

LONG-TERM STABILITY OF A MOORED OPTICAL OXYGEN SENSOR IN AN ESTUARY

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Introduction

Project Goal: Assess the long-term, undisturbed performance of the SBE63 optical oxygen sensor in a high fouling coastal environment over a two-year period. Results indicate stability within +/- 2% in the field.

- Instrument left on the mooring for 2 years without removal, cleaning, or servicing
- Test site was a shallow nearshore estuarine environment at Shilshole Marina, north of Seattle, WA USA
- Test site visited periodically with water samples and CTD profiles collected for field validation of mooring

Why is this important?

Dissolved oxygen (DO) is a key parameter for understanding biological production, deep water mass transport, biogeochemical cycling, and other oceanographic processes. Improvements and assessments of the long-term stability of oxygen sensors contribute to a better understanding of oxygen data quality. An understanding of potential impacts from biofouling can lead to fewer field servicing visits needed at moored sites, and leave more time for data analysis.

Methods:

A SBE37SMP CTD (37) with a SBE63 optical dissolved oxygen sensor (ODO) was deployed on a floating dock in central Puget Sound at 3 m depth, and 4 m above the bottom. Sole biofouling protection was Sea-Bird's standard anti-foulant cartridges installed on the plumbing intake/exhaust (Sea-Bird Electronics, 2015). Instrument sampled every 15 minutes and output in real-time via cellular telemetry.

37-ODO was not disturbed or recovered for 21 months. Periodic field site visits were completed every 1 – 3 months to help validate mooring data, and three major steps were completed with each visit:

- 1) Water samples were manually collected using a Niskin bottle, matching the 37-ODO depth and sample period. Triplicates collected for dissolved oxygen analysis by Winkler titration method (Knap et al., 1996).
- 2) Side-by-side comparisons were made using profiling CTD (SBE19Plus with SBE43 Clark electrode-type oxygen sensor) for reference, hung *in-situ* adjacent to the 37-ODO.
- 3) A vertical profile was completed using same profiling CTD. Water column structure and stratification were assessed to provide context of the mooring relative to gradients. Spatial variability and position relative to surface mixed layer are considered when comparing the mooring to water samples.

