Summer 2011

An Analytical Study of Air-Sea CO2 Gas Exchange in the Northwest Mississippi Bight Region

Andrea Kathryn Braatz
University of Southern Mississippi

Follow this and additional works at: https://aquila.usm.edu/masters_theses

Part of the Marine Biology Commons, and the Other Ecology and Evolutionary Biology Commons

Recommended Citation
https://aquila.usm.edu/masters_theses/217

This Masters Thesis is brought to you for free and open access by The Aquila Digital Community. It has been accepted for inclusion in Master's Theses by an authorized administrator of The Aquila Digital Community. For more information, please contact Joshua.Cromwell@usm.edu.
An Analytical Study of Air-Sea CO2 Gas Exchange in the Northwest Mississippi Bight Region

Andrea Kathryn Braatz
AN ANALYTICAL STUDY OF AIR-SEA CO₂ GAS EXCHANGE IN THE
NORTHWEST MISSISSIPPI BIGHT REGION

by

Andrea Kathryn Braatz

A Thesis
Submitted to the Graduate School
of The University of Southern Mississippi
in Partial Fulfillment of the Requirements
for the Degree of Master of Science

Approved:

__Stephan D. Howden____________________
Director

__Laodong Guo________________________

__Steven E. Lohrenz_______________________

__Susan A. Siltanen_______________________
Dean of the Graduate School

August 2011
ABSTRACT

AN ANALYTICAL STUDY OF AIR-SEA CO$_2$ GAS EXCHANGE IN THE NORTHWEST MISSISSIPPI BIGHT REGION

by Andrea Kathryn Braatz

August 2011

With the continued increase of carbon dioxide (CO$_2$) emissions, researchers are concerned with accumulation of excess CO$_2$ within the atmosphere. The ocean is an important sink for the drawdown of atmospheric CO$_2$ concentrations. Due to high spatial and temporal variability, CO$_2$ fluxes in the coastal ocean are not as well characterized as those for the open ocean. More specifically, data for the northern Gulf of Mexico (GOM) coastal region is lacking. A time series analysis of air-sea CO$_2$ flux rates from May through December 2009 was conducted using data collected by The University of Southern Mississippi’s Central Gulf Ocean Observing System 3-meter discus buoy, located within the northwest Mississippi Bight region (MBR). Data collected by the buoy included wind speed and direction, sea surface temperature, sea surface salinity, pressure, and $p$CO$_2$. Four hypotheses were addressed. One hypothesis was the region was a weak net sink for atmospheric CO$_2$ with an alternative hypothesis that the region was a net source that varied seasonally. Air-sea CO$_2$ flux rates calculated from the buoy data indicated the northwest MBR was a weak net source during the month of July, but was overall a net sink for CO$_2$ from May through December. The mean daily CO$_2$ flux rate from May through December ranged from -4.23 to -5.96 mmol m$^{-2}$ d$^{-1}$. A third hypothesis was uptake of CO$_2$ in the coastal northern GOM would exceed release of CO$_2$
in the remainder of the GOM. Net annual flux for the entire coastal northern Gulf of Mexico region was estimated at approximately -3.78 to -5.33 Mt C yr\(^{-1}\), while the net annual flux for the remainder of the GOM was estimated at approximately 14.33 to 19.82 Mt C yr\(^{-1}\). Sea surface salinity, net primary productivity, and wind speed were the environmental variables which had the strongest correlations with CO\(_2\) flux rates.

Although air-sea flux calculations should use the wind speed relative to surface water, the wind speed relative to fixed geographic coordinates (Eulerian reference frame) is customarily used. The final hypothesis was surface currents would have an appreciable affect on CO\(_2\) flux rates throughout the region. An investigation of CO\(_2\) flux rates computed from wind speeds relative to surface water resulted in a decrease in CO\(_2\) flux rates of 2.06 to 2.84%. This difference in CO\(_2\) flux rates was statistically significant; however, fell within the margin of error involved in estimating the Eulerian flux rates.
DEDICATION

To those lost but never forgotten.

