Full Paper

Use of Voltammetry to Monitor O_2 Using Au/Hg Electrodes and to Control Physical Sensors on an Unattended Observatory in the Delaware Bay

Tommy S. Moore,*[a] *Donald B. Nuzzio*,[b] *Timothy W. Deering*,[a] *Martial Taillefert*,[c] *George W. Luther III*[a]*

[a] University of Delaware, College of Marine and Earth Studies, Cannon Laboratory, 700 Pilottown Rd, Lewes, DE 19958, USA
*e-mail: tsmoore@udel.edu; luther@udel.edu
[b] Analytical Instrument Systems, P.O. Box 458, Ringoes, NJ 08822, USA
[c] School of Earth & Atmospheric Sciences, Georgia Institute of Technology, 311 Ferst Drive, Atlanta, GA 30332-0340, USA

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Abstract
A voltammetric analyzer was used to control an observatory mooring in the Delaware Bay at the same time oxygen data were collected with solid-state gold-amalgam (Au/Hg) electrodes. Oxygen, temperature and salinity data were collected for 8 days and sent wirelessly back to the shore-based laboratory. Observed oxygen saturations ranged from 70 to 171%, with a mean of 107%. The highest oxygen concentrations were observed when there were low tides during the solar maximum, indicating higher rates of production within the Delaware Bay than in coastal Atlantic Ocean waters which passed the mooring at high tides, as expected based on previous shipboard studies. Lower percent saturations indicated respiration, the decomposition of organic matter by oxygen, as the dominant process and corresponded to night periods. Upon recovery the electrodes were free of bio-fouling. This study demonstrates that voltammetric techniques and equipment can be used in observatory and mooring systems.

Keywords: Voltammetry, Delaware Bay, Ocean observing, Oxygen, Mooring, Observatory

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1. Introduction

In recent years our understanding of the oceans has greatly increased, and with this understanding has come the realization that traditional, ship based measurement techniques are not sufficient to address some oceanographic issues. Two areas currently being focused on are the need to understand ecosystem response to short-lived events and the need to have longer observation times for seasonal and interannual processes [1]. Ocean observatories, both permanent emplacements and mobile assets, are the current solution to this issue. The need for a large-scale network of observatories has long been recognized, and was brought back into mainstream thinking in 2004 by the U.S. Commission on Ocean Policy (www.oceancommission.gov). The Ocean Observatories Initiative (OOI) and the Ocean Research Interactive Observatory Network (ORION) are NSF's contribution to establishing a national ocean observatory network, which can then provide necessary research assets that can become part of the Global Earth Observation System of Systems (GEOSS).

A number of analytical techniques are suitable for use in observatories, including flow injection analyzers, optodes and electrochemical techniques. Electrochemical techniques are the most common, and range from simple conductivity, temperature and depth sensors (CTD), to more elaborate electrode techniques. The major electrochemical techniques are conductimetric (e.g., salinity), potentiometric (e.g., pH), and amperometric/voltammetric (e.g., O_2, H_2S). Voltammetric techniques using solid-state Au/Hg amalgam micro-electrodes to scan applied potential and measure current are advantageous over other methods because they are nonselective and can provide data on a number of chemical species present including (but not limited to) O_2, H_2S, Fe^{2+}, Mn^{2+}, Fe and S species [2–5]. Detection limits are (sub)micromolar for these species when deposition steps are not used.

In previous work [6], we have documented the intercomparison of commercial optrodes and Clark amperometric sensors with Winkler O_2 titrations and the solid state Au/Hg voltammetric electrode to monitor O_2. In that work, we observed that the Winkler O_2 titrations and the solid state Au/Hg voltammetric electrode gave identical data and more reliable information compared to the other two. There are two principal reasons for these observations. First the Clark sensor has a high O_2 consumption rate at the electrode when on, so that O_2 measurements can be lower than the Winkler O_2 titrations and the solid state Au/Hg voltammetric electrode. Second, the optode has a membrane covering the Ru dye and its thickness did not allow for accurate determination of rapid changes $\geq \Delta$ 10 μM O_2 min^{-1}) in O_2 concentration, which are commonly observed in the environment. In addition, commercial optrodes and Clark amperometric sensors are rated for O_2 concentrations and saturations of up to 500 μM and 120%, respectively. Many coastal and estuarine environmental systems can have up to 900 μM and over 300% saturation [7].