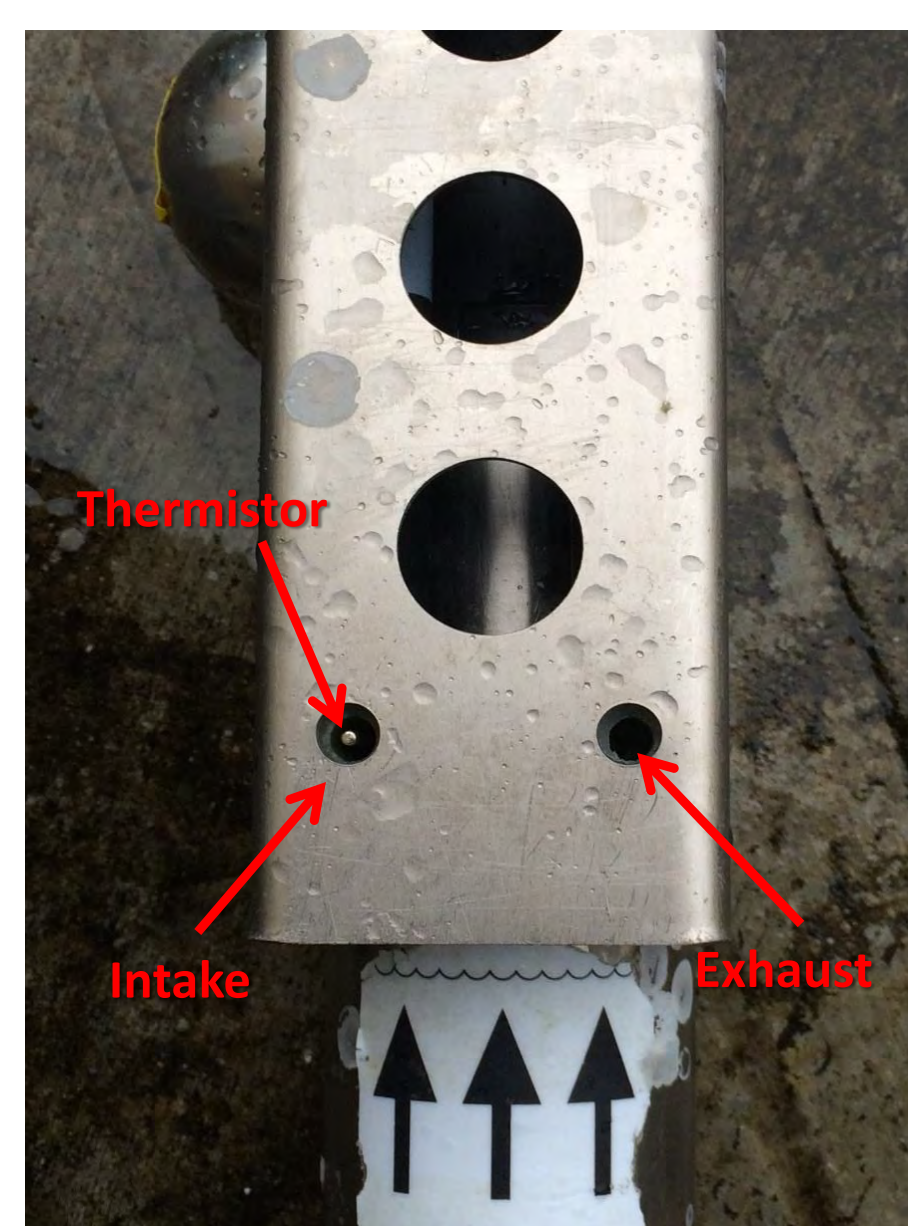


Fig. 2A Prior to deployment: Close-up of SBE37-ODO intake/exhaust. Temperature, conductivity, and oxygen sensors are all contained within the pumped flow path.