John D. Michalowske

&

Harold G. Braatz
ACKNOWLEDGMENTS

First and foremost, I would like to thank my advisor Dr. Stephan Howden for all the help and guidance, without which I could not have completed this research. I would also like to thank my committee members, Dr. Steven Lohrenz and Dr. Laodong Guo, for their time and feedback.

I am grateful for funding received for this research, which was provided by The Central Gulf Ocean Observing System. Use of data collected by the $pCO_2$ sensor onboard the USM buoy was critical for this study. I want to thank NOAA and the Pacific Marine Environmental Laboratory for providing this data and Dr. Christopher Sabine for authorizing use of this data. Nutrient and chlorophyll data was obtained from the Northern Gulf Institute.

A number of USM staff members and students have also earned my gratitude. Buoy maintenance and repair work was performed by Richard Slaughter, and all buoy communications were handled by James Davis. NGI nutrients and chlorophyll data was processed by and obtained from Allison Mojzis. Guidance for processing satellite imagery was provided by Brooke Denton.

Finally, I would like to thank Jerry Braatz and Jason Dale for proofreading this thesis and offering valuable comments and suggestions.
TABLE OF CONTENTS

ABSTRACT..................................................................................................................ii

DEDICATION..............................................................................................................iv

ACKNOWLEDGMENTS..............................................................................................v

LIST OF TABLES........................................................................................................viii

LIST OF ILLUSTRATIONS........................................................................................ix

CHAPTER

I. INTRODUCTION.......................................................................................................1

   The Carbon Cycle
   Air-sea CO₂ Gas Exchange
   Study Region and CenGOOS Buoy
   Objectives/Hypothesis

II. METHODS.............................................................................................................15

   Bulk CO₂ Flux Equation
   Data Sources and Missing Data
   CO₂ Flux Rates
   Productivity Data

III. CENGOOS BUOY DATA ANALYSIS.................................................................27

   Environmental Variables
   pCO₂ and CO₂ Flux Rates
   Influence of Environmental Variables on CO₂ Flux Rates
   Synthesis of Maximum and Minimum CO₂ Flux Rates

IV. ANALYSIS OF LAGRANGIAN CO₂ FLUX RATES.......................................43

   CenGOOS Buoy Data
LIST OF TABLES

Table

1. Mean Monthly SSS, SST (°C), Wind Speed (m/s), and Wind Direction (Degrees) Measured from True North.................................................................28

2. Mean Monthly $pCO_2$ (µatm) and CO$_2$ Flux Rates (mmol m$^{-2}$ d$^{-1}$)......................33

3. Results of Sensitivity Analysis Showing Percent Increase/Decrease in CO$_2$ Flux Rates When Variables Were Changed by the Values Indicated. For Pressure Values Were Divided by 100 (0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5).........................37

A-1. Mean Monthly River Discharge (m$^3$/s) for All Major Rivers Contributing to MBR From May to December, 2009.................................................................59

A-2. Mean Climatological River Discharge (m$^3$/s) for All Major Rivers Contributing to the MBR From May to December, 2009.................................................................59
LIST OF ILLUSTRATIONS

Figure

1. Broad overview of the global carbon cycle (a) and the marine carbon cycle (b) which demonstrates two pathways for carbon storage in the sediments...........1

2. Map of major rivers influencing the MBR region with locations of USM CenGOOS buoy, and NDBC buoys 42007 and 42012..........................12

3. Buoy timeline.................................................................18

4. Location of USM CenGOOS buoy and NDBC buoys 42007 and 42012........18

5. Comparison of wind data for all three buoys from May through August, 2009 with a one-way ANOVA of wind direction for all three buoys (a) and a one-way ANOVA of wind speed for all three buoys (b).................................19

6. Comparison of SST for all three buoys from May 13 through August 30, 2009. One-way ANOVA of SST for all three buoys (a), SST correlation between USM buoy and 42007(b), and SST correlation between USM buoy and 42012 (c)..................................................................20

7. One-way ANOVA of measured CenGOOS SSS and linearly regressed SSS for May through September, 2009.................................................................22

8. Gas transfer relationships at low to intermediate wind speeds in the NW MBR from May through December, 2009......................................................23

