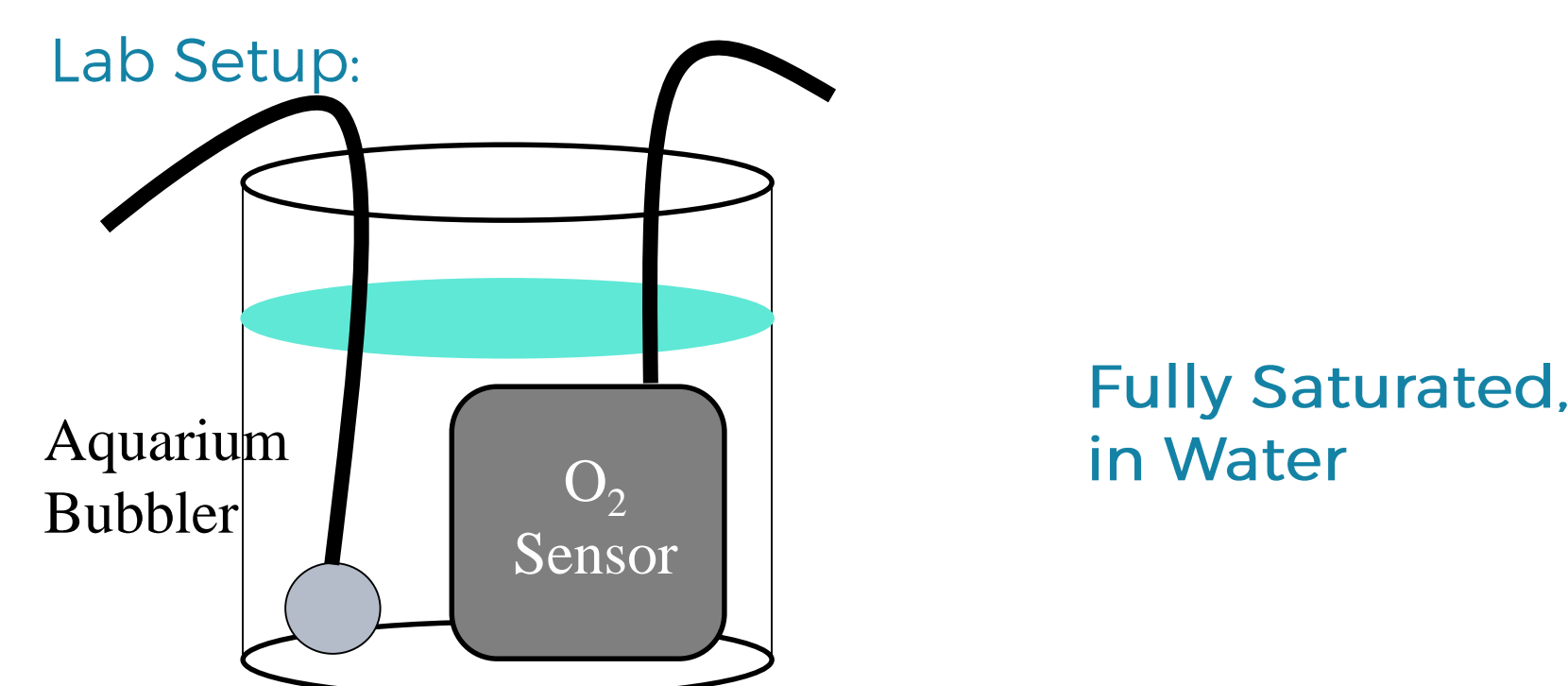
Our concern is time drift of the coefficients after factory calibration, which has been documented by others (ex: Bittig and Kortzinger, 2015). This time drift can be periodically recorded and corrected with a gain and offset correction, calculated from a two-point calibration with an $[O_2]$ observation at full saturation and zero saturation (Bittig et al., 2018):