In other work we have tested the long term stability of the Au/Hg voltammetric electrode [5]. The electrode showed better than 2% precision over 2 months in laboratory solutions and up to a week in field tests off the University of Delaware dock. Calibrations were performed twice or more daily in the field tests and showed that the Au/Hg electrode provided excellent data and held calibration.

Any sensor array used on a moored system is also susceptible to some degree of fouling, sometimes to such an extent that the sensor is no longer useable. Membrane bound electrodes are susceptible to fouling at the membrane surface, requiring frequent recalibration and replacement [8]. This sensor maintenance contributes greatly to the cost and time required to maintain an observatory. The OOI calls for the development of new sensor technology to be used by ocean observatories, and reliable chemical sensors are greatly needed. Voltammetric techniques using Au/Hg are resistant to fouling because conditioning or cleaning potentials can be applied, and normal use of the electrode via scanning a range of potentials will serve to clean it [2, 5].

Our objective was to show that voltammetric equipment and electrodes could collect adequate data as an observatory. Voltammetry using a Au/Hg electrode was used in this study since it is sensitive to oxygen and has no problems detecting high O_2 concentrations and % saturations as do commercial optrodes and Clark amperometric sensors. Once developed the system may be readily deployed in a variety of systems with no changes. Voltammetric equipment normally has the capacity to control other devices, and this feature was used to show that voltammetric equipment could control observatory functions.

2. Experimental

2.1. Study Site

The Delaware Bay (Fig. 1) is a shallow, nearly vertically homogenous estuary in the mid-Atlantic portion of the United States. The Delaware River is the largest source of water into the bay, supplying 58% of the mean annual flow [9]. The Schuylkill River supplies an additional 15% of the mean annual discharge, and no other river supplies more than 1% of the discharge [9]. During mean flow conditions the water column is nearly homogenous[10], although stratification in the lower bay can occur during spring runoff, with fresher runoff water overlying the more saline bay water [11]. Tidal currents in the bay are ca. 1 m/s, subtidal currents are ca. 0.1 m/s and the tidal excursion range is 10 to 20 km [12].

Primary production in the Delaware Bay has been found to be principally light-limited [11, 13, 14], and only the lower bay has been found to be nutrient-limited [13]. The upper regions of the bay are heavily urbanized and highly eutrophic [15], and often experience high-nutrient, low-growth conditions that are related to light limitation [14]. Additionally, it has been observed that bacterial respiration can exceed primary production in all regions of the bay, leading to negative oxygen balance [16]. Observed oxygen saturation values, calculated from discrete samples followed by Winkler oxygen titrations, range from > 170% to < 60% [15–17], and can drop 170% to 70% overnight (Sharp, personal communication).

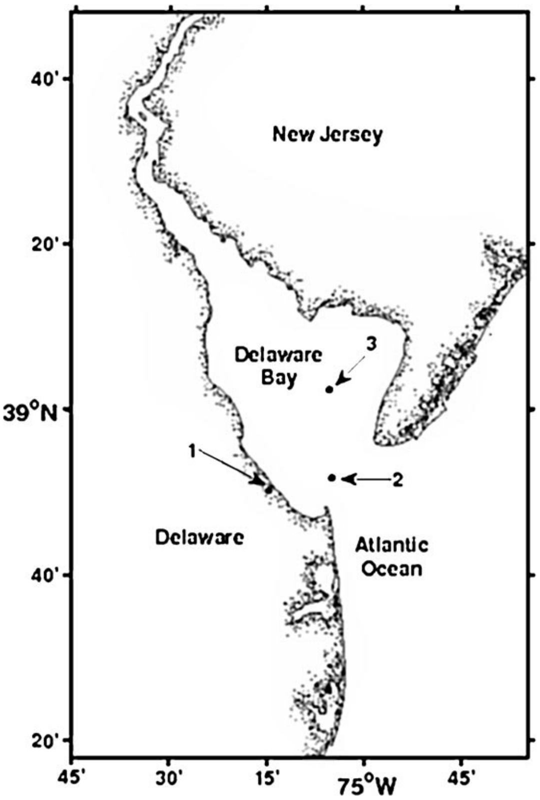

Fig. 1. Map of the Delaware Bay and surrounding area. 1) College of Marine and Earth Studies in Lewes, DE. 2) Buoy deployment site. 3) NOAA NDBC station 44009.

