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Getting More Mileage out of Dissolved Oxygen Sensors in Long-Term Moored Applications

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***Abstract* - The SBE 43 dissolved oxygen (DO) sensor is a complete redesign of the Clark electrode oxygen sensor and is engineered to provide stable, rapid-response dissolved oxygen measurements for profiling and long-term mooring applications. Customers as well as scientists at Sea-Bird are demonstrating that the SBE 43 DO sensor provides high quality moored DO data within 5% accuracy for five or more months, even in high biological fouling coastal environments. As with all instruments, including optical DO sensors, biofouling ultimately interferes with the quality of moored measurements. When the SBE 43 DO sensor experiences a shift in calibration, it is primarily due to fouling of the membrane, which affects the slope of the sensor's response. The stable zero offset and the fact that the drift is confined to a linear slope means the calibration is easily corrected with a single reference point taken either in the field while the instrument remains moored, or during post processing of data after the sensor is recovered and validated in the lab.**

INTRODUCTION

This paper describes the merits of using the SBE 43 dissolved oxygen sensor for long-term moored applications, suggests deployment techniques that minimize the impact of bio-fouling, and presents a simple means of maintaining measurement accuracy in deployments lasting several months. A case study of a real-time oxygen monitoring application is used to demonstrate a simple procedure for calibrating and assessing the condition of SBE 43 sensors while they remain sampling in the field, saving time and money in terms of maintenance and factory servicing. As an alternative, a method for correcting data during post processing is also given.

ADVANTAGES OF THE SBE 43 DISSOLVED OXYGEN SENSOR

Sea-Bird developed the SBE 43 DO sensor correcting the limitations of the traditional Clark electrode technology. These are the long time required after power-up to achieve a stable response (polarization), the requirement of flow (stirring) of sample water past the electrode, and the drift of sensor accuracy caused by electrolyte consumption and membrane fouling.

The time required after power-up to achieve a stable response is eliminated in the SBE 43 by maintaining continuous polarization of the electrode with internal lithium batteries. Continuous polarization does allow the sensor to react with ambient oxygen. However, based on several years of factory calibrations, significant electrochemical drift has not been observed, existing somewhere below the sensor level of uncertainty of 1 uM/kg. Estimates of in-field drift rates are less than 0.5 % over 1000 hours of ventilated operation (sample on-time), based on drift analysis of ARGO profiling floats with deployment histories greater than three years.

For moored applications, the SBE 43 DO sensor is deployed with a unique plumbing arrangement that traps water surrounding the sensor and allows the sensor to drive that water anoxic between measurements. The anoxic environment reduces the flux of oxygen to the electrode when the instrument is between samples. This diminishes the electrochemical drift for long-term deployments. Pumping 30 seconds prior to each measurement flushes the low oxygen water out of the plumbing, bringing fresh sample water through to the sensor as the sample is acquired.

An additional benefit of the plumbed housing design is that it protects the DO sensor from continuous and direct contact with the external environment. The placement of broad spectrum, EPA-approved anti-foulant cartridges at both the intake and exhaust of the plumbing allows the antifoulant to diffuse into the water trapped within the plumbing while the instrument is not sampling. This helps prevent attachment and growth of any biota that may have entered the system during the previous flush. Black plenums with black tygon tubing block light and hinder algal growth inside the DO sensor housing.

Adjusting a Single Linear Slope Term Maintains Accuracy

The SBE 43 DO sensor output is highly linear with respect to oxygen partial pressure (oxygen concentration) and maintains a stable output at zero oxygen. These essential characteristics reduce the calibration drift to a simple change in the slope of the linear output (a change in *SOC*) (1).

$$Oxygen(ml/l) = SOC * (V + V_{offset}) * T_{cor} * P_{cor} * OXSOL \tag{1}$$

SOC is the linear slope scaling coefficient, *V* the sensor output voltage, and V_{offset} the sensor voltage at zero oxygen. T_{cor} and P_{cor} are correction functions for the sensor's response to temperature and pressure, respectively. OXSOL is the conversion coefficient for the fugacity of oxygen gas as a function of Tand S [1].

The stable V_{offset} and linear slope means the ratio of measured to true concentration remains constant over the whole range of the sensor (0-10 ml/L). The other parameters that correct for the effects of temperature and pressure are lower order terms in the equation. Therefore, adjusting the slope *SOC* in the calibration equation is the focus of maintaining sensor accuracy.