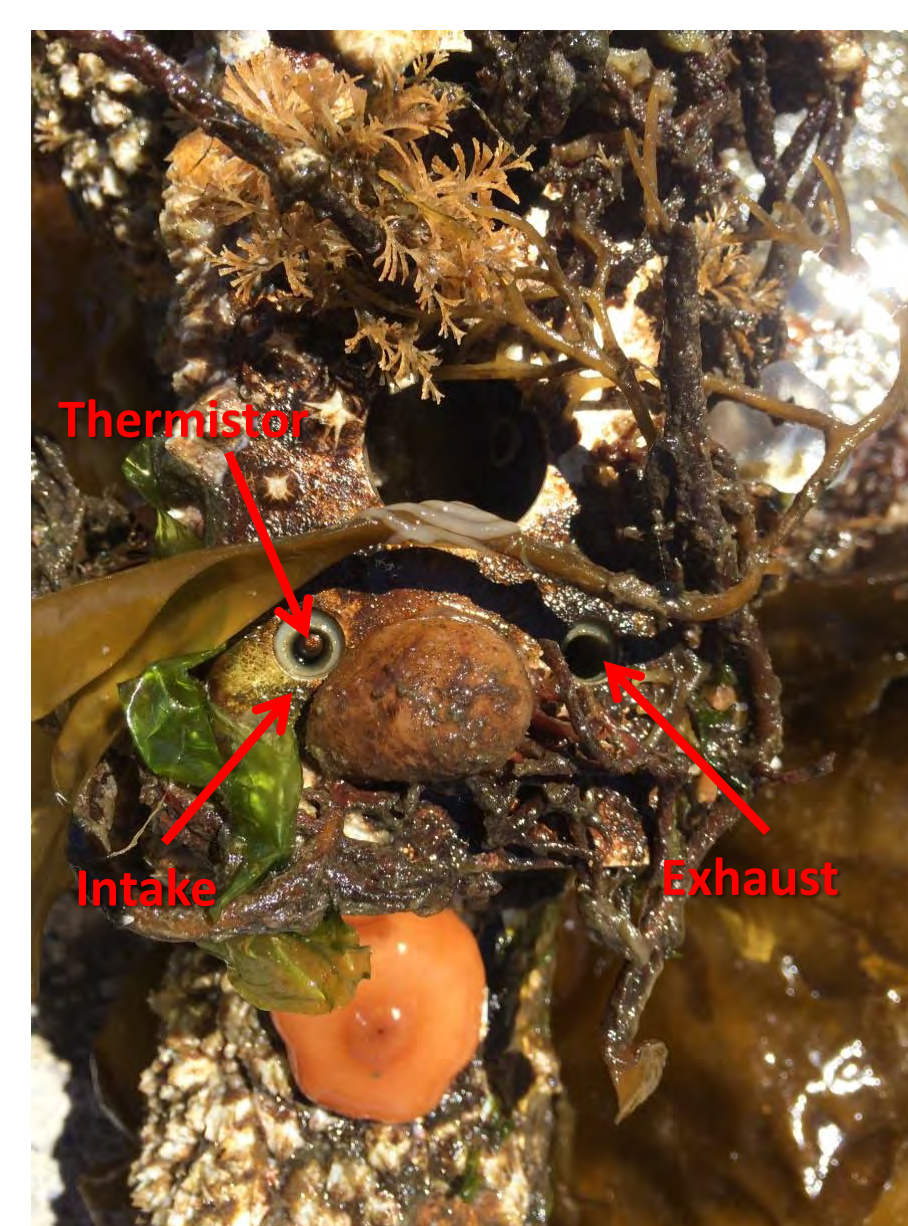


Fig. 2B After 21-month deployment: Same close-up of SBE37-ODO. Note the clear area around the white anti-foulant cartridges on the intake/exhaust.

Results

Time series of mooring data shows seasonal and diurnal oxygen variability over the deployment period, and field validation data also mapped the same features. In particular, oxygen super-saturation events from phytoplankton blooms are captured, with DO reaching as high as 185% oxygen saturation (up to 12.2 mL/L), shown in Fig. 1.

Near the end of the deployment, salinity showed less tidal fluctuation, while DO dropped to 0, presumably due to clogging of the sensor/plumbing. Then, mooring was pulled and recovered in June 2015, after 21 months at the estuarine site. The extent of biofouling on recovery is shown in Fig. 2 and 4. Note the clear path around the anti-foulant cartridges at the intake/exhaust that remains, confirming the efficacy of the anti-foulant in high growth environments.

After recovery, housing exterior was cleaned, and sensors lightly flushed with DI water only. Calibration was completed at Sea-Bird to assess drift, shown in Fig. 3. The post calibration of the ODO sensor shows a slope drift of -1.2%, where the sensor was deployed for 21 months of the two year period. This result falls within the initial accuracy specification of the ODO sensor (+/- 2%), showing negligible impacts from biofouling at this site.