2.2. Instrumentation and Methods

2.2.1. Electrochemical Analyzer

Analyses were performed using an Analytical Instrument Systems, Inc. In-situ Electrochemical Analyzer (AIS-ISEA-III). The instrument is a potentiostat with six current range scales between 0–100 nA up to 0–10 mA, and can perform scans at rates up to 10 volts/second. It communicates through a RS-232 serial interface, and can be operated in real-time, with the data files stored on the host computer, or as a logger, repeating a user-defined sequence of experiments at a specified time step and storing the data for future uploading. The instrument was configured as a standard 3-cell electrode, using a platinum wire as the counter, and a Ag/AgCl wire as the reference, and the instrument can cycle between four working electrodes (see below). As an added precaution against electrical noise, the instrument can be grounded to the shield wire on the reference electrode. Up to three auxiliary analog devices (±5 V output) can be monitored, and the analyzer can record data from a Seabird SBE 37-SM MicroCAT CTD, which provides salinity, temperature and depth data.

2.2.2. Electrodes and Voltammetric Techniques

Four 100 μm gold amalgam micro-electrodes, as originally described by Brendel and Luther [2] and Luther et al. [4], were used for working electrodes in this study. A 100 μm diameter gold wire was soldered to a conductive copper wire, and then placed within a 2–3″ length of 0.125″ polyethyletherketone (PEEK) tubing, and the void space filled with a non-conductive marine epoxy (West System 105 epoxy resin and 206 hardener). Single-pin underwater connectors were soldered to the free end of the conductive wire to ensure a water-tight fitting between the electrode wires and the cell-cable, and to allow for easy deployment of electrodes. The PEEK–conductor wire end and the single-pin electrode were waterproofed by applying two alternating layers of 3M Scotchkote electrical coating and Scottchfil electrical insulation putty.

Once constructed, each working electrode surface was sanded with 400 grit paper, and then polished with four diamond polishes of successively smaller sizes (15, 6, 1, and 0.25 μm). Finally each electrode is plated with Hg by reducing Hg(II) from a 0.1 N Hg/0.05 N HNO_3 solution for 4 minutes at a potential of −0.1 V, while purging with N_2. The mercury/gold amalgam interface was conditioned using a 90 second −9 V polarization procedure in a 1 N NaOH solution (Au/Hg on the negative terminal and Pt wire on the + terminal). The electrode was then run in linear sweep mode from −0.1 to −1.8 V versus a Saturated Calomel Electrode (SCE) or Ag/AgCl electrode several times in oxygenated seawater to obtain a reproducible O_2 signal.

The counter and reference electrodes were modified from previous studies in order to make them more robust. The Ag wire for the reference electrode was soldered to a conductive copper wire, and at the same time an additional copper wire was soldered to the aluminum shielding braid that surrounded the copper wire. Both wires were then potted in 3/8″ Teflon tubing using the same marine grade epoxy as above, leaving ca. 5″ of Ag wire exposed. A perforated 1/2″ Teflon tubing guard was then fitted over the 3/8″ tubing as an additional protective measure. The same procedure was used for the counter electrode using 1/4″ and 3/8″ tubing.

2.2.3. Standardization and Stability

Electrodes were standardized by performing linear sweep voltammetry (LSV) scans in oxygen-saturated filtered seawater, conditioned at −0.1 V for 2 seconds, then scanning from −0.1 to −1.8 V at 2 V/s. O_2 reduces to H_2O_2 and H_2O_2 reduces to H_2O at the Au/Hg surface Equations 1 and 2, at an $E_{1/2}$ of −0.3 V for Equation 1 and an $E_{1/2}$ of −1.30 for Equation 2.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad (2)$$

Minimum detection limits are 3 μM for O_2 and H_2O_2, as previously determined by Brendel and Luther [2] using statistical comparison of blanks with standard solutions in seawater. Precision was found to be better than ±1%. In a comparative study of the Au/Hg electrode, Glazer et al. [6] found that the electrodes offer highly accurate measurements as compared to a Clark-type electrode and Winkler titrations, and that the response time for the Au/Hg electrodes is faster than both the Clark-type electrode and an optode system.

