# Time-Series Measurements of Atmospheric and Oceanic $CO_2$ and $O_2$ in the Western Gulf of Maine

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***Abstract-*** ***A collaboration has been established between the University of New Hampshire's (UNH) Joint Center for Ocean Observing Technology and NOAA's Pacific Marine Environmental Laboratory (PMEL) to adapt and deploy an autonomous carbon dioxide measurement system on a moored platform in the coastal Western Gulf of Maine. This buoy provides high-resolution time-series measurements of atmospheric and oceanic $CO_2$ values and is useful for the estimation of air-sea $CO_2$ fluxes and monitoring coastal zone biochemistry dynamics. In addition, with its close location to the coast, it allows study of terrestrial air mass effects on marine air-sea $CO_2$ exchange. This paper provides details on the overall system including field validation of buoy observations. This validation includes data from a nearby UNH AIRMAP atmospheric observing station on Appledore Island and a monthly shipboard cruise transect made by the UNH Center for Coastal Ocean Observing. These assets permit evaluation of dissolved oxygen and both air and water $CO_2$ levels.***

## I. INTRODUCTION

The Gulf of Maine is a biologically-productive, temperate latitude, semi-enclosed continental shelf sea. It has 7,500 miles of coastline and is sheltered from the Northwest Atlantic Ocean by Georges and Browns Banks. Numerous large rivers feed into the Gulf as do waters from the Scotian Shelf to the north. Carbon fluxes at the land-ocean boundary are one area of uncertainty in current coastal $CO_2$ budget analyses as is the control by biological productivity. Cai et al. [1] has suggested that mid-to-high latitude continental shelves should act as sinks for atmospheric $CO_2$ but little data to evaluate this exists in the Gulf of Maine. These reasons led to our deployment of a $CO_2$ air-sea flux platform in this coastal region. Our long-term goal is to work collaboratively with NOAA Pacific Marine Environmental Laboratory (PMEL) and others to determine if the coastal NW Atlantic is a net source or sink of $CO_2$ through the collection of both temporal and spatial data using a variety of sampling methods including moored platforms.

In June of 2006, through a joint effort between the University of New Hampshire (UNH) and PMEL, the first UNH $CO_2$ buoy was deployed in the Gulf of Maine allowing high temporal measurements over a sustained period. This buoy is deployed approximately 12 km off the coast of Southern Maine, just north of the Isles of Shoals in 70 m of water. It is one node in NOAA/PMEL coastal network. As of May 2008 the NOAA $CO_2$ Program, working with several collaborators, has expanded the moored array to 10 open ocean and 4 coastal ocean $pCO_2$ moored systems. The primary objectives of this note are to describe specific details related to the UNH installation and operation of the NOAA system, the overall system performance to date, and forthcoming upgrades.

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Figure 1. The UNH $CO_2$ buoy deployed in the coastal Gulf of Maine in North of the Isles of Shoals.

## II. BUOY

### *A. Buoy Design*

The UNH buoy (Fig. 1) chosen to deploy the $CO_2$ sensor is a buoy developed at WHOI for GLOBEC and then used as a prototype in the Gulf of Maine Ocean Observing System (GoMOOS) [2]. This buoy was designed to be a flexible ocean-observing platform, allowing for instruments to be installed and removed as needed and to be easily upgraded with new sensors at a minimal cost. It is 2 meters in diameter and 3.5 m tall with a Surlyn foam flotation collar (Gilman Corporation). The Surlyn foam was cut with two chines so that the bottom of the foam resembles a sphere. Thus there is minimum tilting force due to the surface wave slopes - minimizing buoy pitch and roll effects. The buoy hull is 5400 series aluminum with zinc protection and has shown no corrosion with about 10 years in the water. With the majority of the flotation in the lightweight foam, the buoy with full

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suite of instruments weights about 700 kg. The relatively small size and weight of this buoy makes it ideal for deployments off small R/V's and fishing boats available in our region (Fig. 2). In GLOBEC and GoMOOS configurations, the buoy used solar power to charge four 12 V power 34 Ah glass mat batteries using four 20-watt solar panels through standard shunt regulators.