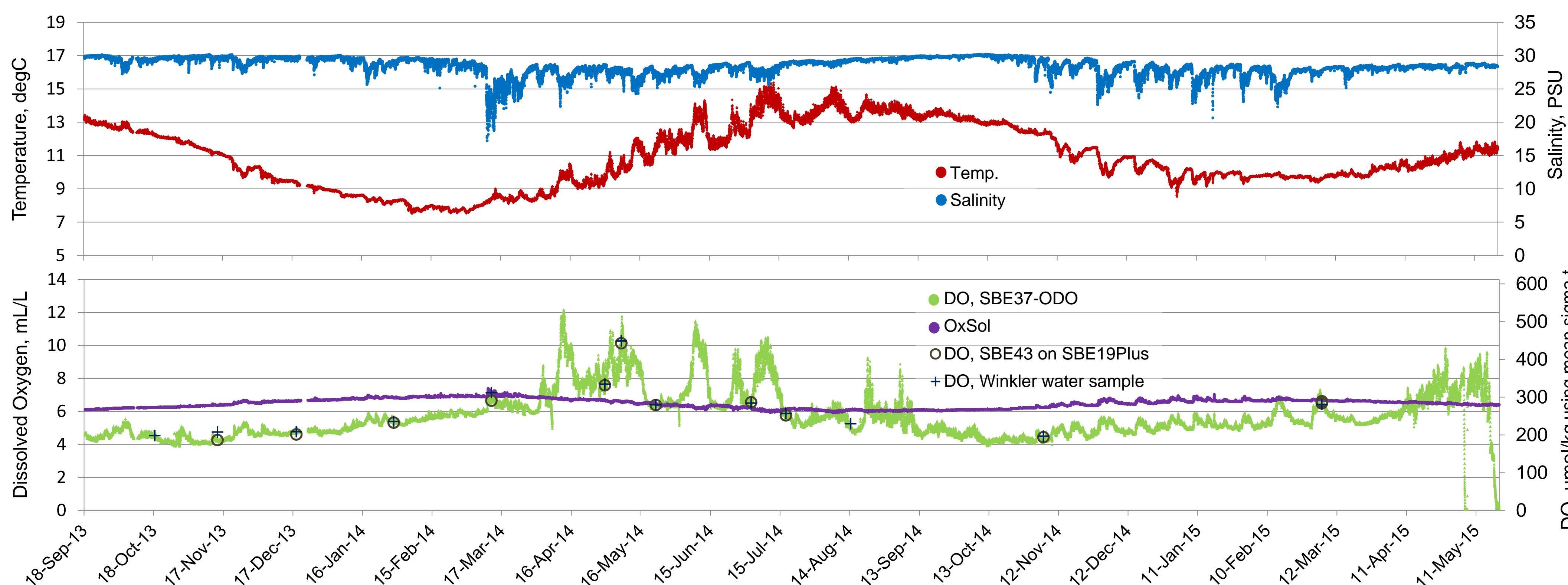
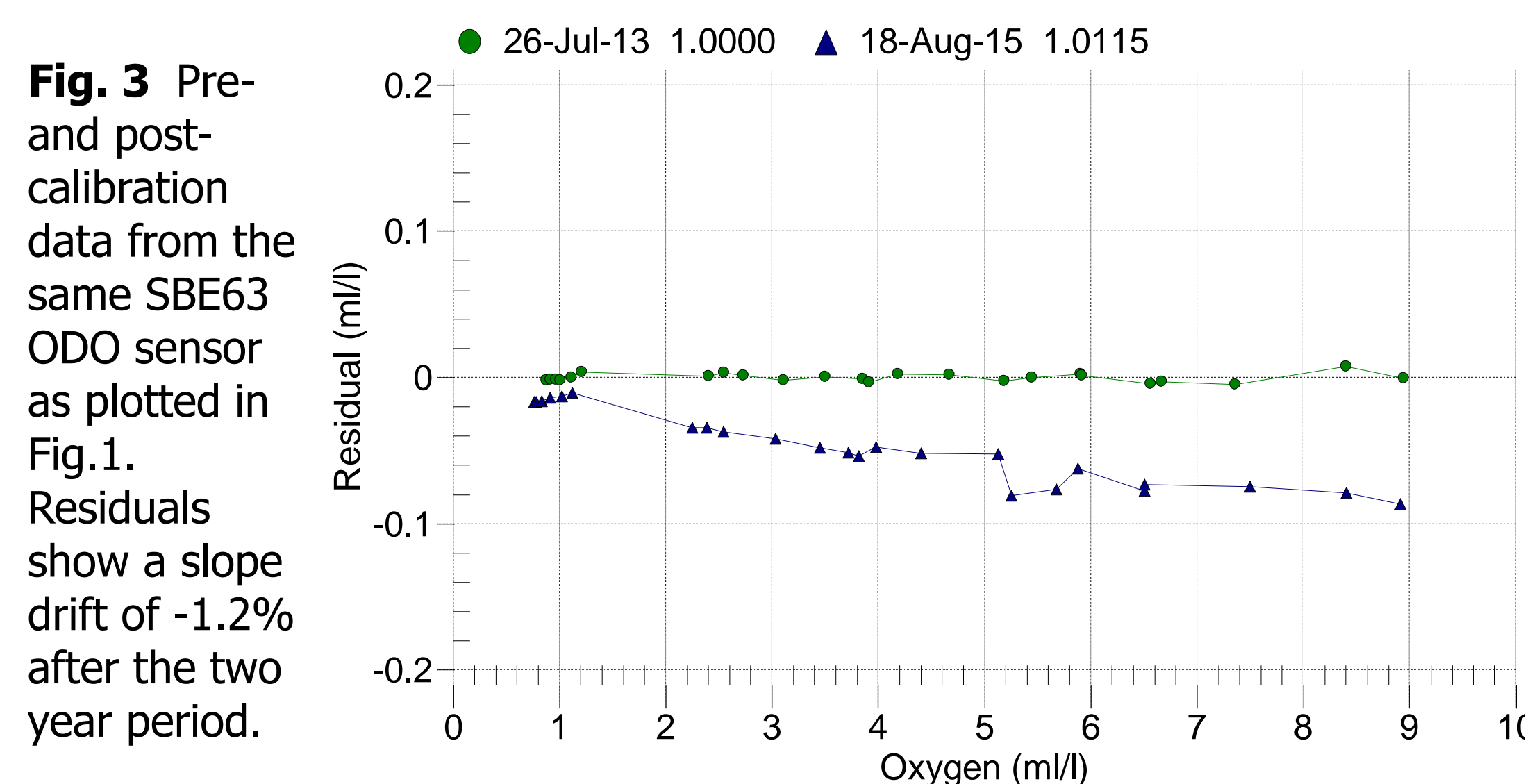