Previous studies [18] have shown that the change in electrode sensitivity is constant at flow rates greater than 1.7 cm/s, typical of water movement at high and low slack water. The electrode has been calibrated over a range of salinities and temperatures up to 50 °C [5].

Au/Hg electrodes have been found to be stable for a period of over 2 months (7,909 scans) [5] in an electrochemical cell measuring oxygen in filtered seawater that was replaced daily. The relative standard deviation of the experiment was better than 2%, with most of the deviation attributed to changes in laboratory temperature as a thermostatted cell was not used. Stability of an electrode was also tested for five days off of a dock at the University of Delaware Marine Operations Building. The results show a sinusoidal pattern indicative of tidal changes. The electrode was tested twice daily in oxygen-saturated seawater, with excellent reproducibility.

2.2.4. Unattended Buoy

The electrochemical analyzer, along with all other non-sealed electrical equipment, was mounted in the watertight well of an unattended buoy designed by Mooring Systems, Inc (Fig. 2). The buoy was deployed in Delaware Bay near its meeting with the Atlantic Ocean, outside of the outer breakwater, approximately five miles off-shore by the R/V *Cape Henlopen* on August 26, 2005, (Fig. 1) in 10 m of water. This location was selected due to its close proximity to our facilities and to measure the chemical and physical properties of the Delaware Bay coastal current, which affects the Atlantic Ocean coast off Delaware [19]. While connected to the host computer, the instrument was controlled manually in order to test each electrode and to verify that the MicroCat CTD was working properly. After this test, any data stored on the instrument were uploaded to the host computer for analysis and the instrument was returned to logger mode. In logger mode the instrument was configured to run 5 LSV scans from −0.1 to −1.8 V at 2 V/s on each electrode every 15 minutes (80 scans/hour). Prior to each voltammetric scan, salinity, temperature and depth data were logged into each scan's raw data file. Data were manually uploaded daily.

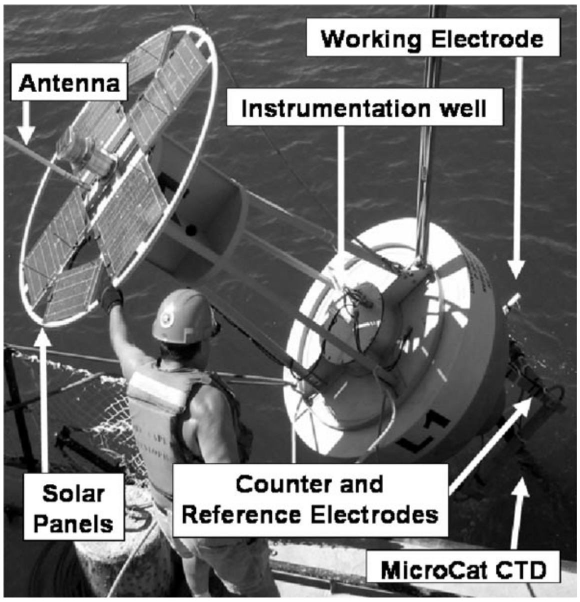

Fig. 2. Image of the buoy during deployment. The instrument was powered by three 12 V DC batteries that were recharged by ten 0.5 A solar panels. Connection between the instrument and the host (shore-based) computer was done using a 900 mHz radio. Electrode and MicroCat cables were passed through the stainless steel instrumentation well and controlled by the AIS-ISEA-III.

Electrodes were mounted at three different depths along the mooring cable (1.5 m, 5 m and 8 m), and one working electrode, along with the counter and reference electrodes, was mounted to the frame on the bottom of the buoy (1 m deep), and the MicroCat CTD was mounted 1.5 m down on the mooring cable. Of the four electrodes, the deepest two failed immediately due to cabling/connector failure because deploying the system placed significant strain on the connectors. The 1.5 m deep electrode lasted for ca. 1 day before connector failure. The electrode mounted on the buoy frame was protected from hazards during deployment and stress on the cables/connectors due to the tidal currents, and collected data for 8 days. After 8 days, the buoy was struck by lightning, prematurely ending our study. For future deployments the system will be modified to incorporate a lightning arrestor and stronger cables.

