Long-Term Performance of Aanderaa Optodes and Sea-Bird SBE-43 Dissolved-Oxygen Sensors Bottom Mounted at 32 m in Massachusetts Bay

MARINNA MARTINI AND BRADFORD BUTMAN

U.S. Geological Survey, Woods Hole Science Center, Woods Hole, Massachusetts

MICHAEL J. MICKELSON

Massachusetts Water Resources Authority, Boston, Massachusetts

(Manuscript received 13 March 2006, in final form 11 January 2007)

ABSTRACT

A field evaluation of two new dissolved-oxygen sensing technologies, the Aanderaa Instruments AS optode model 3830 and the Sea-Bird Electronics, Inc., model SBE43, was carried out at about 32-m water depth in western Massachusetts Bay. The optode is an optical sensor that measures fluorescence quenching by oxygen molecules, while the SBE43 is a Clark polarographic membrane sensor. Optodes were continuously deployed on bottom tripod frames by exchanging sensors every 4 months over a 19-month period. A Sea-Bird SBE43 was added during one 4-month deployment. These moored observations compared well with oxygen measurements from profiles collected during monthly shipboard surveys conducted by the Massachusetts Water Resources Authority. The mean correlation coefficient between the moored measurements and shipboard survey data was >0.9, the mean difference was 0.06 mL L^{-1}, and the standard deviation of the difference was 0.15 mL L^{-1}. The correlation coefficient between the optode and the SBE43 was >0.9 and the mean difference was 0.07 mL L^{-1}. Optode measurements degraded when fouling was severe enough to block oxygen molecules from entering the sensing foil over a significant portion of the sensing window. Drift observed in two optodes beginning at about 225 and 390 days of deployment is attributed to degradation of the sensing foil. Flushing is necessary to equilibrate the Sea-Bird sensor. Power consumption by the SBE43 and required pump was 19.2 mWh per sample, and the optode consumed 0.9 mWh per sample, both within expected values based on manufacturers' specifications.

1. Introduction

A field evaluation of two new oxygen-sensing technologies, the Aanderaa Instruments AS optode model 3830 and the Sea-Bird Electronics, Inc., model SBE43 has been carried out over a 19-month period at about 32-m water depth in western Massachusetts Bay. These measurements were carried out cooperatively by the U.S. Geological Survey and the Massachusetts Water Resources Authority (MWRA) as part of long-term oceanographic observations made at site LT-A, (Butman et al. 2004). This site was typically within 200 m of 42°22.703′N, 070°46.969′W, located 9.5 miles east of Boston, Massachusetts, near the Massachusetts Bay sewage outfall. The recurring 4-month deployments made this monitoring program a good place to evaluate the new oxygen technologies and to complement other shorter-term evaluations (ACT 2004; Fulford et al. 2005). Units of milliliters per liter (mL L^{-1}) will be used but can be easily converted using the relation 7 mL L^{-1} = 10 mg L^{-1} = 312.5 μM.

Corresponding author address: Marinna Martini, U.S. Geological Survey, Woods Hole Science Center, 384, Woods Hole, MA 02543.
E-mail: mmartini@usgs.gov

DOI: 10.1175/JTECH2078.1

2. Instrumentation

In the past, in situ measurement of dissolved oxygen has been based on the Clark cell, a membrane diffusion technique developed in the 1960s and adapted for long-term moored marine deployment in the 1980s with limited success. Because accurate long-term moored measurements of dissolved oxygen remain a technical challenge, Aanderaa Instruments AS and Sea-Bird Electronics, Inc., have recently developed new sensors designed to obtain reliable and stable in situ oxygen measurements in the open ocean over long periods of time.

a. *The Aanderaa optode*

The Aanderaa optode (model 3830) is an optical sensor. It uses a micro-optode (Tengberg et al. 2003) that measures fluorescence lifetime quenching using a sensing foil developed by Precision Sensing GmbH. Chemicals in the foil are excited by light of a certain wavelength, and the duration of the emissions is a measure of the oxygen content in the water. The accuracy of the Aanderaa optode is specified as 0.18 mL L^{-1}, with a resolution of 0.02 mL L^{-1} and a settling time of <25 s. The optode nominally requires 960 mW of power (Aanderaa Instruments AS 2004). Aanderaa optode technology is intended to remain stable and accurate for a period of 1 yr before requiring a new two-point calibration and replacement of the foil, a procedure that can be performed by the user. The foil is held in place by a window-frame type of surround. Fouling may be inhibited by the installation of an optional copper surround for the optical window instead of the standard plastic material.

b. *The Sea-Bird SBE43 dissolved-oxygen sensor*

The Sea-Bird SBE43 oxygen sensor uses a membrane polarographic oxygen detector, an upgraded Clark cell, redesigned and optimized to reduce drift and hysteresis effects (Carlson 2002; Sea-Bird Electronics, Inc., 2002a). The accuracy of the Sea-Bird SBE43 is specified as 2% of saturation (Sea-Bird Electronics, Inc., 2005b), which is 0.16 mL L^{-1} for a solubility of 7.8 mL L^{-1} at 32 ppt and 2°C, or 0.12 mL L^{-1} for a solubility of 6.2 mL L^{-1} at 32 ppt and 12°C. The SBE43 specifications state a stability to within 2% of calibration per 1000 h if the membrane is kept clean and moist. Sea-Bird recommends an equilibration time of 30–36 s for the SBE43, or 5 to 6 multiples of the response time (Sea-Bird Electronics, Inc., 2002b). Flushing is a requirement to achieve the accuracy and measurement stability as stated in the sensor's specifications; otherwise, the sensor would deplete the oxygen in the measurement volume. The SBE43 requires 60 mW, and an SBE05T pump can draw up to 1800 mW. Sea-Bird recommends that the SBE43 be recalibrated by Sea-Bird after every long-term in situ deployment. Fouling may be inhibited by application of tributyl-tin leaching tips on the intake and discharge of the sensor.

3. Field experiment

This paper makes use of moored data, shipboard surveys, and laboratory testing performed over 19 months from the fall of 2002 through the spring of 2004 to evaluate the moored performance of the optode and SBE43 sensors.

