A Multiyear Assessment of Biological Pertubations of CO_2 in the Northeast Channel of the Gulf of Maine

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Abstract—**The University of New Hampshire (UNH), in collaboration with the University of Maine at Orono (UMO) and the University of Montana, has been monitoring surface ocean dissolved carbon dioxide and oxygen in the Northeast Channel, at a site on the northeast flank, of the Gulf of Maine for the last several years. UMO has maintained a buoy at this site (Buoy N) since 2004, and UNH has deployed two instruments (the SAMI-CO_2 Sensor (Sunburst Sensors, LLC) and an Aanderraa Instrument Oxygen Optode 3835) since March 2008. The controls on the CO_2 system are examined to determine the dominating biological seasonal influences that occur alongside physical processes. We evaluate several approaches to isolate these factors and processes using the buoy data and following previous studies. Preliminary results suggest measurable interannual biochemical variability may be attributed to water mass dynamics at this site.**

Keywords-CO_2 air-sea flux; ocean DIC; Gulf of Maine; ocean carbon cycle; biochemical sensors; dissolved oxygen

I. INTRODUCTION

Since the beginning of the industrial revolution, the atmospheric concentration of carbon dioxide (CO_2) has increased from 280 ppm to 380 ppm. Most of this increase resulted from the anthropogenic burning of fossil fuels, but to a lesser extent, from land use changes. Atmospheric concentrations of CO_2 have decreased from the oceanic uptake of CO_2. Several studies in this region show tis shelf region to be a weak source of atmospheric CO_2 but the data are insufficient to conclude that this is a persistent and long-term result [1]. However, the oceans ability to continue the uptake of anthropogenic released CO_2 is decreasing as sea surface temperatures increase and pH decreases [2]. Other factors influence the partial pressure of CO_2 (pCO_2) in seawater, such as temperature, salinity, the concentration of dissolved inorganic carbon (DIC), and alkalinity [3]. The atmospheric CO_2 that the ocean takes up increases that anthropogenic DIC component of seawater, which increases ocean acidification [3].

The pCO_2 in the surface waters of the ocean is controlled by a variety of parameters, including total CO_2, total alkalinity (TA), temperature, salinity, phosphate ion, and silicate [4]. There are physical (mixing and advection, warming and cooling, gas exchange with the atmosphere, and diffusive transport of CO_2), biological (photosynthesis and respiration), and chemical (carbonate formation and dissolution and photooxidation) controls on the total CO_2 (essentially DIC) in the upper mixed layer of the ocean [3, 5, 6].

What makes it difficult to quantify the controls that change CO_2 concentrations is that more than one factor is often responsible for CO_2 changes [5, 7]. Measuring dissolved oxygen (O_2) concentrations along with DIC can help determine which process is dominating control over CO_2 in the water column [7]. Reference [7] observed that an undersaturation of pCO_2 along with a supersaturation of O_2 with respect to the atmosphere implies photosynthesis dominating DIC; conversely a supersaturation of pCO_2 and an undersaturation of O_2 indicate net respiration. Variations in O_2 do not merely reflect biological processes, but also reflect air-sea gas exchange [8]. However, during strong blooms, CO_2 and O_2 fluxes can present a significant inverse correlation, which may be indicative of air-sea gas exchanges driven by biological processes [5]. Temperature changes often explain warming of surface waters that leads to outgassing and a corresponding decrease in pCO_2 [1].

Lack of coincident physical and biogeochemical observations associated with the CO_2 flux has made it difficult to determine the contributions of the coastal ocean to the global air-sea CO_2 flux [3]. CO_2 and DIC in the coastal ocean can be highly variable, with larger variability than seen in the open ocean [1, 3]. Some reasons for this are that the coastal ocean receives large inputs of organic and inorganic matter and nutrients from land and river runoff, exchanges large volumes of matter and energy with the open ocean across the continental slopes, and is one of the most biologically active areas of the biosphere [9, 10]. The coastal ocean has been largely neglected in global carbon budgets even though the flows of carbon and nutrients are disproportionately high in comparison with the surface area [9]. This neglect is largely caused by the uncertainty in the role of continental shelves in the air-sea exchanges of CO_2, and also because the exchange is highly variable with time and space [2].