2.2.5. Data Analysis

Once the raw data files were uploaded from the instrument, they were then converted from a binary file to a text file and analyzed using custom designed Matlab programs. Scans were examined to make sure that the electrodes were functioning properly (Fig. 3), smoothed using an 11 point moving average in order to remove any electrical noise, then analyzed amperometrically by subtracting the limiting current of the oxygen wave (the mean current between -0.5 V to -0.8 V) from the residual current over the range -0.1 V to -0.15 V or from the current at the half wave potential (ca. -0.3 V) determined by taking the derivative of the LSV. The latter was done due to noise at the beginning of some scans which made it difficult to accurately measure the residual current. The H_2O_2 peak was not quantified due to excessive noise. Currents were converted to concentration using the standard curve determined in the lab, corrected for changes in temperature and salinity. Then all the measurements that were taken during the same time period (oxygen, temperature and salinity) were averaged together, giving a data point every 15 minutes. Because our voltammetric scans were taken at 5 s-intervals, each O_2 measurement is from a different water mass (i.e, water is continually flowing while the measurements are being recorded). The mean % variation in the samples was typically 5% (consistent with titrations from water samples collected before and after deployment) but on some occasions was up to 14%. By comparison, O_2 concentrations varied by more than a factor of two over the course of the study. In samples taken by bottles and placed into a voltammetric cell, the variation is better than 1–2% [5, 6] and is a measure of the true reproducibility of the electrode. Additional data for the tidal height and solar radiation were collected from the NOAA data station at the Lewes ferry terminal (station 8557380; http://tidesandcurrents.noaa.gov/index.shtml) and NOAA NDBC station 44009 (http://seaboard.ndbc.noaa.gov/), respectively.

3. Results and Discussion

O_2 was the only chemical species measured by voltammetry because the bay is a relatively healthy ecosystem, and no other electrochemically-active species were present at detectable concentrations. O_2 increases occur primarily due to photosynthesis (Eq. 3) although storms and wave action enhance atmospheric O_2 mixing across the air-water interface. O_2 decreases are due primarily to respiration (reverse of Eq. 3).

$$CO_2 + H_2O \rightleftharpoons CH_2O + O_2 \qquad (3)$$

Over the course of 8 days, 4,756 LSV scans were recorded from the surface electrode and the MicroCat CTD. The data are presented in Figure 4, along with tidal height information recorded at the Lewes ferry terminal and solar radiation data from station 44009. O_2 concentrations at the study site were also determined by Winkler titration shortly after deployment of the buoy, and values obtained from the buoy at that time are within 2–5% of the titrated value. The Delaware Bay is normally a well-mixed estuary, with fresher water coming from the upper reaches of the bay and saline water coming from the mouth of the bay (Fig. 1). In summer the less saline, more productive bay water is warmer than that coming from the Atlantic, and our buoy was well positioned to monitor the differences between these two water sources, reflecting conditions from further up the bay at low tide and conditions at the mouth of the bay at high tide. As a result, salinity and temperature are out of phase, and salinity is in phase with the tides (Fig. 4). During this time, the maximum solar radiation was initially lagging