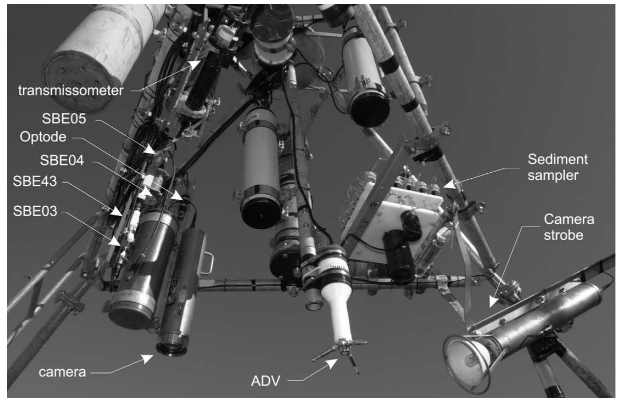

FIG. 1. View of tripod 717 from below the frame showing the locations of the Aanderaa optode and the Sea-Bird sensors. Also deployed on this tripod are an SBE04 conductivity cell, SBE43 oxygen sensor, SBE05T pump, and SBE03F temperature cell, a Sontek acoustic Doppler velocimeter, a Benthos still camera, Sea Tech transmissometer, a sediment sampler, and an RDI ADCP (not visible).

a. *Moored data*

The long-term U.S. Geological Society–Massachusetts Water Resources Authority (USGS–MWRA) monitoring program deployed on the seabed instrumented stainless steel tripod frames that are 4.6 m high and 3.7 m long on each of three sides (Fig. 1). The tripods were instrumented to provide a suite of oceanographic measurements. In addition to the oxygen sensors, instrumentation measured three-axis current velocity, temperature, salinity, light transmission, pressure, and collected suspended sediment. The tripods were designed so that the area 1.5 m above the bottom (mab) was relatively unobstructed for near-bottom current velocity measurements.

Tripods were exchanged 3 times a year, typically in February, May, and early fall (September or October). Each deployment is assigned a reference number (USGS mooring number), which is used to identify each data series referenced in this paper. Table 1 lists sampling intervals for each sensor.

Oxygen sensors were added to the tripods in May 2002. The oxygen sensors were mounted at heights ranging from 1.54 to 2.33 mab. Oxygen sensor data were recorded by USGS-designed dataloggers and Aanderaa RCM 9 MkII dataloggers. A 4-month comparison between the optode and SBE43 took place from 24 September 2003 to 5 February 2004. Data collected from October 2002 through May 2004 are compared with shipboard survey data for sites near LT-A.

TABLE 1. Deployed tripods, heights above bottom, and sampling intervals for sensors used in the oxygen sensor comparisons. Aanderaa = internal optode or RCM9 thermistor, SBE03F = Sea-Bird temperature cell, SBE04 = Sea-Bird conductivity cell, SBE37 = Sea-Bird microcat (combines SBE03F and SBE04 technology with a datalogger), and SBE43 = Sea-Bird oxygen sensor.

	Tripod 697	Tripod 708	Tripod 717	Tripod 756
Deployment dates	10/24/02–5/21/03	3/30/03–9/24/03	9/24/03–4/7/04	2/5/04–5/19/04
Tripod depth	33.4 m	30.9 m	31.8 m	31.7 m
Temperature	Aanderaa (3.75 min, 2.3 mab)	SBE03F (3.75 min, 1.9 mab) Aanderaa (30 min, 1.5 mab)	SBE03F (5 min, 1.7 mab*) SBE37 (60 min, 2.5 mab*) Aanderaa (5 min, 2.3 mab*)	SBE03F (3.75 min, 1.8 mab) Aanderaa (20 min, 1.6 mab)
Oxygen	Optode 123 with plastic window (3.75 min, 2.3 mab)	Optode 113 with copper window (30 min, 1.5 mab)	Optode 123 with plastic window (5 min, 2.3 mab*) SBE43 253 with pump (5 min, 1.7 mab*)	Optode 113 with copper window (20 min, 1.6 mab)
Salinity	None	SBE04 with pump (3.75 min, 1.9 mab)	SBE04 with pump (5 min, 1.9 mab*) SBE37 (60 min, 2.5 mab*)	SBE04 (3.75 min, 1.9 mab)

* All the sensors on tripod 717 were about 0.5 mab after the tripod tipped over.

Operational difficulties provided additional opportunities to evaluate sensor performance. A tangled recovery line and a toppled tripod delayed the retrieval of the tripods scheduled for recovery on the February 2003 and February 2004 refurbishment cruises, respectively. To maintain continuous, high-quality measurements, the replacement equipment was deployed as planned, so that for a period of time, two fully instrumented bottom tripods with oxygen sensors were present simultaneously about 300 m apart. Data from these overlapping deployments provide comparison between sensors near the end of a 4-month deployment and newly deployed sensors. While the toppling of tripod 717 provided an opportunity for optode versus optode comparison, it also modified the optode versus SBE43 test. In addition, the SBE43 exhausted its power before the planned recovery. The tripod's orientation on its side placed many of the sensors within 0.5 m of the bottom, which increased the amount of exposure to fouling by suspended sediment.

This series of deployments from 25 October 2002 through 19 May 2004 provide three time periods to compare data, indicated in the top graph in Fig. 2. The first comparison is between the shipboard survey data and the moored time series from October 2002 through November 2004. The second comparison is between optodes on two different tripods separated by 348 m due to the delayed recovery of tripod 697 in May of 2003. The third comparison is between an optode and SBE43 both mounted on tripod 717 and deployed on 24 September 2003.

The Sea-Bird oxygen and conductivity sensors must be flushed to circulate water past the sensors. The SBE43 oxygen sensor was flushed for 30 s prior to sampling to reach equilibrium. The USGS has found it necessary to flush conductivity cells deployed on stationary platforms near the seabed to prevent sediment accumulation in the cell. Three to five seconds of flushing prior to sampling has proved adequate to refresh the water in the conductivity cell and to remove sediment. This flushing technique was used for all tripod-deployed conductivity cells with one exception: the SBE37 Microcat that was connected to the Sontek ADV on tripod 717. The Sontek's electronics could not support the power required by the pump.

Several techniques were employed to prevent fouling from affecting the oxygen measurements. Optodes deployed on tripods 708 and 756 were deployed with a copper plate that surrounded the foil window. Optodes on tripods 697 and 717 had no fouling protection. The Sea-Bird SBE43 (tripod 717) had tributyl-tin leaching tips mounted on the pump discharge and oxygen sensor intake. This leaching technique has been used successfully by the USGS in the past to prevent fouling of Sea-Bird conductivity cells and transmissometers (Strahle et al. 1994).