Figure 2. The UNH $CO_2$ buoy aboard the UNH Research Vessel Gulf Challenger ready to deploy.

*B. PMEL $pCO_2$ Sensor, installation, and deployment*

In 1992 researchers from the Monterey Bay Aquarium Research Institute (MBARI) developed a method for the equilibration of dissolved gases and subsequent *in situ* infrared gas analysis using proven $pCO_2$ measurement technology [3]. In 1993 they deployed this $pCO_2$ system on a moored platform and collected hourly $\Delta pCO_2$ data for a 70-day period with an accuracy of 1-2 ppmv (parts per million per volume) [4]. Working with MBARI, PMEL researchers developed a new generation autonomous pCO2 system that uses a Licor-820 detector together with a calibration gas to make accurate $pCO_2$ measurements in seawater and the atmosphere. Atmospheric and seawater oxygen partial pressures are also measured using a motion stable galvanic cell oxygen probed (MAX-250, Maxtec, Inc.). The present version of the PMEL $CO_2$ sensor system is packaged in three separate pressure cases containing the electronics, a reference (span) $CO_2$ pressurized gas tank for *in situ* calibration, and a D-Cell battery pack. The system also includes a MBARI-style equilibrator with a PMEL-developed atmospheric inlet device (airblock) (Fig. 3). The data is recorded internally and also telemetered daily to PMEL via Iridium satellite for processing and display on the www.

For the UNH platform, the electronics, battery, and Span gas tank units were each mounted within the 0.5 m diameter by 1 m deep instrumentation well (see Fig. 4). Wooden and PVC inserts at the well bottom secure the PMEL subsystems. The tops of the cases are bolted to vertical bars welded to the inside of the pressure case insuring a rigid installation (Fig. 4). The PMEL battery pack is used solely to power the $CO_2$ system. The buoy's solar power, now with one battery, is used to power the navigational light as well as one Aanderaa oxygen Optode sensor and Persistor-based data recorder. A self-powered Seabird Microcat temperature and salinity sensor is mounted at a depth of 0.5 m on the buoy substructure and provides serial data to the PMEL data logger and also logs data internally. The Optode unit is mounted alongside the Microcat. The buoy is moored with a traditional chain catenary mooring with a 1,200 kg anchor. Five meters of ¾" chain are used just below the buoy, then 60 meters of ½" chain in the water column, a 5 ton swivel and another 70 meters of ¾" chain to the anchor.

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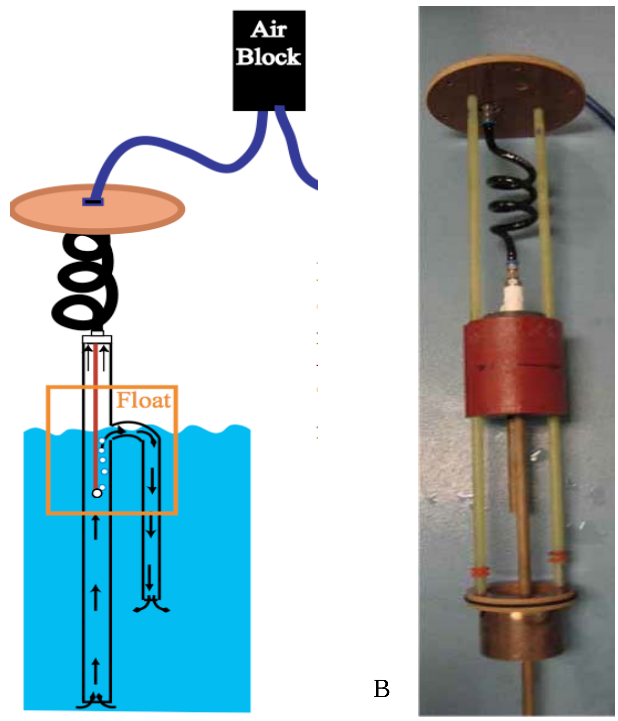


Figure 3. (a) Diagram of the buoy's equilibrator and airblock demonstrating recirculating water filling the head space with gas. The water is typically recirculated for 10 minutes. (b) Photo of the equilibrator with float.