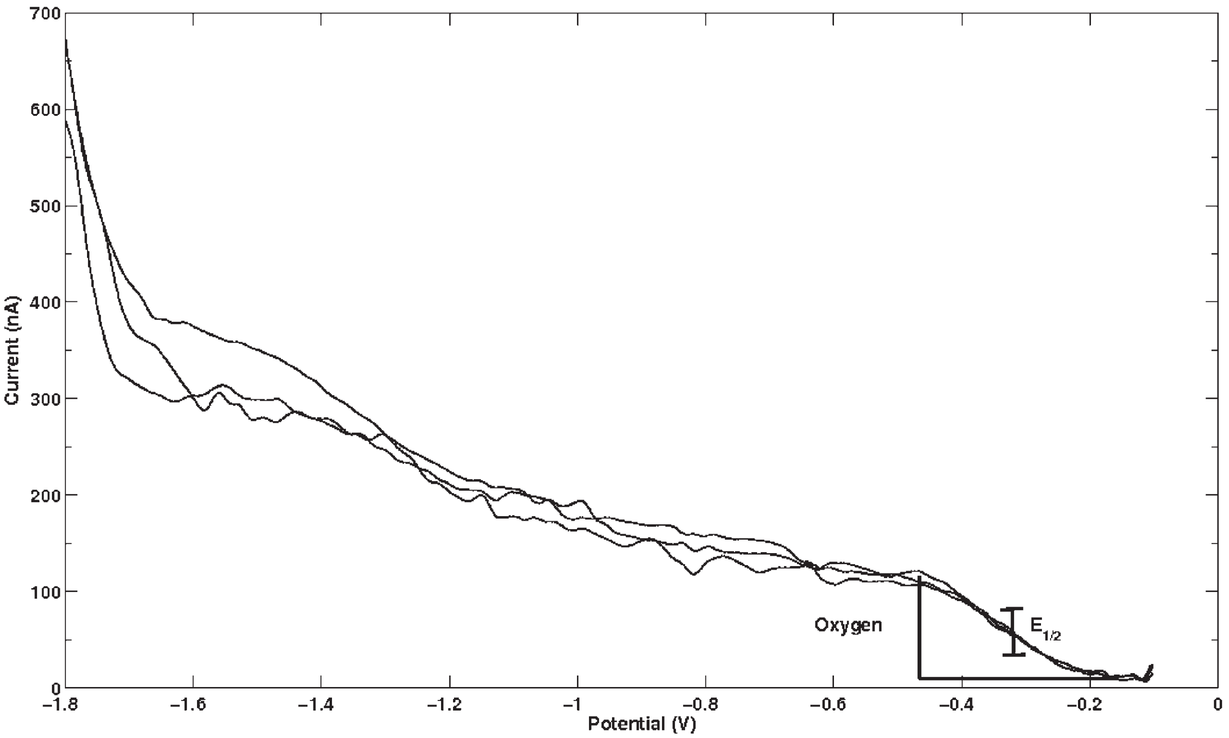

Fig. 3. Three smoothed LSV scans taken every 5 seconds on the surface electrode. Indicated is the $E_{1/2}$ for oxygen and its current. Scans are reproducible for the oxygen signal but can get noisier after the oxygen signal. At a scan rate of 2 V s^{-1} in flowing water, a S shaped wave is seen.

behind the daytime high tide by ca. 3 hours, and by the end of the data collection it was leading the daytime high tide by ca. 2 hours. While this did not significantly affect the water temperature, it did have a number of implications for the dissolved oxygen concentrations observed. Higher O_2 concentrations towards the end of the 8 days of data collection appear due to the increase in solar radiation during the low tide period at our site.

Observed oxygen concentrations ranged from 174 μM to 373 μM, with a mean of 236 μM. Average oxygen saturation in micromolar units for the observed temperature and salinity range is 221 ± 2 μM (O_2 saturation was calculated using the empirical relationship derived by Weiss [20], and will increase with decreasing temperature and salinity). The observed oxygen saturations ranged between 70 and 171%, with a mean of 107%. O_2 over-saturation is common in this system, and is due to photosynthesis [15–17]. Our data showed significant variability, as O_2 saturations could drop from 150% to 70% during the brief overnight period (e.g., Fig. 4, 8/29 to 8/30), as organic matter decomposition is the dominant process in the dark. Other rapid changes during daylight hours appear to be due mainly to cloud cover and mixing of water masses.

Due to the short length of our time series we performed a wavelet transform of the oxygen data using Matlab software designed by Aslak Grinsted (http://www.pol.ac.uk/home/research/waveletcoherence/) instead of using a Fourier transform. A wavelet is a function with a mean of zero that is localized in both frequency and time, and a continuous wavelet transform allows for the recognition of localized intermittent oscillations in a time series [21]. While lacking the precision of a Fourier transform, wavelet transforms have the advantage of being able to use shorter time-series data sets. Using a wavelet on a short time series must be done with caution as it is possible to generate erroneous results. The wavelet transform of the oxygen data (Fig. 5) revealed a strong periodicity at 0.5 and 1 day. A cross-wavelet transform (a comparison of two wavelets, revealing areas of high common power) of the oxygen data with the tide height show an area of high common power that was 180° out of phase at a period of 0.5 day. A cross-wavelet transform of the oxygen data with solar radiation show an area of high common power that is in phase at a period of 1 day.