In order to provide a reliable estimate of air-sea CO_2 exchange in the coastal environment, high temporal and

spatial coverage is needed [10]. Historically, sparse oceanographic measurements have limited our ability to quantify the air-sea flux of CO_2 on the continental shelves [2]. To remedy this, continuous measurements of physical and biogeochemical parameters are needed [1, 10]. One approach, which we will examine, is via autonomous biochemical sensors and several recent studies show that long-term ocean CO_2 observations can be achieved with reasonable accuracy [11].

A. Northeast Channel in the Gulf of Maine

The Northeast Channel (NE Channel) in the Gulf of Maine is one of two deep water access points to the Atlantic Ocean (the other is the Great South Channel), and has a depth of approximately 230 m [12]. The NE Channel has several noteworthy features. There are strong semidiurnal tidal currents here that contribute a strong inflow on the eastern side of the NE Channel, and a strong outflow on the west side [13]. Most of the time, there is a deep inflow of slope water into the NE Channel, but occasionally, fresher surface water from the Scotian Shelf (SSW) is also observed [12, 13]. The SSW is distinguishable by its low salinity and temperatures [14]. UMO Buoy N is located at 42.33 N; 65.91 W on the NE flank of the channel (Fig. 1).

B. Buoy N Instrument Cluster

The University of New Hampshire (UNH) and the University of Montana (UM) have been supporting nearly continuous biochemical observations in the NE Channel since March 2008. To our knowledge, this site represents the first offshore coastal shelf CO_2 time series in the NW Atlantic Ocean. Buoy N resides in 230 m of water, and consists of a string of autonomous physical oceanographic instruments attached at various depths (http://gyre.umeoce.maine.edu/data/gomoos/buoy/). At a depth of 3-5 m, an instrument cage holds two key instruments (Fig. 2) for this study, the SAMI-CO_2 Sensor (Sunburst, LLC) and the Oxygen Optode 3835 (Aanderraa Instruments). CO_2 data have been collected at this site over three separate deployments since April 19, 2008 at a depth of 3 m (Oceans Processing Analytical Lab, UNH). This analysis will look at time series data from April 19, 2008 until August 19, 2010 when the instruments on Buoy N were last serviced. Data on temperature, salinity, pCO_2 and dissolved oxygen are all measured at this site.

II. QUALITY CONTROL OF PCO$_2$ DATA

Studies have shown exceptionally long-term stability and sensitivity in the Submersible Autonomous Moored Instrument for CO_2 (SAMI-CO_2) sensor [11]. The operating characteristics have been calculated to having an accuracy of $\pm$ 1 µatm and a precision of $\pm$ 2 µatm [11]. The main difference between other CO_2 sensors and the SAMI-CO_2 is that the SAMI-CO_2 sensor is able to periodically renew its indicator solution, thus enhancing the stability and sensitivity in the sensor [11].
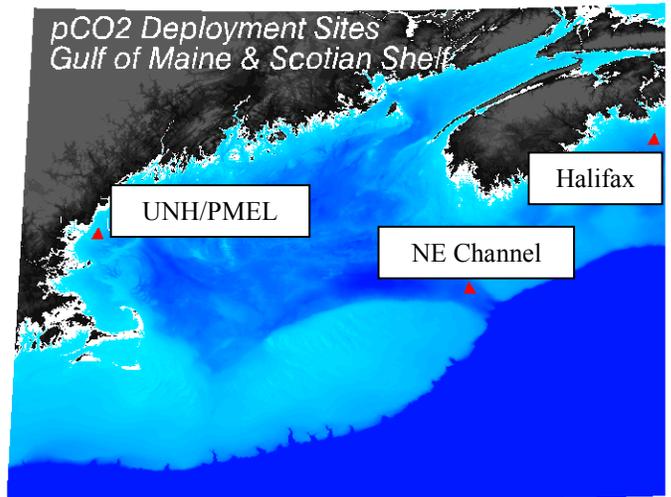