In order to properly employ the system's dissolved gas equilibrator, the buoy's floatation collar needed to have a hole bored through it. The Gillman Corp. successfully upgraded the foam without comprising the buoyancy of the buoy. The lower leg of the equilibrator is located a depth of 0.6 m below sea level. Two versions of the gas equilibrator have been deployed. The first had a 70/30 Cu to Nickel ratio while the latest version has a 90/10 ratio. The change is made in an attempt to reduce biofouling. The airblock is mounted to the buoy tower near the top of the solar panels, 1.5 above sea level (Fig. 1). This device also serves as a manifold for the equilibrator. The buoy's bulkhead penetration plates (Fig. 4) can easily handle all cables and tubes leading to and from the electronics case to the airblock. As a safety feature, a pressure release valve is incorporated into one penetration plate to assure the lid of the well will not blow open were the span tank to leak.

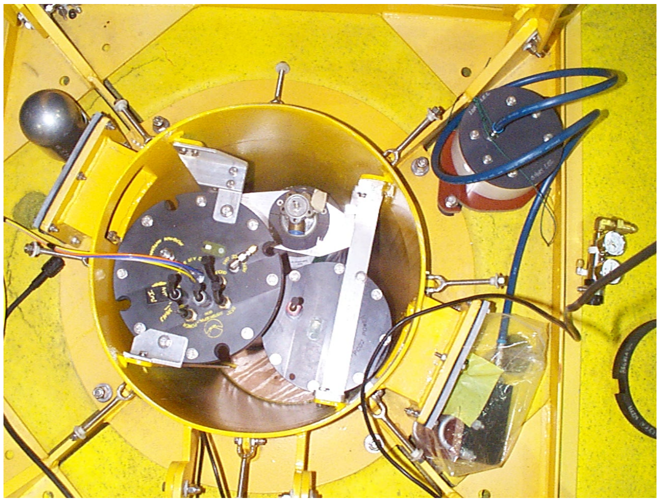

Figure 4. Top view of the electronics (left), span gas tank (top) and battery pack (right) installed in the buoy well. The bulkhead penetrator plates are seen in the upper left and lower right with three penetrations in each plate. The top of the equilibrator is the round PVC plate on top of the 6” hole in the surlyn. The airblock is shown in the lower right in a plastic bag beside the bulkhead penetrator plate and has yet to be mounted in the tower.

The system is operated in a manner consistent with typical PMEL default settings. Data are collected at the top of the hour using a 12 minute measurement cycle that includes Licor calibration using air drawn through a soda lime chamber for zero and the span tank sample with a 505 ppmv $CO_2$ reference value. Temperature and system pressure are closely monitored and recorded. The equilibrator is operated roughly 10 minutes and then headspace air is measured for both $CO_2$ and $O_2$ along with relative humidity. For the Gulf of Maine deployment, we have set the system to record data at time intervals including 2, 3, and 6 hours. The rate is now controlled via Iridium from PMEL and has been adjusted to adapt to sampling needs and battery limits, helping to extend mission length while capturing gas dynamics at all scales longer than 6 hours and often at a two hour time step. The system has been deployed and recovered to date using the UNH R/V Gulf Challenger. Deployments have been from March-Nov. 2006 and Mar. 2007 – June 2008 with more than 20 months of successful operation. Data can be viewed at the PMEL website (www. pmel.noaa.gov/co2/coastal/NH/data_070w-14d.htm).