Based upon the trends observed in the wavelet analysis, both a tidal and day/night trend were present in the oxygen data, as expected based on Equation 3. At high tide the oxygen concentration decreased, due to the lower productivity in the Atlantic Ocean waters, and oxygen concentrations were consistently at or below saturation at these times. This trend was most readily seen during the high tides on 8/28. Productivity in the Delaware Bay was higher than that in the Atlantic Ocean, and the maximum productivity was observed at the buoy when the maximum in solar radiation happened at low tide (i.e., when the Delaware Bay waters' signal is strongest). This trend was most clearly seen between 8/29 and 8/30.

The buoy was recovered after 6 weeks, as the R/V Cape Henlopen was in use on other projects. Upon recovery the MicroCat CTD was overgrown in algae, but still serviceable.

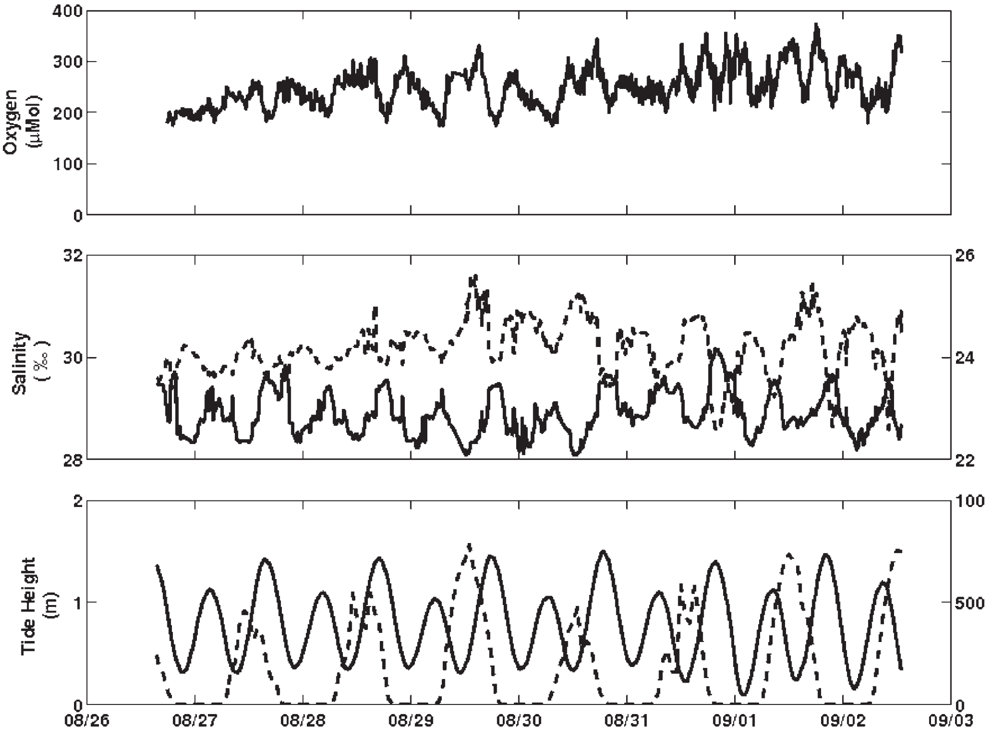

Fig. 4. Top Panel: Oxygen concentration collected every 15 minutes (each point is the average of 5 scans taken at the same time). Middle Panel: Salinity (solid line) and temperature (dashed line) collected by the MicroCat CTD. Lower Panel: Tide height (solid line) from the NOAA data station that the Lewes ferry terminal and solar radiation (dashed line) from the NOAA NDBC station 44009.