Power consumption for the optode and SBE43 was examined during the optode–SBE43 comparison period on tripod 717. For this comparison, an Onset Tattletale 6 computer controlled sampling and independent power switching of a suite of Sea-Bird sensors (SBE43 oxygen sensor, SBE05T pump, SBE04 conductivity cell,

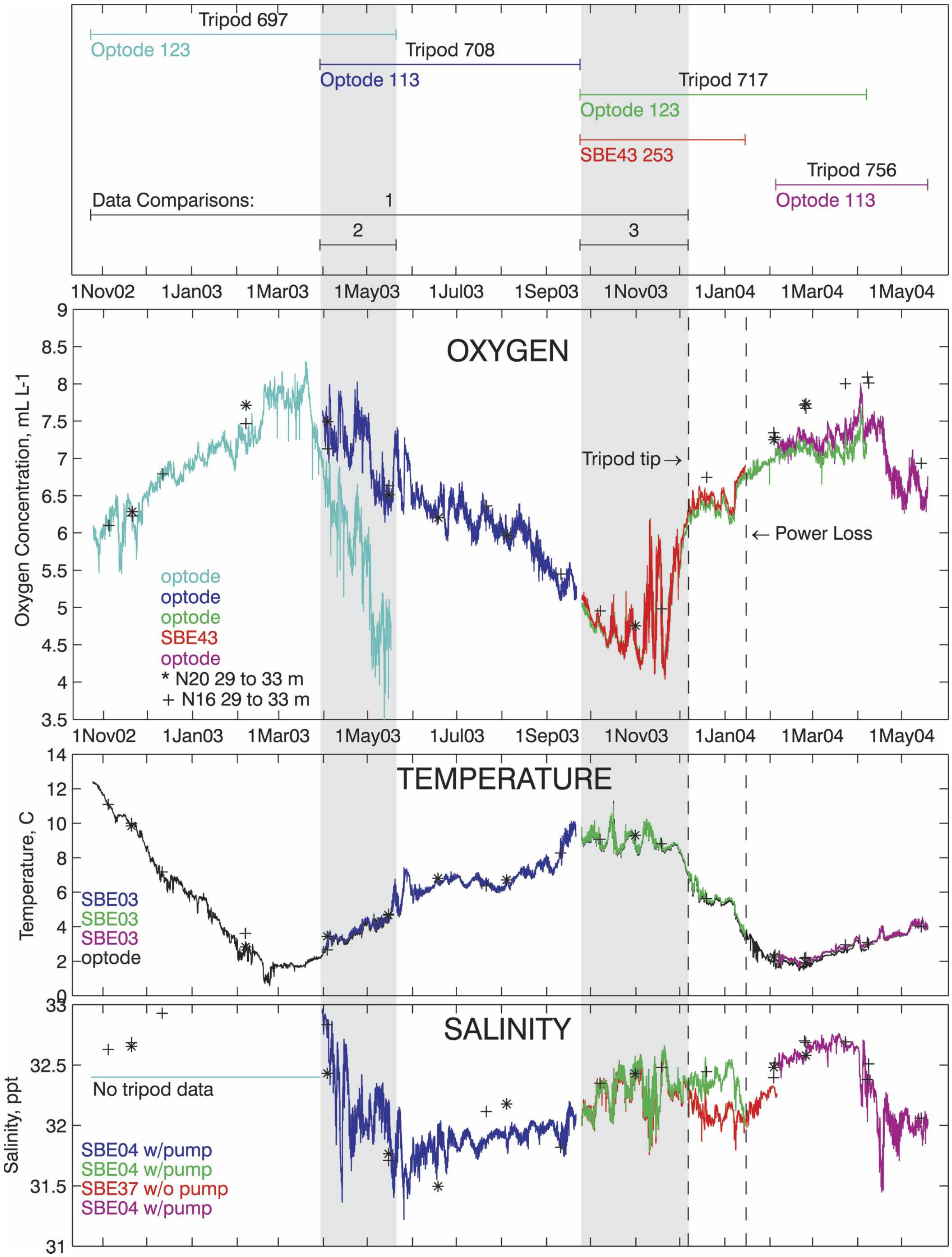

FIG. 2. Plots of the 19-month time series of hourly averaged dissolved-oxygen concentration, temperature, and salinity for all sensors and the nearest stations from the MWRA shipboard surveys. Data are color coded by sensor. Oxygen concentration profile samples from within ±3 m of the tripod depth of 32-m MWRA data are shown. During comparison 3, the SBE43 (red) and the optode (green) data coincide and only the SBE43 data are visible in this plot.

TABLE 2. Results of HIF evaluation of a Sea-Bird SBE43 and Aanderaa optode dissolved-oxygen sensors in a freshwater bath. SBE = Sea-Bird SBE43 oxygen sensor 253, optode = Aanderaa optode 123, Winkler = Azide Modification of Winkler buret titration, Method 8229 from the Hach Company, accurate to ± 0.21 mL L^{-1}, DO Sat. = dissolved-oxygen saturation, T = temperature.

	DO measurement (mL L^{-1})			DO Sat.		Difference (mL L^{-1})		
Date (2003)	SBE	Optode	Winkler	(mL L^{-1})	T (°C)	Sensor − DO Sat.	Sensor − Winkler	DO Sat. − Winkler
19 Aug	9.37	—	8.99	9.45	3.1	−0.08	0.38	0.45
19 Aug	6.33	—	6.12	6.37	20.2	−0.04	0.21	0.24
19 Aug	5.37	—	5.07	5.32	30.4	0.06	0.30	0.24
30 Jul	—	9.54	9.31	9.38	3.0	0.16	0.23	0.07
31 Jul	—	9.31	9.10	9.38	3.0	−0.06	0.22	0.28
31 Jul	—	6.29	6.23	6.37	20.0	−0.08	0.06	0.14
31 Jul	—	5.33	5.18	5.25	30.0	0.08	0.15	0.07
Mean of the difference						0.01	0.22	0.21
Std dev of the difference						0.09	0.10	0.14

and SBE03F temperature cell) and an optode. The Sea-Bird sensors, optode, and datalogger were powered at 12 V by independent 21-V batteries and voltage regulating circuits. The sampling interval for all sensors was 5 min.

The Sea-Bird oxygen and conductivity sensors were sampled by flushing for 30 s by the SBE05T pump, then the SBE43, SBE04, and SBE03F's outputs were recorded. The pump was set to operate at 1600 rpm and was connected to antifouling tips, 10 cm of tygon tubing, and conductivity and oxygen sensors in series. A pump in this configuration can draw as much as 1800 mW at 12 V depending on flow resistance and rotational speed (Sea-Bird Electronics, Inc., 2005d). All the Sea-Bird units were powered by a 630-Wh battery that lasted for 114 days, consuming 19.2 mWh per sample [(630 Wh × 1000 mW W^{-1})/(144 days × 288 samples per day)] or 2304 mW over 30 s of operation. From laboratory measurements of the Sea-Bird sensors' current drains it is possible to estimate the actual power consumption by the pump to be 1792 mW at 12 V (2304 mW total − 116 mW SBE04–227 mW SBE03F − 60 SBE43–109 mW voltage regulator).