9. Map of region used to estimate area of northern GOM..........................24

10. Map of CODAR sampling region boundaries......................................26

11. Average SSS, SST, pressure, and wind measured by the CenGOOS buoy (and NDBC buoys).................................................................28

12. Eight day averages (left) and mean monthly values of NPP in mg C m$^{-2}$ d$^{-1}$ estimated from MODIS satellite imagery for the region located within 28.5°N, -90.0°W, 31.0°N, and -87.0°W. ..................................................29

13. NGI Chlorophyll and nutrient data from station 8 for the months of May, June, August, and November of 2009. ............................................30
14. Average values for pCO\textsubscript{2} and CO\textsubscript{2} flux rates
15. Relationships between CO\textsubscript{2} flux rates and pCO\textsubscript{2\text{atm}}, pCO\textsubscript{2sw}, and \Delta pCO\textsubscript{2}
16. Time series of daily averaged wind speed and CO\textsubscript{2} flux rates from May through December, 2009
17. Time series of eight day averages and monthly averages of NPP and CO\textsubscript{2} flux rates from May through December, 2009
18. Results of sensitivity analysis of changes in wind speed on CO\textsubscript{2} flux rates
19. Time series of wind speed, SST, SSS, and \Delta pCO\textsubscript{2} from May through December, 2009
20. Mean monthly NPP plotted with \Delta pCO\textsubscript{2}, pCO\textsubscript{2\text{atm}}, and pCO\textsubscript{2sw}
21. Monthly averages for CO\textsubscript{2} flux rates and most influential environmental variables
22. Mean monthly CenGOOS buoy surface current speeds for May through September 2009. For the \textit{u} component (a) positive values indicate eastward flow while negative values indicate westward flow. For the \textit{v} component (b) positive values indicate northward flow while negative values indicate southward flow
23. CenGOOS buoy mean monthly CO\textsubscript{2} flux rates from May through September calculated with (blue dashed line) and without (red solid line) surface currents data
24. Mean monthly CenGOOS percent differences between Lagrangian and Eulerian flux rates (Eulerian-Lagrangian)
25. CenGOOS mean monthly difference in flux rates (dflux), NPP, SSS, and \Delta pCO\textsubscript{2}
26. Mean monthly CODAR surface current speeds for June through November 2009. For the \textit{u} component (a) positive values indicate eastward flow while negative values indicate westward flow. For the \textit{v} component (b) positive values indicate northward flow while negative values indicate southward flow
27. CODAR mean monthly CO\textsubscript{2} flux rates from June through November calculated with (blue dashed line) and without (red solid line) surface currents data

x
28. CODAR Mean monthly percent differences between Lagrangian and Eularian flux rates………………………………………………………………………………………50

29. Contour plot of mean dflux (a). The black arrows represent mean surface currents. Mean wind speed and direction is indicated to the right of each plot. Values were averaged over the time period from June 30 to November 9, 2009. Regions where the difference in flux rates was positive are represented by red and yellow shading and are displayed in a magnified portion of the plot to the left (b). Below is a contour plot of hourly wind, surface currents, and flux differences from hour 1 of August 1, 2009 (c). Negative differences are represented by green and blue shading…………………52

30. Mean daily CenGOOS buoy winds, surface currents, and differences in flux rates from May through September 2009………………………………………………53

31. CODAR mean monthly dflux, NPP, and dpCO\textsubscript{2}……………………………………54

A-1. Mean monthly river discharge for all major rivers influencing the MBR.............59

D-1. Map of northern Gulf of Mexico region used to calculate net annual CO\textsubscript{2} uptake…………………………………………………………………………..62

E-1. Images of 8-day averaged NPP from day 137 to day 168, 2009.........................63

E-2. Images of 8-day averaged NPP from day 169 to day 200, 2009.........................64

E-3. Images of 8-day averaged NPP from day 201 to day 232, 2009.........................65

E-4. Images of 8-day averaged NPP from day 233 to day 264, 2009.........................66

E-5. Images of 8-day averaged NPP from day 265 to day 296, 2009.........................67