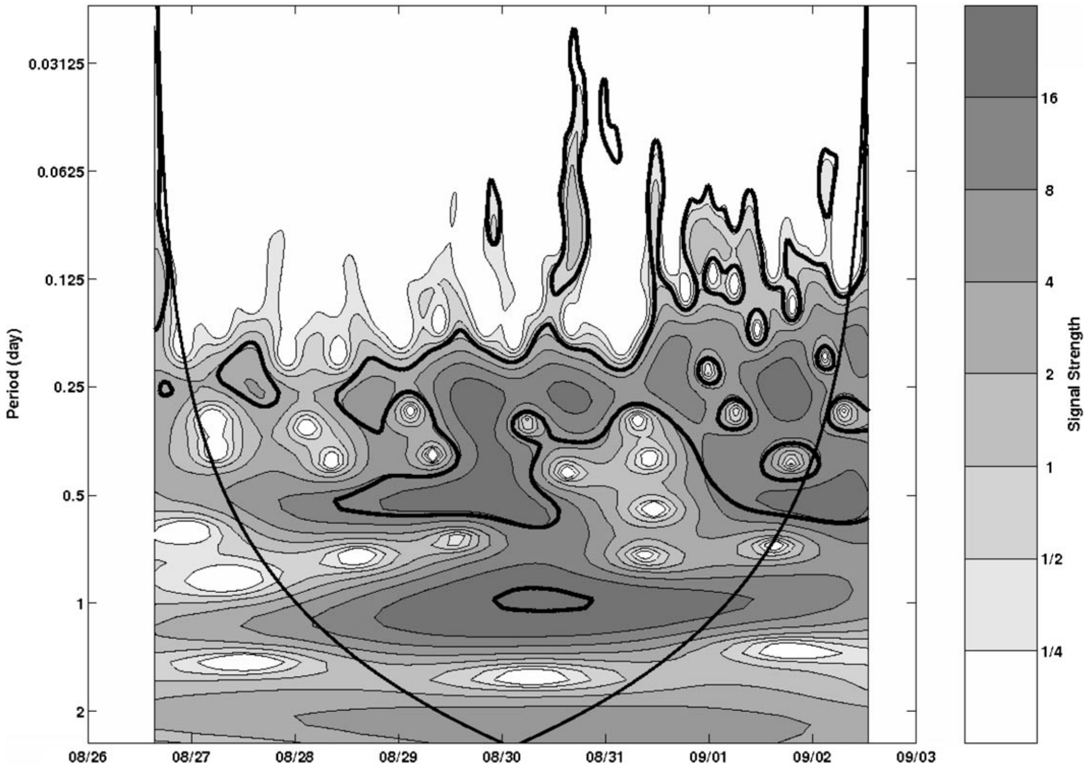

Fig. 5. Continuous wavelet transform of the oxygen data performed using Matlab software designed by Aslak Grinsted. Darker areas indicate areas of high signal power, thick black contours designate the 5% significance level against random noise, and the thin black line is the cone of influence, outside of which edge effects might distort the wavelet.

The counter and reference electrodes had significant overgrowth on the protective Teflon guards, and test O_2 scans performed in the lab after recovery found them to be in good working condition. The working electrodes were recovered with no significant fouling observed, but the working electrode was not at the same calibration upon recovery (due to a lack of use after the lightning strike).

4. Conclusions

The need for observatories, which can perform continuous time-series measurements in oceanography, has been recognized, and this study demonstrates that voltammetry at a Au/Hg working electrode and voltammetry equipment can be useful on observatory and mooring systems. The system used here would readily provide even more information if used in a system that experiences seasonal anoxia (e.g., the Chesapeake Bay [22, 23] and the Gulf of Mexico off the Louisiana coast [24 – 27]), as the working Au/Hg electrodes used are non-selective and sensitive to H_2S as well as other reduced chemical species. Our 8 day study from a relatively healthy, well-mixed estuary revealed how complex a seemingly simple system can be. The variability in the data presented here demonstrates the importance of time-series measurements, as discrete sampling from a ship followed by traditional shipboard analyses would have missed much of the variability seen here. These data revealed both tidal and day/night trends at this site, and the combination of these two processes in lowering oxygen is important for the recruitment and settlement of oxygen sensitive biological species (e.g.; fish and crabs [28, 29]).

5. Acknowledgements

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