The optode makes a measurement immediately when powered up. For each sample, it was left on for 5 s to allow the datalogger to acquire the data using serial communications. Laboratory measurements show that the optode and power regulator draw 1.05 mWh per sample when operated this way (0.9 mWh optode + 0.15 mWh power regulator). The optode was powered by a 210-Wh battery. The optode ran for the entire deployment, 196 days, at the end of which the battery voltage drop indicated that 35% of the battery capacity was used [(22.5 V − 20.6 V)/(22.5 V − 17.0 V)].

For the other deployments, the optode was connected to a standard Aanderaa RCM-9 Mk-II datalogger. Internal optode temperature was not recorded by the RCM; instead an external thermistor measurement was recorded.

b. Shipboard surveys

A series of surveys were performed by Battelle for the MWRA as part of an outfall monitoring program (Libby et al. 2005). These surveys measured dissolved-oxygen profiles 17 times per year. Stations N16 and N20 were located within 2.6 and 3.0 km, respectively, from LT-A and were the closest sites having observations within ±3 m vertically of the sensors mounted on the tripods. Prior to 25 September 2003, the oxygen sensor on the CTD profiler used in the shipboard surveys was a Sea-Bird SBE13; afterward the sensor was an SBE43.

c. Calibrations and testing

The USGS Hydrologic Instrumentation Facility (HIF) tested the SBE43 and optode sensors prior to the intercomparison deployment on tripod 717. The sensors were placed in temperature-controlled baths where oxygen concentration was maintained at saturation using an aquarium pump. The optode was submerged in the tank while freshwater was pumped from an intake near the optode through the SBE43. The bath was allowed to stabilize for several hours. Winkler titrations were performed using a Hach dissolved-oxygen kit (Hach method 8229) with an accuracy of ±0.21 mL L^{-1}. Table 2 summarizes the results of comparisons between the sensors and Winkler titrations for saturated freshwater. The mean difference between the Sea-Bird and Winkler measurements was 0.30 mL L^{-1} and between the optode and Winkler measurements was 0.17 mL L^{-1}. Given the sensor and Winkler accuracies, the differences suggest that both sensors were performing within specifications prior to deployment on tripod 717.

Tests were also conducted at the HIF to verify the stabilization time of the SBE43. The sensor repeatedly achieved 99.6% of its stable reading within 30 s of power up, when flushed by an SBE05T pump. During repeated tests in a bath containing 13.50 mL L^{-1} of oxygenated freshwater, the SBE43 reached 13.41 and 13.44 mL L^{-1} at 29 and 30 s from power up, respectively. Sea-Bird states that 5–6 time constants of 6 s are required for stabilization of the SBE43.

Factory calibrations of sensors and laboratory checks were performed on both the optode and SBE43 on several occasions. Two optodes (113 and 123) were exchanged during the course of the four deployments in this dataset. For tripod 697, a new optode (123) calibrated at the factory was put in service. After deployment, this sensor was tested at the HIF (Table 2). For tripod 708, a new foil was installed in optode 113 by an Aanderaa technician. For tripod 717, optode 123 did not receive a new foil, but prior to deployment the fouling was removed from the old foil and then the sensor was tested at the HIF (Table 2). For the deployment of optode 113 on tripod 756, the foil was not replaced, and a postrecovery comparison to a recently calibrated SBE43 was done in an aerated bath at the USGS Woods Hole Marine Operations Facility, where optode 113 was found to be 10% (0.64 mL L^{-1}) lower than the SBE43. The SBE43 (253) deployed on tripod 717 was calibrated at the factory immediately before and after deployment.

d. Processing

Both sensors depend on the permeability of a sensing foil or membrane. Corrections for in situ conditions were applied to both the Aanderaa and Sea-Bird dissolved-oxygen measurements. For the SBE43, dissolved oxygen was calculated using formulas provided by Sea-Bird (Sea-Bird Electronics, Inc., 2002a), which makes corrections for pressure, salinity, and temperature to compensate for the permeability of the membrane. Salinity was calculated using measurements from the adjacent SBE04 conductivity and SBE03F temperature cells. The nominal deployment depth of the oxygen sensor (32.5 m) was used for the pressure correction. The optode requires correction for in situ salinity. A nominal salinity value to be applied by the optode in situ can be set in the optode prior to deployment. However, during the deployments reported here, this value was set to 0, and the salinity correction was applied during postprocessing using values measured in situ. For tripod 697, a nominal value of 32.5 ppt was used based on the typical salinity value measured during winter at LT-A. For tripod 717, after the pumped oxygen sensor and salinity cell ran out of power, salinity data from the Sea-Bird SBE37 cell on the same tripod was applied. A pressure adjustment was not needed for the deployed depth of 32.5 m. The response of the optode sensing foil decreases 4% for every 1000 m of water depth (Aanderaa Instruments AS 2004), and this was negligible (0.13% or 0.009 mL L^{-1} for a nominal value of 7 mL L^{-1}) at 32.5-m depth. The optode outputs data (μM) and is already corrected for temperature using a thermistor located in the optode housing; μM is converted to mL L^{-1} by dividing by 44.66 (Aanderaa Instruments AS 2004). All moored comparison data were aligned in time to within 6 min and then hourly averaged.

The effect of accuracy and response time of the temperature and salinity sensors used to correct the oxygen data is negligible. Oxygen solubility changes by 0.05 mL L^{-1} ppt^{-1}, and 0.10 mL L^{-1} $°C^{-1}$. Manufacturers' recommended formulas were used to determine the effect of changes in temperature and salinity on oxygen measurements. These formulas apply both solubility corrections and calibration corrections for the effects of temperature on the sensors' components. Optode oxygen concentration changes by about 0.04 mL L^{-1} ppt^{-1} and 0.01 mL L^{-1} $°C^{-1}$. Sea-Bird measurements change by about 0.05 mL L^{-1} ppt^{-1} and 0.17 $°C^{-1}$. The response time of the SBE04 conductivity cell is 0.7 s with an accuracy and stability of ± 0.0003 S m^{-1} $month^{-1}$ when kept clean and unfouled (Sea-Bird Electronics, Inc., 2005a). The accuracy of the SBE03F temperature cell is 0.001°C. The response times of the temperature sensors were different from the oxygen sensors; however, both were well within the 5 min or greater datalogger sampling interval. The SBE03F temperature probe has a response time of 0.7 s (Sea-Bird Electronics, Inc., 2005c). The temperature probe was not included in the flow path of the pump used to flush the oxygen sensor and conductivity cell. The optode relies on temperature readings from a thermistor inside a 36-mm titanium case. In this configuration, the optode's temperature measurements have a response time of $<$10 s.