Figure 1. Map of the pCO_2 deployment sites in the Gulf of Maine and Scotian Shelf. The red triangles indicate where the pCO_2 monitoring sites are off the coast of Halifax, the Northeast Channel, and the UNH/PMEL buoy off the coast of Portsmouth, NH (image provided by D. Vandemark).
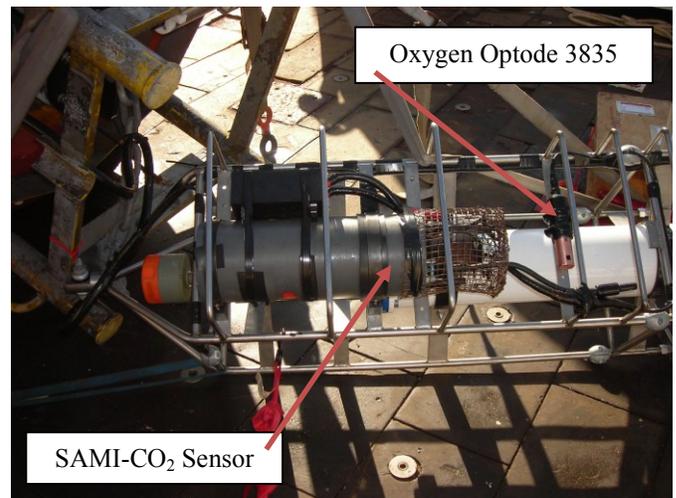

Figure 2. This instrument cage is found at a depth of 3-5m on Buoy N in the Northeast Channel of the Gulf of Maine (image provided by S. Shellito). The SAMI-CO_2 sensor and the Oxygen Optode 3835 collect the pCO_2 and the O_2 data for UNH.

The SAMI unit performs a calibration measurement using deionized (DI) water every 3.5 days. As a result, baseline measurements of the 440 and 620 nm (the absorbance maxima of the acid and base forms of the bromothymol blue indicator used by the SAMI-CO_2) are determined [11]. The resulting time series of blank measurements are used to inspect, adjust, and flag bad data within each 3.5 day block of data.

To further ensure the quality of the pCO_2 data, preliminary checks were performed. The entire time series of pCO_2 data were plotted. Any abnormally high or low values were removed from the data set (data valid between the tested operating range of 200 – 600 µatm, [11]). Additionally, pCO_2 was calculated from the DIC and the TA using the CO_2SYS program [15]. The measured pCO_2 data are (Fig. 3). In Fig. 3, there are times when the modeled pCO_2 and measured track
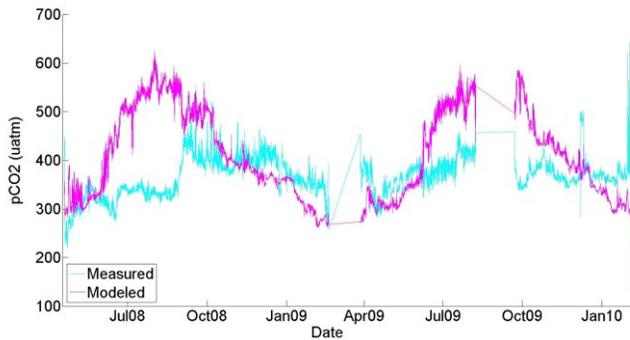
Figure 3. During the three year deployment, there were two gaps in the data where the buoy was removed for maintenance. Sometimes the modeled pCO$_2$ (magenta) tracks well with the measured pCO$_2$ (cyan), other times one is greater than the other which could indicate biological processes like photosynthesis and respiration. Short time scale jumps in the data could indicate the mixing of two water masses.

fairly close together. At other times, the modeled pCO$_2$ is greater than the measured, which could be due to biological activity drawing down inorganic carbon from the system for primary productivity. Other times, the measured pCO$_2$ is greater than the modeled, which could indicate periods of high respiration or ventilation of deeper waters. The two largest jumps in the data occur when the buoy was pulled from the water for servicing. Other smaller shifts in both the modeled and measured pCO$_2$ could indicate the mixing of two different water masses. Further quality control checks on the pCO$_2$ data are currently being performed at the University of Montana.