$$[O_2]_{corr} = G * [O_2]_{raw} + \text{Offset}.$$

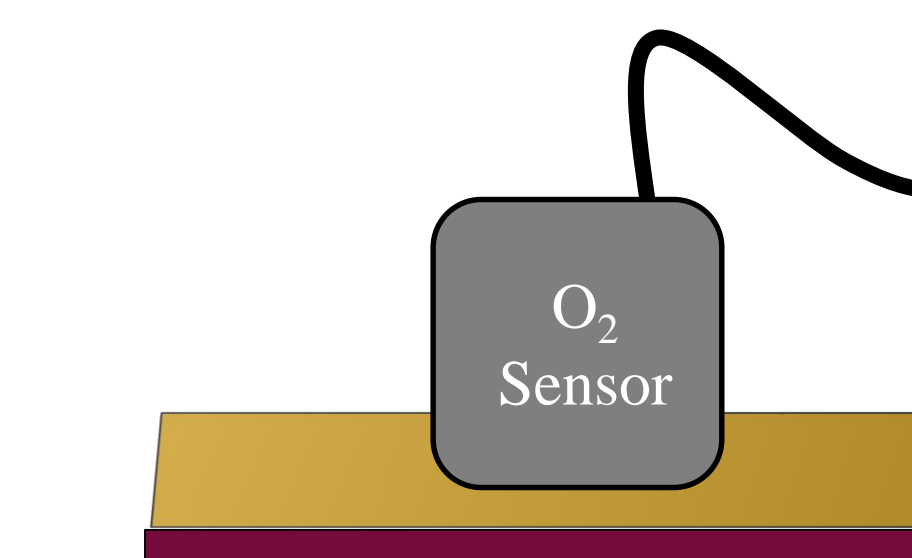
Methodology

We use a lab calibration. All measurements are done at room temperature. Theoretical saturation is calculated using coefficients from Garcia and Gordon (1992) including a full atmospheric pressure correction. Values of atmospheric pressure and relative humidity are obtained from a local weather station and adjusted from sea-level to altitude of the lab at Scripps.

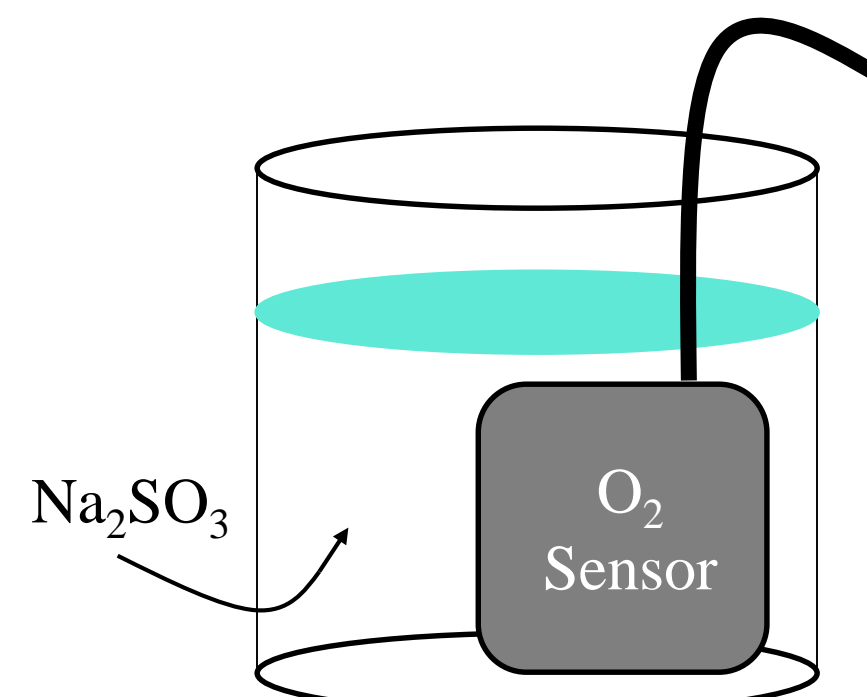
Lab Setup:



Fully Saturated,
in Water



Fully Saturated,
in Air

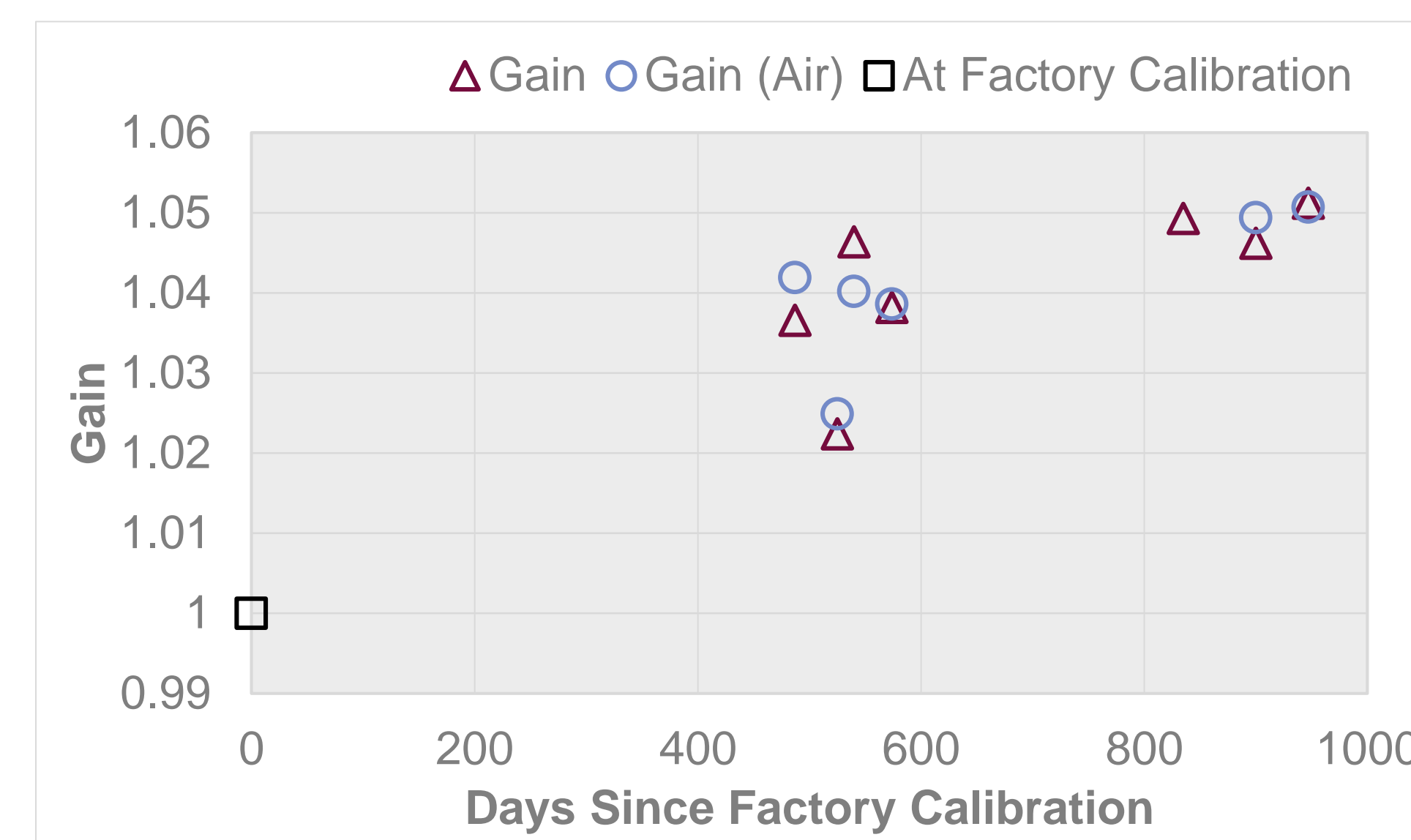


Zero Oxygen, in
Solution

(Sodium sulfite + DI Water)
 $2 SO_3^{2-} + O_2 \rightarrow 2 SO_4^{2-}$ or
 $S^{4+}O_3^{2-} + \frac{1}{2} O_2 \rightarrow S^{6+}O_4^{2-}$