## III. Results and Discussion

### *A. Buoy Data Quality Assessment*

While the NOAA/PMEL $CO_2$ system has been operated in the open ocean with great success, coastal zone measurements can present new challenges due to the larger physical and biochemical signal range and short-scale temporal dynamics. Foremost, biofouling issues are potentially much more significant in biologically productive waters such as the UNH mooring site. For these reasons, close attention is being given to the data quality for all variables in the buoy measurement suite. Focus in this note is mainly on the dissolved gas measurements.

As mentioned, the buoy measurement location is 12 km off the coast in 70 m or water. The site was chosen in part for its proximity to a range of ancillary data measurements that can both help in buoy data quality verification but also scientific data analysis using additional types of atmospheric and oceanic measurements. Nearby GoMOOS Buoy B (NDBC 44030, less that 12 km to the north) provides wave and meteorological data, fluorescent chlorophyll, ADCP current profiles and T/S observations at multiple depths to augment the $CO_2$ buoy data. An NDBC C-Man station (IOSN3) on White Island 6 km to the south of the buoy also provides meteorological data.

Most importantly for this note is the routine measurement of CO2 via two independent sources. First is the UNH AIRMAP (www.airmap.unh.edu) observing station on Appledore Island (AI), ME (42.97N, 70.62W), located 12 km E from the coast of NH at the Shoals Marine Laboratory. Sampling for $CO_2$ has occurred here in summer months 2004-2006, operating in a continuous time-series mode with data recorded at 1 min intervals. Ambient air is drawn from a 5.1 cm i.d. Teflon manifold located atop a World War II-era lookout tower 36 m above sea level (asl). An infrared gas analyzer (Li-7000) samples the air at 0.5 liters per minute (lpm). The Li-7000 is automatically zeroed with Ultra High Purity Nitrogen (UHP $N_2$) every 12 hours and is calibrated every 14 hours with a standard (Scott-Marrin, Inc., Riverside, CA). Calibration standards range between 370 and 400 ppmv ± 1% and used by the system for approximately one year before replacement.

Monthly R/V Gulf Challenger shipboard transects of this same coastal Gulf of Maine region provide an oceanic data calibration source. A continuous sampling of atmospheric $CO_2$ is drawn from a Teflon-lined bow intake at a height of 3 m asl. An infrared gas analyzer (Li-840, Li-Cor ) with custom built sample water vapor removal loop (Nafion filter with $N_2$ gas) is used to measure dry $CO_2$ at a 0.1 lpm flow rate. Prior to implementing this continuous mode atmospheric data in 2006, the airside measurements were acquired periodically over a 3-5 min measurement period during cruises from the same bow intake using a similar IR-based system.

Flow to the shipboard flow-through system was also pumped to an equilibrator (Fig. 5), similar to that described by Wanninkhof and Thoning [5], but consisting of three Plexiglas chambers instead of a single chamber. Equilibrated air was drawn out of the third chamber, while ambient air was drawn into the first chamber and passed through the second and third chambers, equilibrating with the pumped water supply at each step. Equilibrated air was dried and measured as described aboved for atmospheric $CO_2$. Calibration procedures and standards are akin to those used at the AIRMAP site, excepting that the $CO_2$ standard gas span tank used on the ship is nominally 820 ppmv (Scott-Marrin, Inc., Riverside, CA). Monthly Challenger cross shore transects provide data from 3 to 80 km offshore, with the ship passing directly by the mooring on an ESE heading and returning the same day on a reverse course. Data processing filters out any possible ship exhaust contamination influencing the atmospheric $CO_2$

mixing ratio estimates. Measurements from twenty-one cruises between May 2004 and June 2008 are used to support this study. We have recently instituted fixed station sampling near the buoy that includes Winkler titrations for dissolved oxygen as well as inorganic carbon (DIC) and total alkalinity measurements.