Fig. 1 Time series of shallow SBE37-ODO deployed in central Puget Sound from Sept. 2013 – May 2015, undisturbed for duration. Temperature ($^{\circ}$ C, shown in red) and salinity (PSU, shown in blue) on top. On bottom, DO shown in green with oxygen solubility (OxSol; Garcia & Gordon, 1992) shown in purple, plotted with discrete measurements taken from a clean reference SBE43 sensor and bottle samples.



Results and Precautions from Field Validations

Field validation results using both discrete water samples and a clean reference SBE43 sensor are shown below. During well-mixed conditions (Table 2), the samples and moored sensor data agree better than during gradient conditions when sensor and samples were in the oxycline (Table 1). This stresses the importance of understanding vertical and horizontal water column structure when making sensor and water sample comparisons.

Table 1. Station sampled during vertical DO gradient through-out water column (~ 7 m total depth). Note discrepancy between mooring and bottle samples; likely due to sampling in different water masses.

Date	Time (PST)	DO, SBE37ODO (mL/L)	DO, Winkler water samples (mL/L)					DO, ref. SBE43 (mL/L)	%Diff. of ODO from Avg. Winkler	%Diff. of ODO from SBE43
			Rep. 1	Rep. 2	Rep. 3	AVG	STD			
03/12/14	13:00	6.75	7.14	7.32	7.54	7.33	0.20	6.65	-8.0	1.4
04/30/14	11:15	7.55	7.66	7.76	7.86	7.76	0.10	7.58	-2.7	-0.4
05/07/14	13:30	9.93	10.27	10.21	10.10	10.19	0.08	10.13	-2.6	-2.0
11/05/14	12:15	4.25	4.50	4.82	4.96	4.76	0.24	4.44	-10.6	-4.1
03/05/15	12:00	6.47	6.42	6.42	6.42	6.42	0.002	6.50	0.7	-0.5