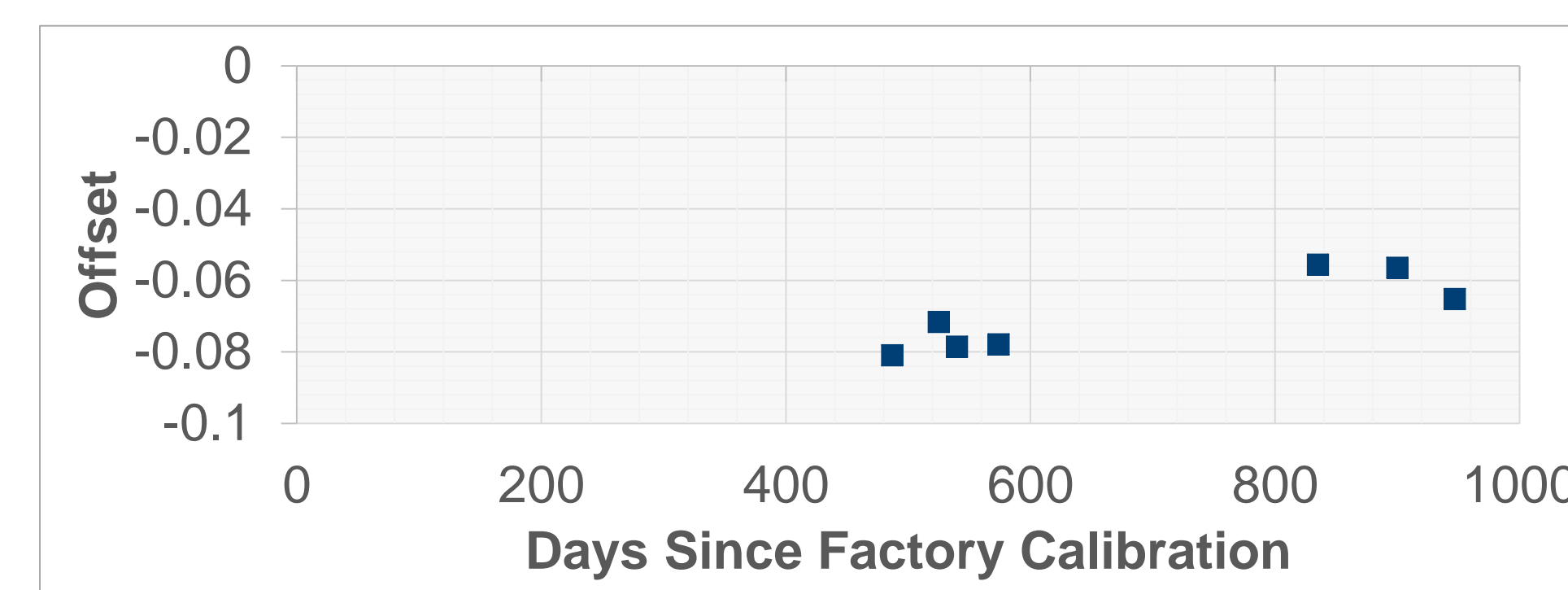
Results

Bench calibration results suggest that there is significant change in the gain over time, on the order of 5% after two years. The gain > 1 means the sensor reads lower than it should.