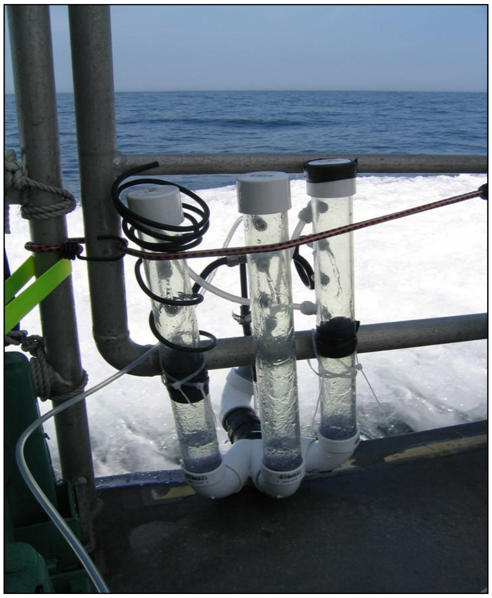

Figure 5. The equilibrator used for the COOA monthly research cruises. Water is sprayed against the walls of the 3 chambers allowing equilibrium within 30 seconds for fast-rate continuous $CO_2$ sampling.

The AI tower atmospheric $xCO_2$ ($CO_2$ concentration in dry air) measurements provide an excellent means to assess PMEL system data quality. Figure 6 presents 30 min. average AI measurements at 36 m asl versus the buoy data at 1.5 m asl. Recall that spatial separation is roughly 7 km along-shore. While only a small segment of the total data is shown, it is given to illustrate the close agreement that we almost always see between these two sites. The offset between the data for this 20 day period is 0.39 ppmv and the standard deviation is 1.7 ppmv. The agreement is impressive and suggests an excellent agreement between the calibration standards and the overall measurement systems. Numerous months of such data indicate the two systems track to an offset below 1.5 ppmv and the standard deviation is typically below 2.0 as well. No baseline drift in either system is observable. Note that there are two outliers in the figure. These points represent cases where freezing spray has blocked the atmospheric intake on the buoy. These points are easily recognized by looking at sea state, winds, and temperature data and are very infrequently seen in the winter operations performed so far.

Figure 7 provides a comparison of $xCO_2$ measurements between the shipboard and buoy observations over the period of our buoy deployments. These ship estimates represent data collected using the flow-through system data collected within a radius of 2 km around the buoy site and within +- 1.5 hours. Clearly the number of samples available is much less than for the AI and buoy atmospheric time series. However, there are still more than 30 measurements for comparison. The bias shows the buoy to be 1.50 ppmv below the shipboard data with a standard deviation of 14 ppmv. These statistics do not include the sample where biofouling (see section III B) is indicated on the figure. Good agreement is seen over a range of inwater values that span 300 uAtm – a much larger range than for the atmospheric data due to the physical and biological controls on the seawater $CO_2$ at this site. The larger standard deviation than for the atmospheric comparison is still quite encouraging. We attribute this number both to solubility effects tied to temporal and spatial sea temperature dynamics near the site both horizontally (e.g. tidal) and vertically. Recent data collected near the buoy by the NOAA R/V Ron Brown also confirmed the inwater buoy pCO2 system is working to an accuracy that is better than 3 ppmv – a level that is excellent for the 10-100 ppmv dynamics for seawater observed near this site.

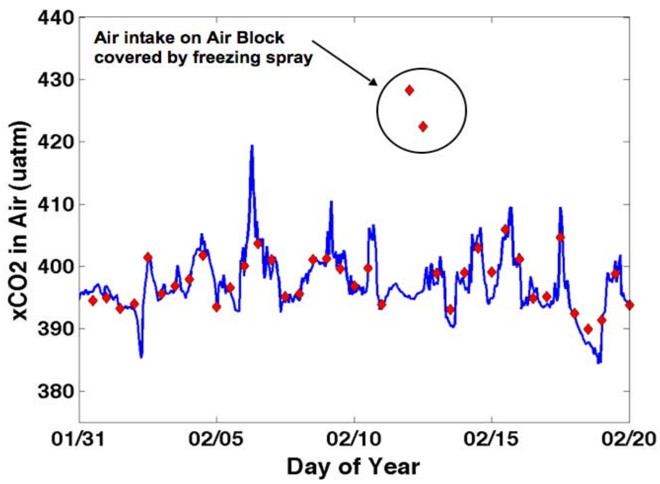


Figure 6. Comparison of Appledore Island atmospheric $xCO_2$ (blue line) to PMEL's buoy atmospheric xCO2 (red diamonds). The offset for the data is 0.39 ppmv and a standard deviation of 1.7 ppmv.