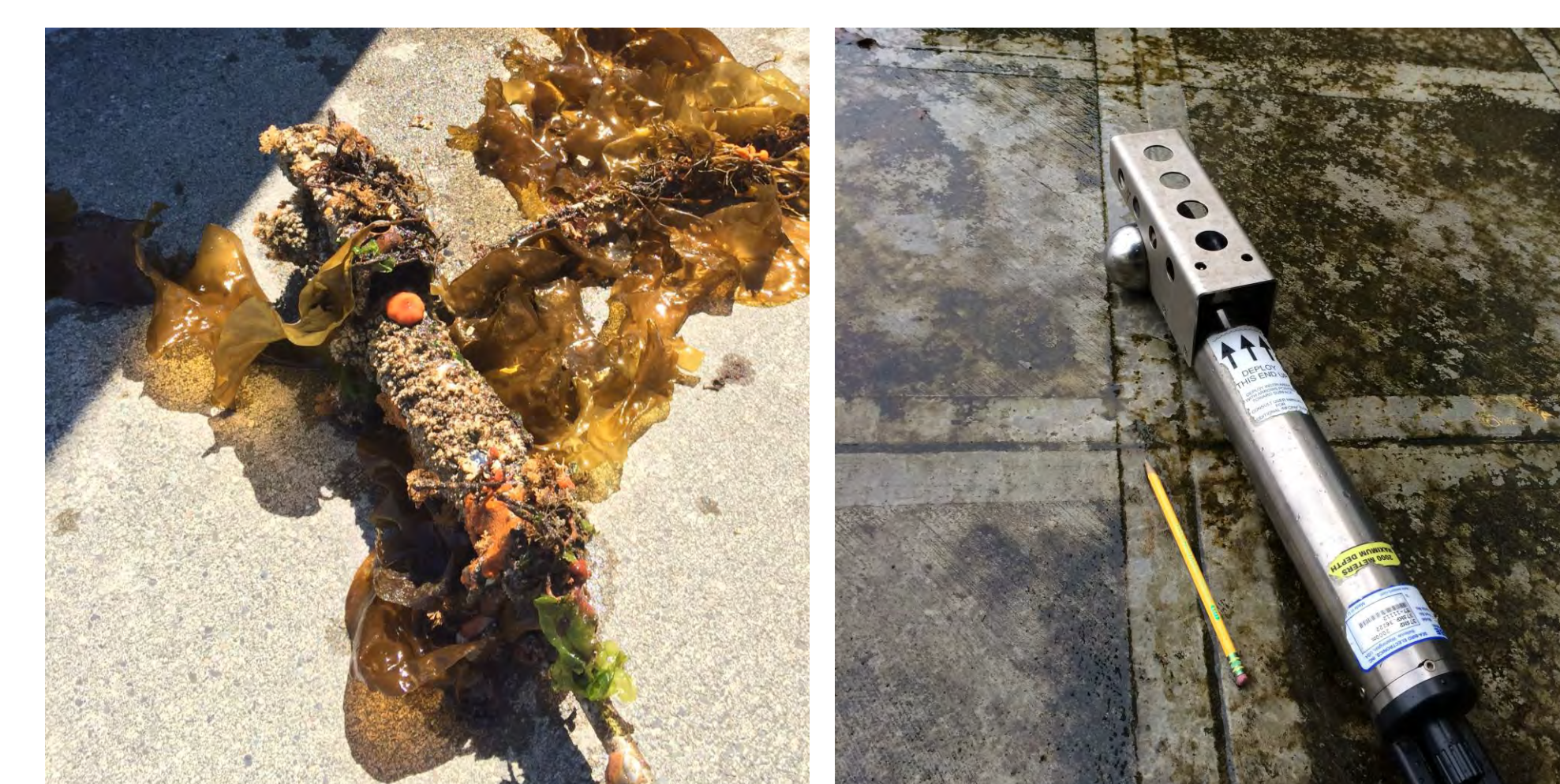


Fig. 4 Photos of the entire SBE37-ODO instrument, both before and after the 21-month deployment with biofouling.