E-6. Images of 8-day averaged NPP from day 297 to day 328, 2009.........................68

E-7. Images of 8-day averaged NPP from day 329 to day 360, 2009.........................69

E-8. Mean monthly May 2009 NPP………………………………………………………….70

E-9. Mean monthly June 2009 NPP………………………………………………………….70

E-10. Mean monthly July 2009 NPP………………………………………………………….71

E-11. Mean monthly August 2009 NPP………………………………………………………….71

E-12. Mean monthly September 2009 NPP………………………………………………………….72

E-13. Mean monthly October 2009 NPP………………………………………………………….72
E-14. Mean monthly November 2009 NPP…………………………………………………..73
E-15. Mean monthly December 2009 NPP…………………………………………………..73

F-1. Sensitivity analysis of CO$_2$ flux rates to changes in SST…………………………74
F-2. Sensitivity analysis of CO$_2$ flux rates to changes in SSS…………………………75
F-3. Sensitivity analysis of CO$_2$ flux rates to changes in atmospheric pressure……….75
F-4. Sensitivity analysis of CO$_2$ flux rates to changes in ΔpCO$_2$…………………..76
F-5. Time series plots of mean daily pCO$_{2sw}$, SST, SSS, and wind speed…………………..76
F-6. Time series plots of mean daily pCO$_{2a}$, SST, SSS, and wind speed…………………..77

G-1. Contour plot of mean dflux for hour 3, July, 2009……………………………………..78
G-2. Contour plot of mean dflux for hour 19, July 21, 2009……………………………..78
G-3. Contour plot of mean dflux for hour 10, August 6, 2009……………………………..79
G-4. Contour plot of mean dflux for hour 21, November 4, 2009…………………………79
G-5. Contour plot of mean monthly dflux for June, 2009……………………………………80
G-6. Contour plot of mean monthly dflux for July, 2009……………………………………80
G-7. Contour plot of mean monthly dflux for August, 2009………………………………81
G-8. Contour plot of mean monthly dflux for September, 2009…………………………81
G-9. Contour plot of mean monthly dflux for October, 2009……………………………..82
G-10. Contour plot of mean monthly dflux for November, 2009…………………………82
CHAPTER I
INTRODUCTION

The carbon cycle is the transformation of the different forms of carbon within and between environments and involves a combination of physical, chemical, and biological processes. Accumulation of excess CO$_2$ within the atmosphere is of major concern because it can alter the carbon cycle and negatively impact biogeochemical processes in terrestrial and oceanic systems. The annual globally averaged concentration of atmospheric CO$_2$ for 2010 was approximately 388.56 ppm (NOAA/ESRL). This was 0.59% higher than the 2009 average, 2.59% higher than the 2005 average, and 5.37% higher than the 2000 average (NOAA/ESRL). Tracking the carbon cycle allows for the establishment of a carbon budget, which can provide valuable information for the management of excess carbon accumulation within the atmosphere.
The Carbon Cycle

The carbon cycle involves exchange of both inorganic and organic carbon between the terrestrial, marine, riverine, and atmospheric environments. Figure 1 illustrates a simplified schematic of the global carbon cycle. CO₂ from terrestrial sources is released into the atmosphere through fossil fuel emissions, fires, volcanic activity, deforestation/land use changes, and respiration. Carbon is released into streams and rivers through erosion, weathering, and inputs of decaying organic matter. Rivers then transport carbon to coastal regions and continental shelves.

In addition to riverine inputs of both organic and inorganic carbon, the ocean also receives CO₂ through exchange with the atmosphere. CO₂ is exchanged between surface waters and the atmosphere directly via diffusion through a thin surface film. CO₂ exchange between surface waters and the atmosphere is affected by biogeochemical
processes, turbulent mixing (wind), and currents. Important biogeochemical processes include CaCO$_3$ precipitation/dissolution and photosynthesis. Carbon is transferred through the layers of the ocean via upwelling and downwelling (Figure 1). The mixed layer of the ocean extends from the surface down to several hundred meters and is characterized by warm (relative to deeper layers) and well mixed waters. The partial pressure of CO$_2$ in the surface of the mixed layer is generally at or near equilibrium with the atmosphere (Trabalka et al., 1985). Below the surface layer is the thermocline region which is characterized by decreasing temperatures with increasing density down to approximately 1000 meters. Water in this region is stratified due to the great amount of energy required to overturn water masses of differing temperatures. The deep ocean is characterized by cold waters and depths greater than 1000 meters. These waters are isolated from surface waters and the atmosphere; however, surface waters can mix down when temperatures are low and salinity is high. These conditions generally occur in Polar Regions (Chester, 2003).