III. QUALITY CONTROL OF O$_2$ DATA

Several checks on the dissolved oxygen data were utilized to ensure that the data were of high quality. Biofouling on the Oxygen Optode sensor has often been observed after several months at sea, when algae grow on the oxygen sensor. The algae produce oxygen during periods of light, which causes the oxygen readings to be extremely high. During the night, autotrophy is minimal, and the probe measures ambient oxygen readings. This is apparent in the data when a time series plot of dissolved oxygen (Fig. 4) is produced and there is high noise in the data between May 2009 and June 2009. By separating out all the day and night data during these periods, the night data may be used. In order to determine whether the noise seen in the raw data is due to biofouling or known tidal variability, a shorter time series was generated (Fig. 5). Over a two week period (from May 13 to May 28, 2009 as depicted in Fig. 5), the oxygen peaks at unrealistic levels once a day and falls back to a lower values once a day. In order to correct for this biofouling, a program was written (minfilter.m, MATLAB). This program finds the minimum value of the oxygen data over intervals of 20 hourly samples over the length of the measured oxygen data. Only where biofouling is indicated will the minimum values replace the measured values of oxygen (Fig. 6, Deployment2).

There are a couple of methods employed to ensure quality in the oxygen data. Before each deployment, the Oxygen Optode is calibrated to a standard to ensure quality. Over the
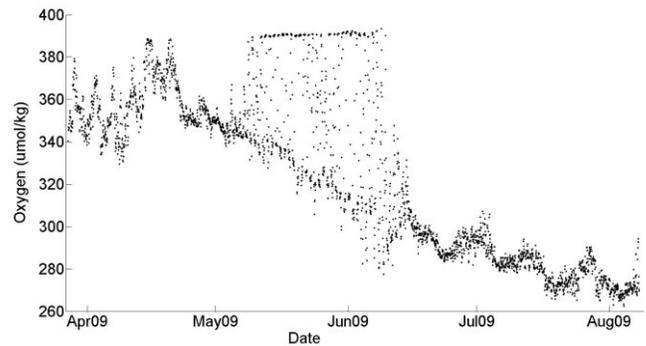

Figure 4. Between the period of May 2009 and June 2009, the measured oxygen data have a large noise signal, indicating biofouling on the sensor.
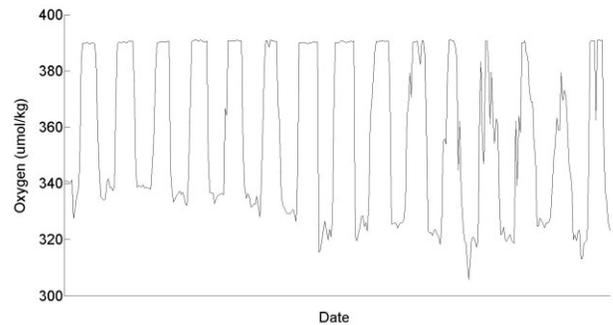

Figure 5. A closer look at the measured oxygen between May 13 and May 28, 2009 indicate that the noise in the data is due to biofouling. Peaks in the data occur once a day during daylight hours, and fall to ambient levels during the night.
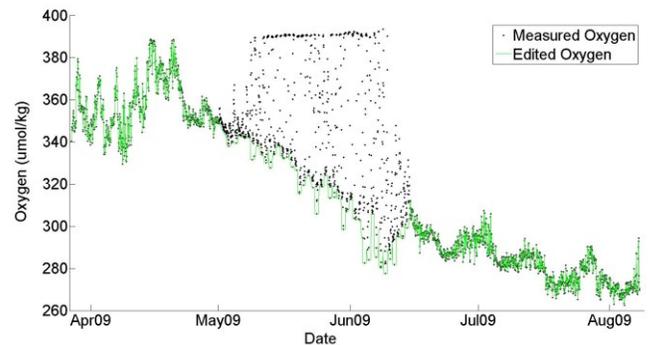

Figure 6. A times series plot of measured oxygen (black) during the second deployment of the Oxygen Optode shows high levels of noise in the data between May and June 2009. After applying the minimum filter to the data (green), the ambient oxygen signal is depicted and agrees with the nighttime values of the measured oxygen.

winter months, storms cause intense mixing in the surface waters in the Gulf of Maine. Consequentially, dissolved oxygen concentrations in the surface waters are in near equilibrium with the atmosphere, which means that the percent saturation of the surface waters is at or close to 100% saturation during the winter [16]. As a means of checking that the Oxygen Optode was providing accurate readings, all the data from the winter months (December, January, and February) were used to produce a time series plot of the

percent saturation (fig. 7). The average winter percent saturation for the first deployment was 100.6%.