Table 2. Station sampled while mooring (SBE37ODO; at 3 m depth) lies in a well-mixed water mass. Mooring DO data is \leq 2% different than bottle samples.

Date	Time (PST)	DO, SBE37ODO (mL/L)	DO, Winkler water samples (mL/L)					DO, ref. SBE43 (mL/L)	%Diff. of ODO from Avg. Winkler	%Diff. of ODO from SBE43
			Rep. 1	Rep. 2	Rep. 3	AVG	STD			
11/14/13	12:30	4.33	4.75*	4.91*	4.92*	4.86*	0.10*	4.26	ND	1.4
12/18/13	11:45	4.69	4.77	4.78	4.80	4.78	0.02	4.60	-1.9	1.9
01/29/14	11:15	5.35	5.39	5.44	5.52	5.45	0.07	5.33	-2.0	0.4
05/22/14	10:46	6.34	6.40	6.40	6.38	6.39	0.01	6.39	-0.8	-0.7
07/02/14	12:17	6.36	6.51	6.50	6.46	6.49	0.02	6.56	-2.0	-3.1
07/17/14	11:16	5.75	5.87	5.86	5.86	5.87	0.01	ND	-1.9	
07/17/14	11:30	5.69						5.76		-1.2

* = Not used as poor water sample collected for Winkler analysis

Example of mooring in Channel Islands, CA

Another example of ODO performance at a nearshore site, in this case with periodic cleaning, from Kapsenberg and Hofmann (2016). Deployment in a kelp forest in northern Channel Islands at Anacapa Island pier from May 2013 – Sept. 2014. Instruments rotated between sites, and cleaned every 2 – 3 months. Results indicate negligible drift in ODO sensors.

Table 3. Comparison between discrete water samples collected at deployment depth and SBE37-ODO's at Anacapa Island show good agreement (< 2.4% difference). (Data from Kapsenberg and Hofmann, 2016).

ODO Sensor S/N:	Date	Time (UTC)	Status	DO, SBE37OD (mL/L)	DO, Bottle water sample (mL/L)	%Diff. of ODO from Bottle sample
0265	06/25/14	21:15	Start interval	5.97	6.01	-0.61
0265	07/09/14	16:45	Mid-interval	4.94	4.97	-0.63
0265	07/09/14	20:45	Mid-interval	5.74	5.76	-0.29
0265	09/20/14	19:15	End of interval	5.32	5.32	0.08
0356	06/25/14	16:45	End of interval	5.43	5.56	-2.37

Status indicates stage of a given deployment interval (each 2-3 months long).