4. Results

A continuous time series of dissolved-oxygen observations from Aanderaa optodes was obtained from 24 October 2002 to 19 May 2004 (Fig. 2). The oxygen sensors performed well and consistently, except when fouled or when battery power was insufficient. Oxygen concentration ranged from 4 to 8 mL L^{-1}, with the lowest concentrations in the fall and the highest concentrations in the late winter. During this time, oxygen saturation calculated from moored temperature and salinity data ranged from 6.1 to 8.1 mL L^{-1}, with the

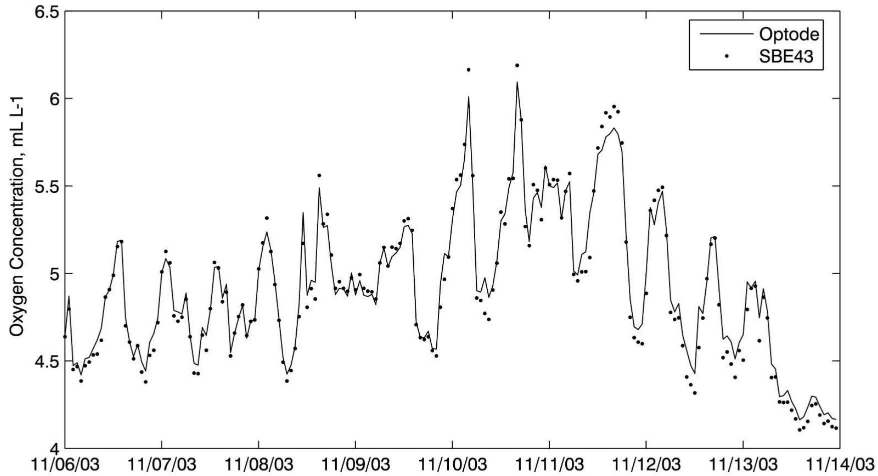

FIG. 3. Selected time series of hourly averaged dissolved-oxygen concentration during comparison 3 when concentrations varied by several 0.1 mL L^{-1} at tidal time scales.

lowest values in the fall and the highest in late winter. Superimposed on this seasonal pattern were fluctuations of more than 1 mL L^{-1} over periods of a few days (Fig. 3).

a. Amount of biofouling

Fouling of the sensors deployed near the seabed occurred during all tripod deployments. Pictures of the optode and SBE43 sensors were obtained before and after deployment (Fig. 4). For example, the optode sensing foil showed varying degrees of fouling ranging from attachment of a few 1–2-mm-sized clams or barnacles (Fig. 4d) to complete coverage of the sensing foil by an encrusting bryozoan colony (Fig. 4c). The decreasing oxygen values that occurred on tripod 697 coincide with decreasing light transmission measured by the adjacent transmissometer consistent with biological growth on both sensors. The optode on tripod 708 had a copper surround and experienced the least amount of fouling of the three documented optodes. This optode was deployed during the summer, typically the heaviest fouling period at this site. On tripod 717, the SBE43's flow intake was kept open by the tributyl-tin impregnated tip (Fig. 4f), but sediment was present on the sensing membrane on recovery (Fig. 4g). Attenuation readings show significant resuspension of sediment during this winter deployment. When the tripod tipped onto its side, the optode sensor moved from its original height of 1.73 mab to about 0.45 mab. On recovery there was significant growth on the optode sensing foil (Fig. 4e). The sensing window of the optode on 756 had a copper window surround and was recovered with a dusting of sediment but was otherwise clean.

b. Calibrations and tests

The following results were obtained from postdeployment calibrations and bath tests: for the deployment of optode 123 on tripod 697, the HIF testing resulted in a mean difference between the optode and Winkler titrations of 0.17 mL L^{-1} (Table 2). Postdeployment calibrations by Sea-Bird showed no unusual drift or other problem with the SBE43 sensor deployed on tripod 717. After recovery, optode 113 deployed on tripod 756 read 0.64 mL L^{-1} below a recently calibrated SBE43.

c. Comparisons

The comparisons are as follows: 1) dissolved-oxygen values between shipboard survey data and moored optode; 2) between two optodes during the overlap between tripod 697 and 708, located about 348 m apart; and 3) between the optode and the SBE43 on tripod 717.

In comparison 1, dissolved-oxygen concentration data from the tripods are compared with the regional MWRA shipboard surveys (Fig. 5; Table 3). Shipboard profile samples were selected between the depths of 29 and 33 m to correspond with the nominal optode depth of 32 m. Using shipboard observations greater than 3 m away from the sensor depth significantly increased the error in observed differences, and given observed vertical gradients of oxygen concentration, were not considered to provide a valid comparison. The correlation coefficients between MWRA shipboard-survey data and the optode is >0.9 for sites N16 and N20 (Fig. 6). The mean differences are 0.07 and 0.05 mL L^{-1}, respec-