IV. INFLUENCES ON DIC

In any aquatic environment, the entire inorganic carbon system can be modeled by knowing two parameters, such as pH and alkalinity, partial pressure of carbon dioxide (pCO_2) and alkalinity, or pCO_2 and dissolved inorganic carbon (DIC). In this case, only the pCO_2 was measured in situ. Following the total alkalinity (TA) modeled from [1],

$$TA_S = 43.2 \times S + 805. \qquad (1)$$

Similarly, the abiotic DIC is modeled [1] as,

$$DIC_S = 46.5 \times S + 546.4. \qquad (2)$$

However, both DIC and TA follow salinity to a first order. Using the salinity measurements and models from [1], TA and abiotic DIC were calculated.

There are several components influencing DIC, where

$$DIC(t) = solubility + mixing_h + mixing_v + R + P, \qquad (3)$$

in the water column, and we can estimate all except the DIC due to R (respiration) and P (production). The abiotic DIC modeled from salinity accounts for the physical components influencing DIC (solubility and mixing). TA is mostly unaffected by multiple biological processes [3], so the modeled TA and measured pCO_2 will be used to determine the DIC. CO_2SYS program [15] is used for the calculation. The biotic DIC is then,

$$DIC_{bio}(t) = DIC - DIC_S \qquad (4)$$

and the difference between the total DIC and the abiotic DIC (Fig. 8). As Fig. 8 shows, there are times when the biotic and abiotic DIC track relatively close to one another. This typically occurs during the winter months when productivity is
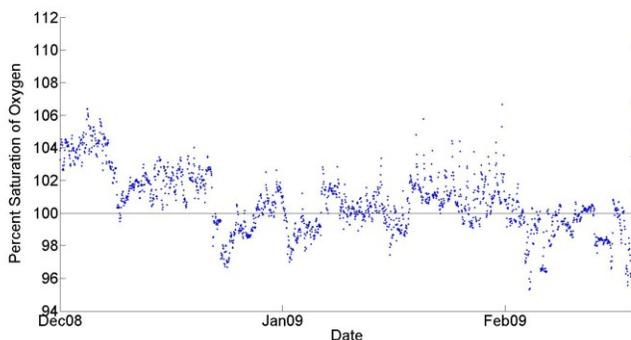
Figure 7. This times series of corrected percent saturation of oxygen is of all winter data (December, January, and February) during the first deployment (start-stop). The average percent saturation during the winter was 100.6% and the 100% saturation line indicated that during these months, the oxygen values were near equilibrium with the atmosphere. This supports the quality of the oxygen data collected towards the end of deployment one.
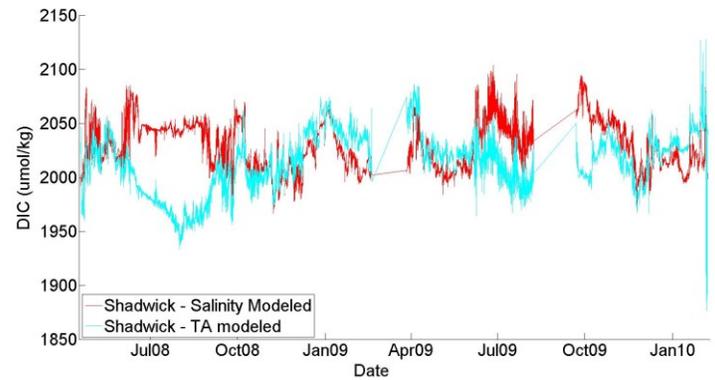
Figure 8. The abiotic DIC (red) shows the DIC modeled after salinity [13]. The DIC (cyan) was calculated from the total alkalinity (modeled from salinity [13]) and pCO_2. The difference between the two lines indicates the influences due to biological activity.

at its lowest. Other times of the year, there are large divergences. This is indicative of when biological activity is drawing down large amounts of DIC for primary production. Other divergences occur in the data, but occur relatively quickly. These divergences are typically due to the mixing of water masses.