Case Study: Real-time Monitoring of Dissolved Oxygen in Cockburn Sound, Western Australia

In November of 2006, a desalination plant went into operation adjacent to Cockburn Sound, a large (100 km^2) coastal lagoon located about 40 km south of Perth in southwestern Australia. When fully operational, the plant will supply Perth with 20% of its freshwater, and will be capable of producing 72 megaliters of drinking water per day. In this process, 50% of the volume of water withdrawn from Cockburn Sound to make freshwater is returned to the Sound at twice the incoming salinity. As part of the environmental operating license agreement for the desalination plant, monitoring of DO is required hourly at multiple sites throughout Cockburn Sound basin to detect reduced oxygen in the saline waters near the Sound floor. Data are reported real-time and used to make management decisions regarding the plant operation.

First Five Months of Dissolved Oxygen Monitoring

Six Sea-Bird 16*plus* Seacats with SBE 43 DO sensors were deployed in Cockburn Sound in June 2006, and set to sample every five minutes. No servicing (cleaning or swapping) was performed on the moored instruments until November 2006, a period of nearly five months. SBE 43 DO sensors were replaced in the servicing of four near-bed instruments in November. Fig. 1 shows data from the North buoy and demonstrates the following key features. The oxygen concentration measured by the North Buoy sensor was consistently below the theoretical oxygen saturation calculated from *in situ* temperature and salinity (Fig. 1–top panel). The outgoing instrument registered lower than the incoming instrument by 5-6%, consistent with reduction of signal from fouling (Fig. 1 – top and middle panels). The sensor accurately measured natural fluctuations in DO as observed in comparison with other moored sensors in the bay. The SBE 43 DO sensor performed well, given that biofouling typically degrades *in situ* DO measurements much more severely within weeks [2,3]. Following the instrument swap, a downward trend in DO was observed between November 9 and December 22, coincident with an increase in temperature (T) (not shown) and salinity (S) (Fig. 1 - bottom panel). The increase in TS would act to reduce the solubility of

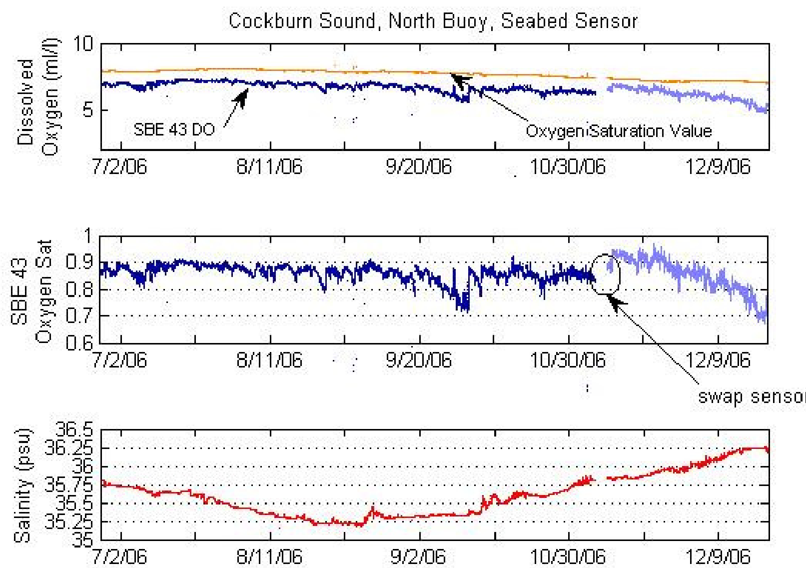

Fig. 1 Near-bed oxygen and salinity at the North buoy in Cockburn Sound for period June 26 – December 22, 2006. SBE 43 sensor 0986 was recovered on November 9, 2006, cleaned and redeployed on a different mooring and is still in the field. Top Panel: Time series of sea-bed measured dissolved oxygen (blue Jun-Nov; purple Nov-Dec) and theoretical saturation concentration (gold); Middle Panel: ratio of SBE 43 measured oxygen to oxygen saturation; Bottom Panel: sea-bed salinity.

oxygen in the water, possibly explaining the decrease in oxygen during this seasonal transition. DO data from other moorings located throughout the bay all experienced the same downward trend before increasing in DO again, suggesting this to be a natural trend rather than an indication of sensor fouling.