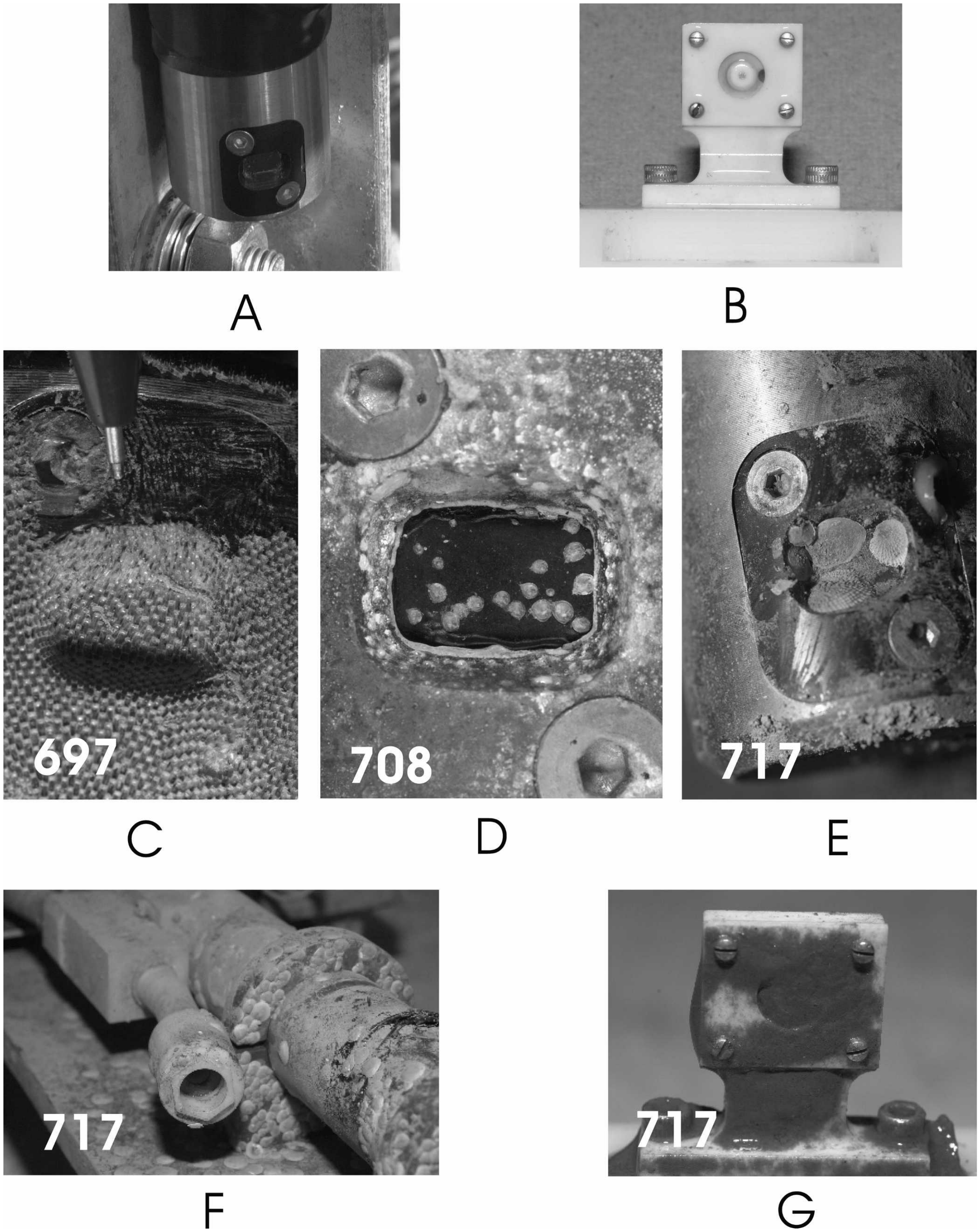

FIG. 4. Images of clean (a) optode and (b) SBE43 membrane assembly before deployment. Optode following recovery from (c) tripod 697 with a plastic window frame, (d) 708 with a copper window frame, and (e) 717 with a plastic window frame. SBE43 from tripod 717 on recovery showing (f) the antifouling tip on the intake and (g) membrane assembly with sediment.

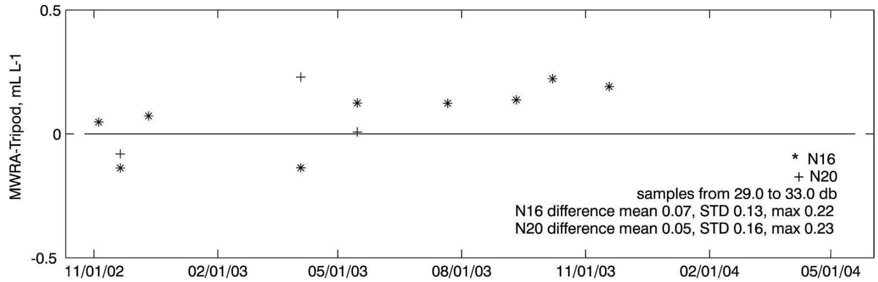

FIG. 5. Plot of the difference between the USGS–tripod optode oxygen concentration measurements and the MWRA shipboard survey data between November 2002 and May 2004.

tively, and the standard deviations are 0.13 and 0.16 mL L^{-1}. The differences between the moored sensors and shipboard-survey data are largest during the spring of 2004, where evidence from postcalibrations and age of the foils suggest that the sensors' accuracy no longer provides a valid comparison.

In comparison 2, data from two optodes are compared. There was an increase in the significant differences between the measurements by the optodes on tripod 697 and tripod 708 during the spring of 2003. Tripod 697's optode's sensing window was completely covered by biological growth on recovery (Fig. 4c). The rapid decline in oxygen concentration recorded by optode 123 from mid-March 2003 to recovery is attributed to the fouling.

During comparison 3, data were collected for 112 days for the optode–SBE43 comparison on tripod 717. For the first 79 days, the mean difference between the optode and SBE43 data on tripod 717 was 0.05 mL L^{-1} and the correlation coefficient was >0.9. The maximum difference was 0.25 mL L^{-1}, which is within the accuracy specified by both manufacturers (0.18 mL L^{-1} for the optode and 0.15 mL L^{-1} for the SBE43). There was an initial difference of 0.15 mL L^{-1} between the sensors just after deployment. This difference slowly decreased over a period of 15 days until the difference was <0.05 mL L^{-1} by 10 October 2003. There is no indication by the transmissometer of fouling this early in the deployment, and temperature sensor readings agree to within 0.01°C.

The greatest difference in oxygen concentration in optode measurements from the end of one deployment to the beginning of the next is −0.61 mL L^{-1}, between tripods 697 and 708. This large difference is attributed to the fouling of optode 123. The difference in optode data for the transition between tripod 708 and 717 is

TABLE 3. Comparison between tripod data and cast data.

Cast date	MWRA ship survey station(s)	Tripod − ship (mL L^{-1})	Tripod statistics* (mL L^{-1})		Shipboard statistics** (mL L^{-1})		
			Mean	Std dev	Mean	Std dev	Shear N16, N20
4 Nov 2002	N16	0.04	6.14	0.05	6.10	n/a	−0.23, n/a
20 Nov 2002	N16, N20	0.05	6.31	0.09	6.26	0.04	−0.54, −0.03
11 Dec 2002	N16	−0.04	6.75	0.05	6.79	n/a	−0.11, n/a
6 Feb 2003	N16, N20	−0.37	7.22	0.07	7.59	0.17	−0.05, −0.05
3 Apr 2003	N16, N20	0.08	7.39	0.17	7.31	0.26	−0.85, −0.05
15 May 2003	N16, N20	−0.14	6.44	0.10	6.58	0.08	−0.42, −0.20
18 Jun 2003	N20	0.08	6.29	0.11	6.20	n/a	n/a, −0.03
21 Jul 2003	N16	−0.13	6.23	0.08	6.36	n/a	−0.09, n/a
4 Aug 2003	N20	0.03	6.00	0.10	5.97	n/a	n/a, −0.19
10 Sep 2003	N16	−0.26	5.19	0.06	5.45	n/a	−0.98, n/a
8 Oct 2003	N16	−0.25	4.71	0.03	4.95	n/a	−0.95, n/a
31 Oct 2003	N20	−0.14	7.62	0.08	4.76	n/a	n/a, −1.30
18 Nov 2003	N16	0.44	5.42	0.36	4.98	n/a	−0.96, n/a

* Tripod data computed from one day before through one day after the date of the cast; tripod position was typically within 200 m of 42°22.703′N, 70°46.969′W at a depth of 32 m.