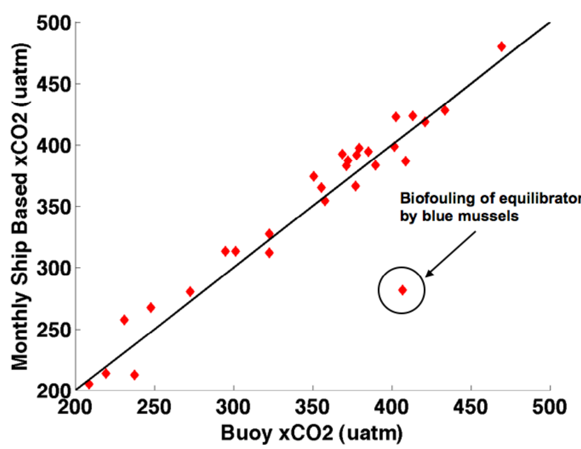


Figure 7. Comparison of monthly COOA cruises in water $xCO_2$ measurement (black line) to buoy measurements in water $xCO_2$ measurements (red diamonds) when boat was within a radius of 2 km around the buoy's location and within +-1.5 hours of a buoy measurement.

Figure 8 provides a comparison of dissolved oxygen (DO) data as measured by two sensors on the buoy, the PMEL Max-250 $O_2$ sensor estimate of equilibrated $O_2$ and the Aanderaa Optode DO sensor mounted at 0.5 m depth. Two Winkler-derived discrete shipboard surface water DO samples are also shown. Several features stand out here. First, the Winkler data agree more closely with the Optode data than with the MAX-250. Second, there is a large offset between the two sensors over this period. Third, the peak-to-peak dynamics of the Optode DO data are much greater than for the MAX-250 data. In general, the Optode measurements are becoming trusted DO estimators with accuracy that typically exceeds 5 uM/l. The Winkler data bear this out. The offset of nearly 50 uM here with the equilibrated $O_2$ is hypothesized to be a problem not with the MAX-O2 sensor (MAX-250 measured atmospheric $O_2$ data is not shown but is close to the expected 20.5 %) but rather with the adequate equilibration of DO into the headspace used to measure the gas. The expectation is that the PMEL/MBARI equilibrator setup is adequate for stripping $CO_2$ but not for the much less soluble $O_2$. The result is the DO derived using the MAX-250 sensor is providing a correlated, but inaccurate estimate of DO. Further comparisons with other Optode and Winkler data are ongoing to ascertain if a post-deployment correction is possible to allow data utilization.

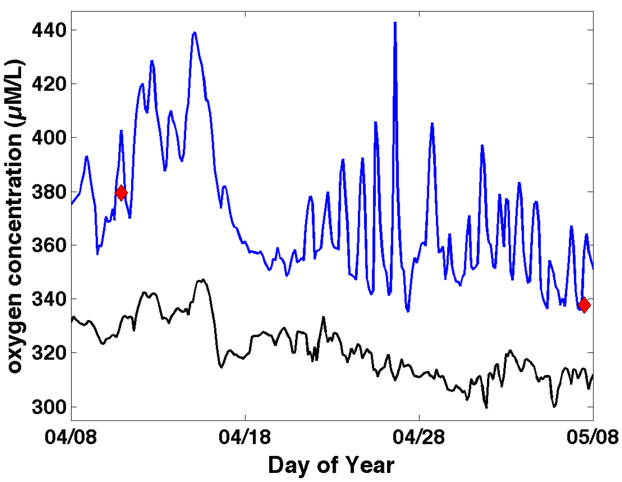


Figure 7. Comparison of dissolved oxygen data. The blue line is data collected from an Aanderaa Optode sensor and the black line is data from the PMEL oxygen sensonr (MAX-250). The red triangles are winklers collected during a COOA research cruise .