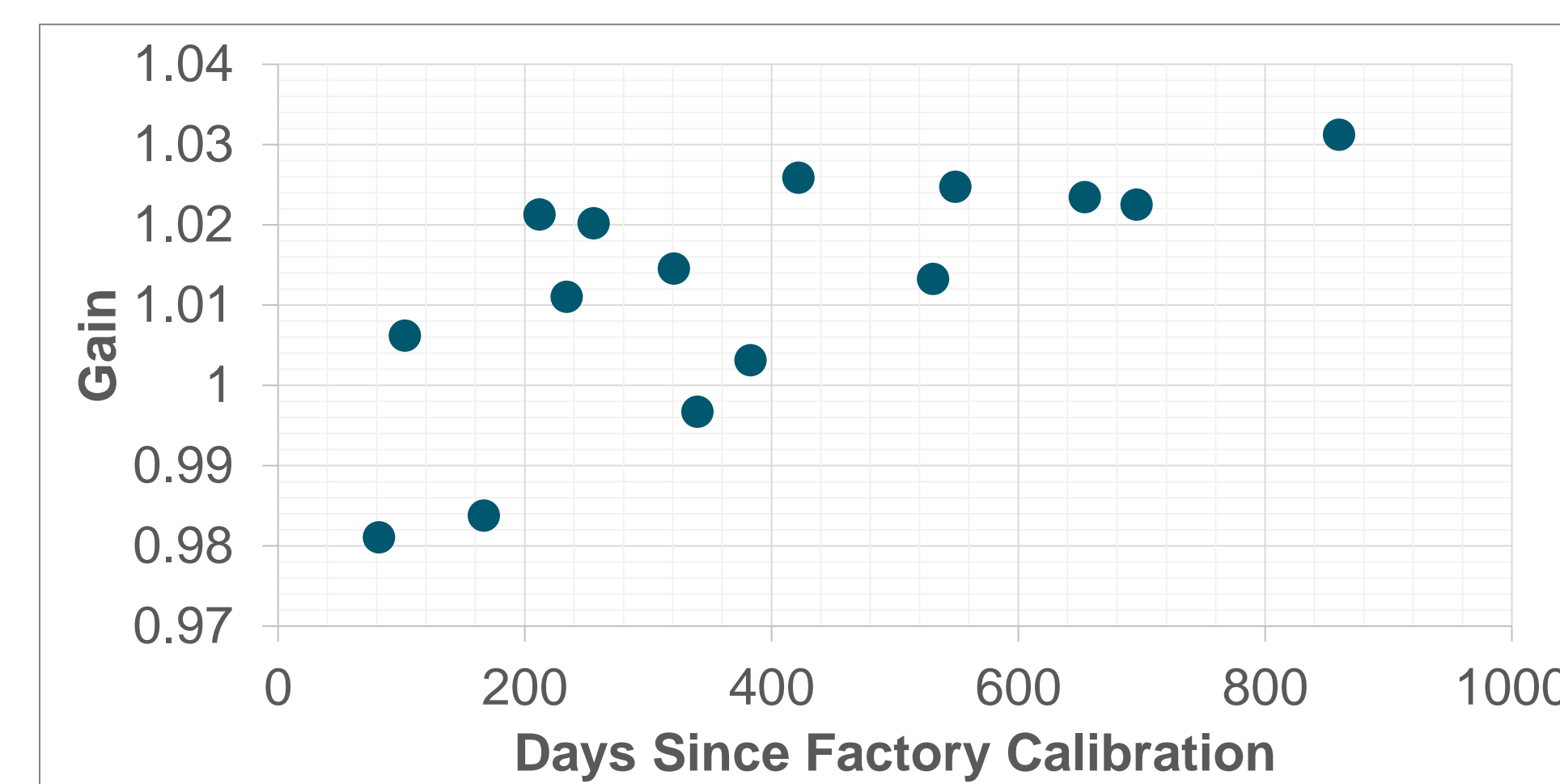
Each plotted data point is an average over a steady 5-minute period during which readings are taken every 10 seconds.

In addition, there is a small, negative offset value. It is on the order of 0.06 ml/l, 1% of saturation, or $3 \mu\text{mol kg}^{-1}$. At zero, the sensor reads higher than it should.