Correcting the Calibration Drift by Adjustment of SOC

Data from two sensors deployed in Cockburn Sound demonstrate the linearity of the calibration drift in SBE 43 DO sensors caused by biofouling after 2 and 8 months deployment in the field, respectively. SBE 43 sensor 1114 was deployed from November 2006 through January 2007, a period of two months during the early summer. Occasional shipboard validation comparisons suggested the moored sensor was reading low of correct anywhere from 3 to 12% near the end of deployment. The sensor was returned to the factory, where it post-calibrated low of correct by 0.8% (less than 1%) (Fig. 2 - triangles). The sensor was cleaned following factory recommendations, and the original calibration value was restored (Fig. 2 - squares).

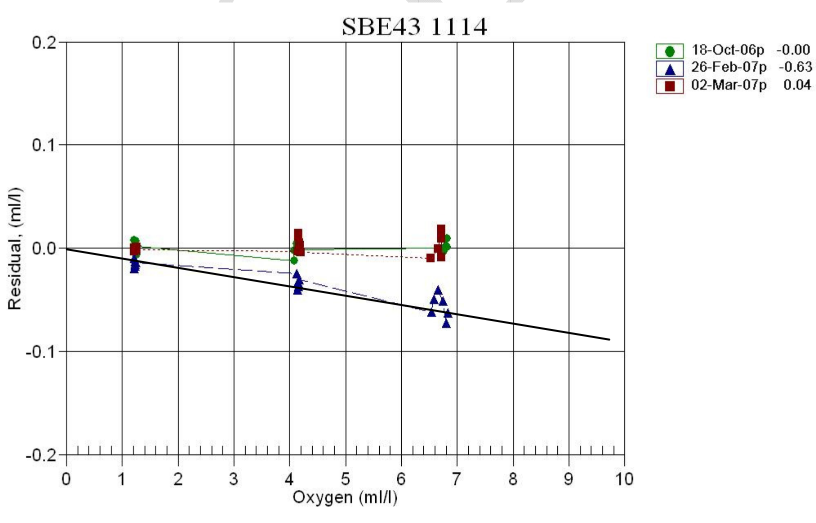

Fig. 2 Calibration results of oxygen concentration (x-axis) and residual concentrations (y-axis) between replicate Winkler water samples and SBE 43 sensor values in a temperature-controlled bath. Dots specify the original calibration, triangles show post-calibration results (prior to cleaning), and squares denote the final calibration results (after cleaning).

In contrast, SBE 43 sensor 1000 was deployed in June 2006, and remained on its mooring for eight months with no maintenance until recovered in late February 2007. The sensor was cleaned following factory recommendations and was redeployed in early March 2007. Despite cleaning, the sensor reported low of correct by 15-20%, based on shipboard validation comparisons made a few days after the March deployment. Inspection of the membrane under a high powered optical microscope at the factory and subsequent taxonomic evaluation indicated diatoms were adhered to the membrane (Fig. 3).

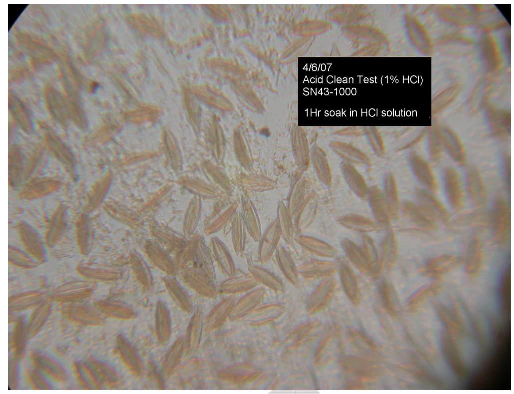

Fig. 3 100X magnification of an SBE 43 DO sensor membrane covered with biological growth. Taxonomic analysis revealed diatoms on the membrane. This sensor was deployed for nine months with no servicing or maintenance in Cockburn Sound, Perth, Western Australia.

Post-calibration of sensor 1000 at the factory indicated the sensor was reading low of correct by 14% (Fig. 4), in agreement with the in-field validation results. Despite the extensive fouling, the slope of the calibration after eight months in the field remained linear, and demonstrated the stable output at zero oxygen. The linear slope term, *SOC*, is corrected in this example using a simple ratio between the reference value and the corresponding sensor output (Table 1). Progressive corrections rely on this simple ratio at different points in time.

Accurately calibrated data is achieved by multiplying the *SOC* value by a ratio factor of 1.2, and applying the new *SOC* value in the calibration equation used for data conversion and processing. Sea-Bird recommends when the *SOC* changes by 15-20% (a correction of ~1.2) and cannot be partially to fully restored by recommended cleaning procedures, that the sensor be returned to the factory for servicing.