** Cast data computed from depths 3 m above and below the nominal tripod depth (29–33 m). Shear is computed from the difference between the bottom two points of the cast, which are not always at the same depth from cast to cast. Data are not available when casts did not extend to within 3 m of the tripod depth. Station N16 was located at 42°23.640′N, 070°45.200′W and station N20 was located at 42°22.900′N, 070°49.030′W.

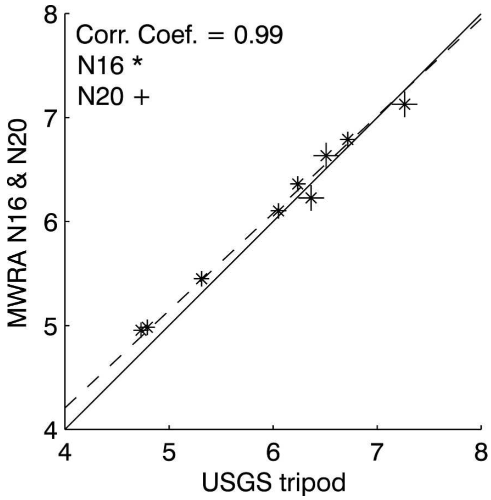

FIG. 6. Regression analysis results of both datasets. USGS tripod data were selected as the nearest hourly average to the time of the shipboard survey. Observations between February 2004 and May 2004 were not included in the regression due to aging of the optode sensing foils.

0.23 mL L^{-1}, and between tripod 717 and 756 is −0.06 mL L^{-1}.

5. Discussion

a. Sensor comparisons

Data from the comparison between the optode and the Sea-Bird SBE43 show that the difference between these sensor measurements were within the manufacturers' stated specifications for accuracy. There was good agreement between the shipboard surveys and tripod data during comparison 3, also within manufacturers' specifications. It is unclear why there was an initial difference of 0.15 mL L^{-1} between the tripod sensors at the beginning of the tripod 717 deployment. While 0.15 mL L^{-1} is well within the accuracy quoted by the manufacturers, agreement is better than 0.05 mL L^{-1} for much of this comparison period. The Sea-Bird sensor maintained good agreement with the optode even when there was indication of entrainment of fine sediment in the sensor and on the membrane. By the time the sensor ran out of power, it had been deployed for a total of 112 days (2688 h). It was still performing within specification when compared to the optode, and was within 0.33 mL L^{-1} of the shipboard survey data. This record exceeds the Sea-Bird specification of stable operation for 1000 h if the sensor is kept clean, which this sensor was not.

The oxygen-concentration sensors compared well with the MWRA shipboard surveys given the factors of fouling, natural variability, and spatial separation. The greatest difference between the moored optodes and the shipboard data occurred between February and March of 2004, with a trend of the optode reading from 0.2 to 0.66 mL L^{-1} lower than the shipboard data. There are two possible explanations: sensor drift and a spatial difference in oxygen concentration. The data suggest that the difference is caused by drift in both optodes. Profiles at sites N18, N16, and N20 from the shipboard survey on 23 March 2004 all measure oxygen concentration near 8 mL L^{-1} at the deepest part of their profiles, while both tripod optodes measure nearer to 7.4 mL L^{-1}. After this date, the moored measurements increasingly diverge from the shipboard readings. It is unlikely that fouling is the cause of this trend because at recovery the optode on tripod 756 was the cleanest of all optodes during these deployments.

This drift seen in tripod data recorded after February 2004 is attributed to the degradation of the optode sensing foil. Aanderaa suggests that optode foils be replaced at least once a year. On 23 March 2004, the foil in optode 113 had been in situ for a total of 225 days, and the foil in optode 123 had been in situ or a total of 390 days. Thus the poor agreement with the shipboard surveys occurred when both optodes were approaching the end of or exceeding their recommended service periods. The foil in optode 113 on tripod 756 had been deployed with a new foil on tripod 708, where it experienced mild fouling (Fig. 4d). This fouling was successfully removed without damaging the foil before the sensor was redeployed on tripod 756. Optode 123 had also been fouled (Fig. 4c) and cleaned. It was tested prior to redeployment on tripod 717, and it performed as close to the claimed specification as could be determined by the HIF (Table 2).

Comparisons of the sensors' performance under different fouling conditions indicate that the optode is tolerant of fouling as long as some part of the window remains clear. The poor optode-to-optode comparison at the beginning of the data from tripod 708 is caused by fouling. The optode on tripod 697 was the most fouled sensor, with the sensing foil window completely covered by a bryozoan colony. The precipitous decline of the dissolved-oxygen measurements from tripod 697 relative to the newly deployed sensor measurements from tripod 708 indicates that the animals may have severely decreased oxygen-molecule transfer to the sensing foil. Fouling conditions of the optode on tripod 717 were also severe; the sensing window was nearly blocked. However, the difference between optode measurements at the beginning of the data from tripod 756 is only 0.17 mL L^{-1}. This difference may also be attributed to the spatial separation of the sensors or temperature differences, as one tripod (717) was tipped over, and its thermistor measurements were lower by 0.19°C.

b. *Effectiveness of antifouling techniques*

Antifouling techniques were used on the optode and the Sea-Bird SBE43. These worked well, given the level of biological growth at 32.5-m depth at the deployment site. The combination of flushing and tributyl-tin leaching tips kept the interior of SBE43, including the membrane surface, free of marine growth. This technique has been observed by the USGS during other experiments as being effective under more severe fouling conditions. For the optode, the data indicate that the copper surround used on the optodes on tripods 708 and 756 resulted in less growth than with the standard plastic window material. In previous testing of the optode, the Alliance for Coastal Technologies (ACT 2004) evaluated the Aanderaa optode for accuracy, precision, and drift with and without a copper antifouling protection screen (ACT 2004). The performance at seven sites during a 4-week test was seen to be dependent on the type of fouling and the perforated plate used to protect the optode foil. The copper perforated plate did not always improve the performance over that of an unprotected optode deployed under the same conditions. The deployments reported here utilized a newer copper window design that differed from the ACT tests in that the foil sensing area was unobstructed (Fig. 4d). The data indicate that this newer copper surround design, used on tripods 708 and 756, was a good compromise between no copper and the perforated copper cover used in the ACT testing. Tripods 708 and 756 were deployed during the most active fouling seasons of spring and summer and showed less fouling than the sensors on tripods 697 and 717.

c. *Power consumption*

Power consumption required by sensing techniques is a key consideration in experimental design and choice of technology for deployments of several months. Both the optode and the SBE43 were sampled so that the least amount of power would be consumed for each sample without affecting accuracy. On tripod 717 the optode was powered for the minimum time required by the Tattletale datalogger to acquire the data using serial communications (5 s). On the other tripods this power-up time is determined by RCM 9 MK II datalogger. The data indicate that both methods were adequate. The SBE43 requires flushing for at least 30 s to achieve steady state, confirmed by the USGS HIF during their testing. Power consumption of the Sea-Bird sensors was within expected values. Power data are provided here in detail to assist future users of these technologies.