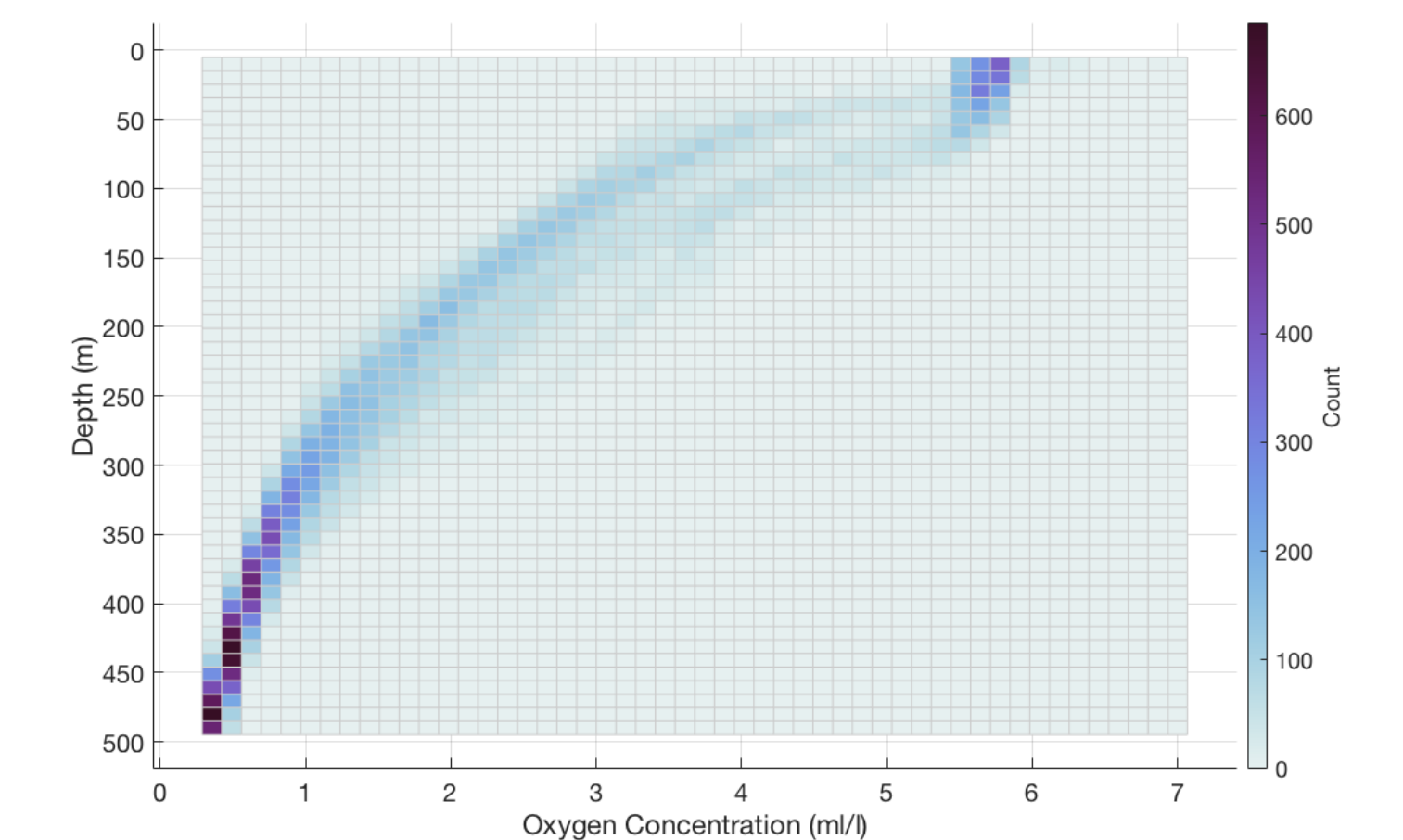
Calculation of a gain using percent saturation and no offset (zero observation) from in-air check values at deployment generally agree with drift to higher gain over time.

The atmospheric data were obtained after-the-fact from historical values from local weather stations. There is only one data point per deployment and no zero oxygen observation. The results have greater variance.



Discussion

-- Comparison of collected data to field observations (CalCOFI Program) were inconsistent due to environmental variability in the surface water column and lack of precision in Winkler titration (0.005-0.01 ml/l) in deeper, more environmentally stable regions of the water column. CUGN gliders dive from the surface to 500m.



-- The glider schedule on CUGN is around 3 months in the field followed by three months in the lab. We plan to isolate the drift during deployment and the "storage drift." Existing work suggests that the sensor drifts less during deployment.

Conclusions and Recommendations

- 1) For long-term studies, a correction or calibration procedure is needed.
- 2) The time drift probably depends on usage of the optode, time in the field versus on the shelf.
- 3) Based on the glider usage, we find that one year after a factory calibration (full calibration) the optode sensors have appreciable drift of over 1%.
- 4) The lab procedure is preferable to field comparisons in our region. This may be the case in other regions as well.
- 5) It appears that calibration in air (full saturation) on the bench is comparable to calibration in water (full saturation).

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Acknowledgements

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