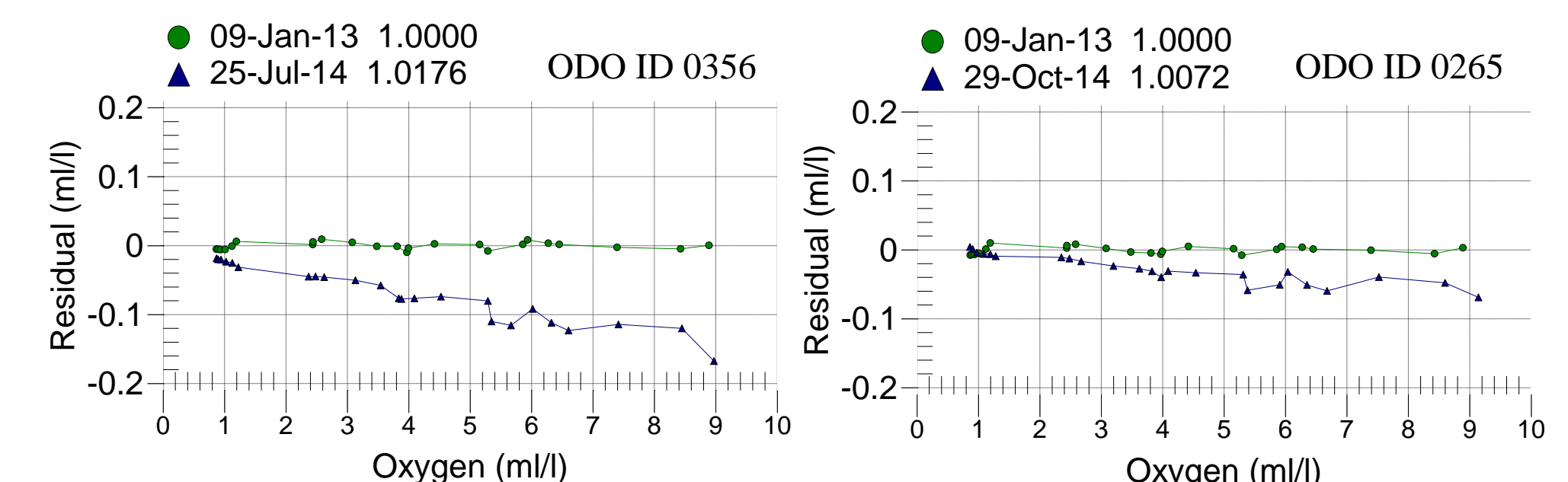


Fig. 5 Pre and post calibrations completed at SBE from ODO sensors deployed in the Channel Islands. Post calibrations show -0.7% drift from ID 0265 and -1.8% drift from ID 0356 over the 1.5 year time period.

Discussion:

What is the mechanism and type of sensor drift?

- Drift characteristic of the SBE63 ODO observed by SBE across numerous factory calibrations indicates sensor drifts linearly low of correct.
- Exact mechanism for drift in optical oxygen sensors is not well understood, and may be due to a combination of factors.
- Bittig and Körtzinger (2015) suggest that reduction of oxygen sensitivity over time could be attributed to a physical change of the sensing membrane such as decreased oxygen accessibility of the luminophore or decreased oxygen diffusivity inside the membrane.
- As with the SBE43, the instrument configuration with plumbing and anti-foulants clearly helps to protect the sensor from external biofouling growth.

How does this compare to drift while in storage?

Drift tests for optical oxygen sensors stored dry at room temperature, completed at Sea-Bird over a three year period, indicate that shelf drift can be on the order of -1.0 to -1.5% per year.

Conclusions

- ODO sensor showed stability within the initial accuracy specification (+/- 2%) and negligible effects from biofouling, until clogging of flow path after 21 months.
- Helps to provide a baseline when deciding how often to service and maintain a mooring in similar environments, which can lead to fewer field visits than typically expected.

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References:

- Bittig, H. and 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.
- Garcia, H. and L. Gordon, 1992. Oxygen solubility in seawater: better fitting equations. *Limnol. Oceanogr.* 37: 1307–1312.
- Kapsenberg, L. and G. Hofmann, 2016. Ocean pH time-series and drivers of variability along the northern Channel Islands, California, USA. *Limnol. Oceanogr.*, early release: DOI: 10.1002/lno.10264.
- Knap, A., A. Michaels, A. Close, H. Ducklow and A. Dickson (eds.), 1996. Chapter 6: Determination of Dissolved Oxygen by the Winkler Procedure; Protocols for Joint Global Ocean Flux Study (JGOFS) Core Measurements. *JGOFS Report 19: 29 – 36.*
- Sea-Bird Electronics, 2015. User Manual for SBE37-SMP-ODO MicroCAT C-T-ODO(P) Recorder. Sea-Bird Scientific: 97 pp.