6. Summary

Observations of dissolved-oxygen concentration have been collected by two different sensors in a coastal marine environment for periods of 4 months. Both the Aanderaa optode and Sea-Bird SBE43 provided measurements accurate to a few tenths of a milliliter per liter and good agreement during overlapping deployments and with shipboard surveys. Significant fouling, either by sediment or growth of marine life on sensing surfaces, affected sensor performance. Both sensors performed within specification. However, the flushing required for Sea-Bird SBE43 resulted in 17 times the power per sample than is required for the optode. Prevention of fouling and power consumption appear to be the biggest considerations when using these sensors in situ for long periods of time.

The data from this test suggest that the optode's sensing foil should be replaced to avoid drift after deployment in situ for about 225 days. Separation of the foil layers has been observed in older batches of optode foils. These were the foils in use during these tests. USGS has also observed layer separation in older foils during subsequent deployments not reported here. However, recent drifter data suggest stability for as long as 600 days (Tengberg et al. 2006).

The tests reported here suggest that accurate measurements of dissolved-oxygen concentration in coastal environments may now be made routinely by sensors over long-term deployments in situ. These technologies significantly advance the ability of scientists to observe and interpret changes in dissolved oxygen over long time periods in situ; however, they still leave room for improvement in comparison to carefully performed Winkler titrations. Winkler titrations can achieve accuracies of 0.1% (Carpenter 1965). Winkler titration accuracy is dependent on the titration used, from a simple dropper in field kits to buret or digital titration in controlled laboratory settings. The World Ocean Circulation Experiment Plan called for accuracies of Winkler titrations of bottle samples of less than 1% and accuracies of 1%–1.5% for sensors used on profilers (World Climate Research Program 1988), noting a lack of adequate sensors when it was written in 1988. The SBE43 sensor was developed during the WOCE program and tested on WOCE cruises. Thus, for applications where is it impractical or impossible to obtain carefully controlled water samples, the Clark cell and optode technologies are the only solution available.

Acknowledgments. We thank Jonathan Borden and Steve Ruane for instrumentation and mooring work; Mary Hastings and Fran Lightsom for data management; the captain and crew of the USCG *Marcus Hanna*, and the captain and crew of the F/V *Christopher Andrew* for help at sea; as well as Dann Blackwood for photography. Trond Gulbrandsoy of Aanderaa, Inc., and Jim Carlson of Sea-Bird Electronics, Inc., provided explanations and calibrations of the optode and SBE43. Suh Yuen Liang and Mike Mickelson provided the MWRA shipboard survey data. William J. Davies and Janice Fulford performed tests at the USGS HIF. This work was funded by the MWRA and USGS. Any use of trade, product, or firm names in this publication is for descriptive purposes only and does not imply endorsement by the U.S. government.

REFERENCES

Aanderaa Instruments AS, 2004: Operating manual oxygen optode 3830, 3930, 3975. Aanderaa Instruments AS, 69 pp.

ACT, 2004: Performance verification statement for the Aanderaa Instruments Inc. dissolved oxygen optode 3830/3930/3835. Alliance for Coastal Technologies Rep. ACT VS04-01, 18 pp.

Butman, B., and Coauthors, 2004: Long-term oceanographic observations in western Massachusetts Bay offshore of Boston, Massachusetts: Data report for 1989-2002. U.S. Geological Survey Digital Data Series DDS-74, DVD.

Carlson, J., 2002: Development of an optimized dissolved oxygen sensor for oceanographic profiling. *Int. Ocean Syst.,* **6** (5), 20–21.

Carpenter, J. H., 1965: The accuracy of the Winkler method for dissolved oxygen analysis. *Limnol. Oceanogr.,* **10,** 135–140.

Fulford, J. M., W. J. Davies, and L. Garcia, 2005: Field comparison of optical and Clark cell dissolved-oxygen sensors. *Proc. 2005 World Water and Environmental Resources Congress,* Anchorage, AK, Environmental and Water Resources Institute of the American Society of Civil Engineers, p. 312.

Libby, P. S., C. Gagnon, C. S. Albro, M. J. Mickelson, A. A. Keller, D. G. Borkman, T. J. Turner, and C. A. Oviatt, 2005: Combined work/quality assurance plan (CWQAPP) for water column monitoring 2002-2005—Tasks 9, 10, 12, 13, 14, 15, Boston. Massachusetts Water Resources Authority, ms-074, 79 pp.

Sea-Bird Electronics, Inc., 2002a: SBE43 dissolved oxygen sensor. Application Note 64, 3 pp.

——, 2002b: SBE43 dissolved oxygen sensor. Application Note 64-2, 6 pp.

——, 2005a: Sea-Bird conductivity sensor SBE04. Specification Sheet, 2 pp.

——, 2005b: Sea-Bird dissolved oxygen sensor SBE43. Specification Sheet, 2 pp.

——, 2005c: Sea-Bird temperature sensor SBE03F. Specification Sheet, 2 pp.

——, 2005d: Sea-Bird Submersible Pump SBE05T. Specification Sheet, 1 pp.

Strahle, W. J., C. Perez, and M. A. Martini, 1994: Antifouling leaching technique for optical lenses. *Proc. OCEANS OSATES'94 Conf.,* Vol. II, Brest, France, IEEE-OES, 710–715.

Tengberg, A., and Coauthors, 2006: Evaluation of a life time based optode to measure oxygen in aquatic systems. *Limnol. Oceanogr. Methods,* **4,** 7–17.

——, and Coauthors, 2003: Optode to measure oxygen in the aquatic environment. *Sea Technol.,* **44** (2), 10–20.

World Climate Research Programme, 1988: Detailed requirements. Vol. I, World Ocean Circulation Experiment Implementation Plan, WCRP-11, WMO Tech. Doc. 242, 174 pp.