Processing Data with Post-Deployment Reference Data

Sometimes, in-field validation is not possible. This restricts correction of any possibly fouled data to occur during data post-processing using a reference validation point taken at the end of the deployment prior to instrument retrieval, or made after the instrument is recovered. The simple assumption is that the change in slope due to fouling is uniform with time, and the data can be back-calibrated using a simple rate of change of *SOC* for the period of suspected fouling. Using sensor 1000 as an example (Table 1), the post-calibration *SOC* value after cleaning the sensor is 0.4931 (0.4109 original factory *SOC* X 1.2 correction factor). A deployment period of eight months amounts to an *SOC* drift of about 0.0003/day. In reality, the moored sensors

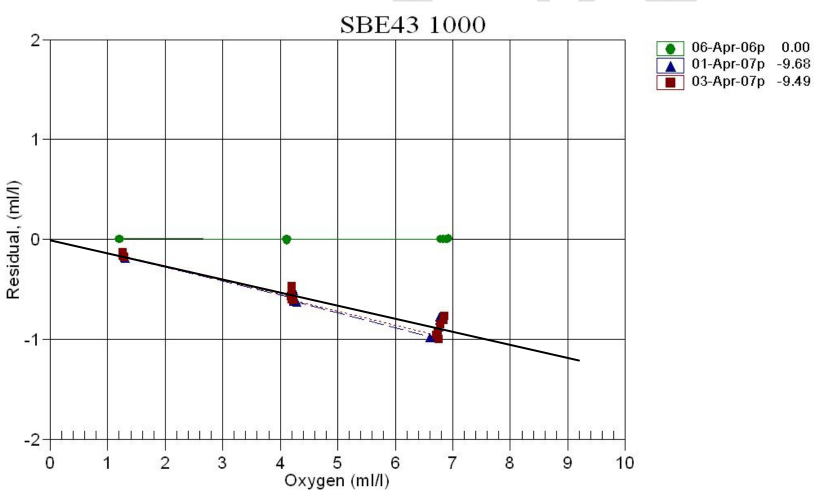

Fig. 4 Calibration results of oxygen concentration (x-axis) and the residual concentrations (y-axis) between replicate Winkler water samples and SBE 43 sensor values in a temperature controlled calibration bath. Dots specify the original calibration; triangles show post-calibration results (prior to cleaning) and the squares denote the final calibration results (after cleaning).

TABLE 1
Reference Winkler water samples and SBE 43 sensor values at three dissolved oxygen concentrations during the final calibration of sensor 1000. The ratio between the Winkler values and corresponding SBE 43 output is used to calculate the SOC correction factor. Note how the SOC correction remains constant at each validation point over the range of oxygen values reported by the sensor.

Winkler DO Of Bath (ml/L)	SBE 43 Output (ml/L)	Residual (SBE 43 -Winkler)	Correction factor (Winkler/SBE 43)
6.8	5.8	-1	6.8/5.8=1.2
4.2	3.6	-0.6	4.2/3.6=1.2
1.2	1.0	-0.2	1.2/1.0=1.2

may not exhibit fouling for several weeks to months, so the user will need to decide how best to determine the time span for data correction of fouled data.

Conclusions

SBE 43 DO sensors have performed well on long-term (5+ months) moorings in high fouling environments with minimal maintenance and degradation of oxygen data. Sea-Bird keeps the anti-fouling approach simple. The plumbed housing isolates the temperature, conductivity and DO sensors from the surrounding environment. A black plenum and plumbing blocks ambient light, and strategically placed anti-foulant cartridges allow anti-foulant to diffuse into the plumbing between samples. Both act to prevent *in situ* growth. An incurred slope change due to any fouling is easily corrected with a single quality reference sample. This allows accurate oxygen measurements to be acquired to within one or a few percent, depending on the reference method used to determine the slope correction. This protocol is being implemented using periodic in-field reference validations on real-time monitoring data that require high accuracy oxygen measurements around the clock in Cockburn Sound, Australia. Correcting data during post-processing is also possible and easy to complete for ocean observing applications where moorings are left in place for several months and in-field validation data are scarce or unavailable. Sea-Bird recommends calibration corrections in excess of 15-20% (an *SOC* correction multiplier approaching 1.2) of the original factory calibration be used as a threshold for determining when the DO sensor needs to be recovered, cleaned, and possibly returned to the factory for servicing. Cleaning of the sensor often restores the calibration and prolongs the field life, saving time and money in factory servicing of the sensor. Of course, the amount of maintenance and validation required will depend on the individual environments being sampled and the accuracy needs of the project.

Acknowledgment

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