*B. Data Losses Due to Environmental Effects*

The buoy was deployed for 8 months in 2006, and for 14 months starting in March of 2007. Several buoy visits have been made within these periods to pull the buoy onboard and change out the optode and T/S sensor and remove subsurface growth of algae, barnacles and mussels. Overall, the $CO_2$ system has performed well and is generally trouble free. During the cold winter storms, ice has infrequently (less than 10 times total) plugged the air block, but the system soon recovers fully. The biggest problem, as yet unsolved, is equilibrator biofouling after extended unattended deployment. Mussel growth has been a problem during long deployments, necessitating routine servicing (buoy pulled on deck in good weather and cleaned) (Figure 8). Modifications to a 90/10 copper-nickel equilibrator to reduce servicing and maintain data quality proved to work up to about May 2008, but the inwater $CO_2$ data once again became inaccurate (see Fig. 6). June 2008 post-deployment assessment showed significant growth of algae and mussels surrounding the equilibrator intake. At this time, we have yet to develop a stand-alone means to identify the time when biofouling begins to degrade measurement accuracy. Finally, the buoy has operated successfully through severe Northeasters including one event exceeding 8 m significant wave height.

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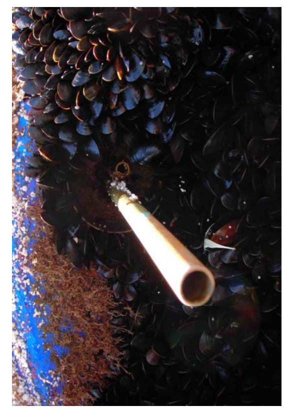

Figure 8. The buoy equilibrator housing (a) before and (b) after biofouling by the blue mussel *Mytilus edulus*. As mussels settle and grow in and around the housing their respiration can start to alter the ambient seawater $CO_2$ signal.

*C. Future Buoy Upgrades*

Plans for the summer 2008 servicing of the mooring and sensors will replace the standard battery pack of alkaline cells with four 42 ampere hour solar charged absorbed glass mat lead acid batteries to power the $CO_2$ system and supporting sensor systems. In order to provide for the larger power requirement of the $CO_2$ system, telemetry and auxiliary sensor system, the solar panels are being upgraded to 4 forty-watt solar panels.

Also, additional sensors and a separate data system with RF telemetry will be added to the buoy system. The new sensors include a Gill 2-D sonic anemometer with KVH digital compass, a Vaisala air temperature, relative humidity and pressure sensor, a WetLabs FLNTU chlorophyll fluorometer and optical backscattering sensor, and a WetLabs CDOM sensor. The Sea-Bird pumped Microcat and Aanderaa Optode will be retained. A Freewaves spread spectrum radio will connect the system to shore, and the two way link will permit routine system and battery state monitoring, and allow sampling changes to be made to both the $CO_2$ system and the auxiliary sensor system. The RF link will be independent from the already successful Iridium link dedicated to the PMEL data collection on the buoy.

The data system for this auxiliary sensing system will be a Triaxys Watchman-500 data system which is a low power microprocessor-controlled system that will switch power to sensors, receive serial data from each sensors, parse it and processe it (average, maximum, mean, standard deviation), and also any additional processing as required. The system will store the data internally on compact flash card, and send it out the spread spectrum radio to shore for integration with the Iridium-linked $CO_2$ system data. Data will be sampled at appropriate rates and averaged to 10 minute samples, and telemetered to shore.

The system will be deployed for 12-16 months in fall 2008 with several planned visits to assess and limit biofouling impacts on the data quality. The ongoing program will also include further calibration and validation of these data using shipboard and AIRMAP sampling.

## ACKNOWLEDGMENTS

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