A Multiyear Assessment of Biological Perturbations of CO₂ 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-CO₂ Sensor (Sunburst Sensors, LLC) and an Aanderaa Instrument Oxygen Optode 3835) since March 2008. The controls on the CO₂ 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—CO₂, 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 (CO₂) 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 CO₂ have decreased from the oceanic uptake of CO₂. Several studies in this region show that the shelf region to be a weak source of atmospheric CO₂ 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 CO₂ is decreasing as sea surface temperatures increase and pH decreases [2]. Other factors influence the partial pressure of CO₂ (pCO₂) in seawater, such as temperature, salinity, the concentration of dissolved inorganic carbon (DIC), and alkalinity [3]. The atmospheric CO₂ that the ocean takes up increases that anthropogenic DIC component of seawater, which increases ocean acidification [3].

The pCO₂ in the surface waters of the ocean is controlled by a variety of parameters, including total CO₂, 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 CO₂), biological (photosynthesis and respiration), and chemical (carbonate formation and dissolution and photooxidation) controls on the total CO₂ (essentially DIC) in the upper mixed layer of the ocean [3, 5, 6].

What makes it difficult to quantify the controls that change CO₂ concentrations is that more than one factor is often responsible for CO₂ changes [5, 7]. Measuring dissolved oxygen (O₂) concentrations along with DIC can help determine which process is dominating control over CO₂ in the water column [7]. Reference [7] observed that an undersaturation of pCO₂ along with a supersaturation of O₂ with respect to the atmosphere implies photosynthesis dominating DIC; conversely a supersaturation of pCO₂ and an undersaturation of O₂ indicate net respiration. Variations in O₂ do not merely reflect biological processes, but also reflect air-sea gas exchange [8]. However, during strong blooms, CO₂ and O₂ 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 pCO₂ [1].

Lack of coincident physical and biogeochemical observations associated with the CO₂ flux has made it difficult to determine the contributions of the coastal ocean to the global air-sea CO₂ flux [3]. CO₂ 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 CO₂, and also because the exchange is highly variable with time and space [2].

In order to provide a reliable estimate of air-sea CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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-CO₂ Sensor (Sunburst, LLC) and the Oxygen Optode 3835 (Aanderraa Instruments). CO₂ 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, pCO₂ and dissolved oxygen are all measured at this site.

II. QUALITY CONTROL OF pCO₂ DATA

Studies have shown exceptionally long-term stability and sensitivity in the Submersible Autonomous Moored Instrument for CO₂ (SAMI-CO₂) sensor [11]. The operating characteristics have been calculated to having an accuracy of ±1 µatm and a precision of ±2 µatm [11]. The main difference between other CO₂ sensors and the SAMI-CO₂ is that the SAMI-CO₂ sensor is able to periodically renew its indicator solution, thus enhancing the stability and sensitivity in the sensor [11].
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. 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 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],

$$\text{TA}_S = 43.2 \times S + 805.$$  (1)

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

$$\text{DIC}_S = 46.5 \times S + 546.4.$$  (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

$$\text{DIC}(t) = \text{solubility} + \text{mixing}_h + \text{mixing}_v + R + P,$$  (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$_2$SYS program [15] is used for the calculation. The biotic DIC is then,

$$\text{DIC}_{\text{bio}}(t) = \text{DIC} - \text{DIC}_S$$  (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 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]).

$$\text{pCO}_2(T_{\text{mean}}) = \text{pCO}_2(\text{obs})[\exp(0.0423(T_{\text{obs}} - T_{\text{mean}}))]$$  (5)

Multi-year pCO$_2(T_{\text{mean}})$ 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 outgassing 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,
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 ≤ 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.

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<table>
<thead>
<tr>
<th>Date</th>
<th>Location</th>
<th>Temp (°C)</th>
<th>Salinity (psu)</th>
<th>DIC (µmol·kg⁻¹)</th>
<th>TA (µmol·kg⁻¹)</th>
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TABLE 1. Listing the DIC (µmol · kg⁻¹) and TA (µmol · kg⁻¹) calculated by UNH on April 19, 2008 and the discrete DIC (µmol · kg⁻¹) and TA (µmol · kg⁻¹) measured by Dalhousie University (DU) on April 17 and April 18, 2008.

REFERENCES