On a seasonal scale, it is possible to determine the dominating influences on pCO_2. The pCO_2 data were first normalized to a constant, mean temperature (6.92 ºC [1]).

$$pCO_2(T_{mean}) = pCO_{2(obs)}[\exp(0.0423(T_{mean} - T_{obs}))] \qquad (5)$$

Multi-year $pCO_2(T_{mean})$ estimates (temperature normalized) were plotted as a function of measured temperature (Fig. 9). All winter data (December, January, and February) were plotted in magenta; spring data (March, April, and May) were plotted in red; summer data (June, July, and August) were plotted in green; fall data (September, October, and November) were plotted in blue. Deviations from the mean atmospheric level of 385 indicate that processes other than solubility control pCO_2. The summer (and fall) data show an early linear decrease with temperature through each season. In the summer, temperatures are increasing leading to out-gassing of CO_2, but the on-going summer photosynthesis overrides this and decreases the normalized pCO_2 in the water column. In the fall, temperatures decrease and pCO_2 increases in the water column as respiration rates and ventilation outpace photosynthesis and cooling, hence the normalized pCO_2 increases through the fall. In the winter, normalized pCO_2 concentrations remain relatively constant. In the spring, a large phytoplankton bloom occurs, which draws down pCO_2. As post-bloom recovery occurs, DIC is again resupplied to the water column and pCO_2 increases (as interpreted in [1, 17]).

V. DISCRETE MEASUREMENTS

Dalhousie University (DU) collected data along a transect intersecting the Northeast Channel. Data were collected on April 17 and April 18, 2008 at three locations within 0.5º of the buoy at a depth of 4 m. Our quality data starts on April 19,
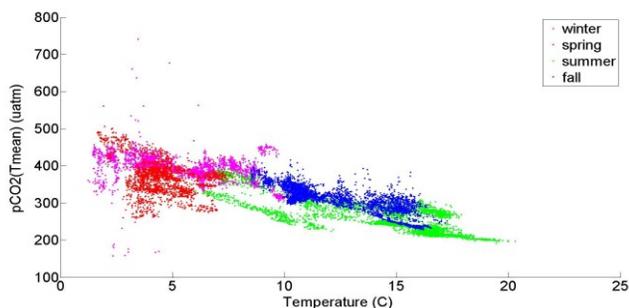
Figure 9. Plot of the pCO_2 corrected to a constant annual mean temperature (6.92ºC) plotted against in situ temperature (ºC). In the winter (magenta) pCO_2 values are relatively consistent. In the spring (red), low pCO_2 values are due to the phytoplankton bloom, while larger values are due to post-bloom recovery when DIC is resupplied due to respiration and remineralization. In the summer (green), pCO_2 is reduced due to on-going photosynthesis and out-gassing driven by warming waters. In the fall (blue) an increase in pCO_2 is observed due to decreasing temperatures.

2008, while the data begun collection in March 2008. For the purposes of direct comparison, data from April 17 and 18, 2008 was analyzed. A t-test (JMP 9.0) compares the DU data with the UNH data (Table 1). There was no significant difference found between the temperature, salinity, DIC, or TA data ($p \leq 0.05$). Additional discrete data collected near the site, ranging between 2008 and 2010, will soon be made available to allow improved validation of the mooring data set.

TABLE 1. Listing the DIC ($\mu mol \cdot kg^{-1}$) and TA ($\mu mol \cdot kg^{-1}$) calculated by UNH on April 19, 2008 and the discrete DIC ($\mu mol \cdot kg^{-1}$) and TA ($\mu mol \cdot kg^{-1}$) measured by Dalhousie University (DU) on April 17 and April 18, 2008.

	Date	Location	Temp (ºC)	Salinity (psu)	DIC ($\mu mol \cdot kg^{-1}$)	TA ($\mu mol \cdot kg^{-1}$)
UNH	4/17/2008	42.33N, 65.91W	4.85	31.892	2035.5	2182.7
UNH	4/17/2008	42.33N, 65.91W	4.82	31.960	2038.4	2185.7
DU	4/17/2008	42.76N, 65.48W	3.83	31.765	2055.1	2170.3
DU	4/17/2008	42.45N, 65.49W	2.20	31.587	1970.6	2165.2
UNH	4/18/2008	42.33N, 65.91W	4.90	31.926	2036.6	2184.2
UNH	4/18/2008	42.33N, 65.91W	5.03	31.919	2035.9	2183.9
DU	4/18/2008	42.12N, 65.50W	5.15	32.609	2062.7	2212.0

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