CO$_2$ is exchanged between the atmosphere and surface waters through a series of reactions. First, CO$_2$ reacts with water to form carbonic acid:

$$\text{CO}_2 (aq) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 (aq) \quad \text{(eq. 1)}$$

Carbonic acid dissociates to form bicarbonate:

$$\text{H}_2\text{CO}_3 (aq) \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \quad \text{(eq. 2)}$$

Bicarbonate dissociates to form carbonate:

$$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \quad \text{(eq. 3)}$$
Nearly 90% of carbon in the ocean is in the form of bicarbonate ions, with the remaining 10% being comprised mainly of carbonate ions (Trabalka et al., 1985). Carbonate ions react with calcium ions to form calcium carbonate:

\[ \text{CaCO}_3 \, \text{eq. (4)} \]

\[ \text{CO}_3^{2-} + \text{Ca}^{2+} \rightleftharpoons \text{CaCO}_3 \]

\[ \text{CaCO}_3 \]
can be buried in sediments in regions with a deep calcite compensation depth (ccd), the depth at which the rate of carbonate accumulation is equal to the rate of carbonate dissolution (Chester, 2003). In regions where the ccd is shallow, CaCO\(_3\) is dissolved before it reaches bottom sediments.

Photosynthesis is a mechanism for removing CO\(_2\) from surface waters, which can result in disequilibrium between atmospheric and surface water CO\(_2\) concentrations. This disequilibrium makes surface waters a sink for atmospheric CO\(_2\). Carbon taken up by surface waters is transported through biological pumping to deeper layers of the water column via falling detritus and decaying organic matter produced during photosynthetic processes. A portion of this carbon is ultimately deposited in bottom sediments and stored (Chester, 2003). The removal of CO\(_2\) from surface waters is partially offset by CO\(_2\) put back into the water (and the atmosphere) via respiration as follows:

\[ \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \]

\[ 6\text{CO}_2 + 6\text{H}_2\text{O} + \text{Light Energy} \rightleftharpoons \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \, \text{eq. (5)} \]

where the forward reaction represents photosynthesis and the reverse reaction represents respiration. Together these processes are important for recycling of carbon within the system. The net amount of CO\(_2\) taken up by phytoplankton is expressed as net primary production (NPP) which is simply the gross primary production minus respiration (Sarmiento & Gruber, 2006).
The carbon cycle in coastal margins is strongly influenced by carbon and nutrient input from rivers and terrestrial runoff and involves numerous processes, including: upwelling and mixing, photosynthesis at the surface, sinking of organic matter, respiration, and air-sea CO$_2$ fluxes (CCSP, 2007). Net primary productivity in these regions is substantially higher, and the biological pump is much more efficient than in open waters (CCSP, 2007).

**Air-Sea CO$_2$ Gas Exchange**

Cumulative increases in atmospheric concentrations of CO$_2$ can be attributed primarily to fossil fuel combustion, with changes in land use and land cover also playing a major role (CCSP, 2007; IPCC, 2007). The combustion of fossil fuels releases CO$_2$ that was previously stored in geological sinks into the atmosphere. Possible consequences of increased atmospheric concentrations include ocean acidification, rising sea level, increased air temperatures, decreased snow and ice cover, and increased precipitation (IPCC, 2007). Ocean acidification occurs as a result of increased uptake of atmospheric CO$_2$ which increases hydrogen ions released into the water column according to equations 1 and 2 (Doney et al., 2009). The hydrogen ions bind with CO$_3^{2-}$ ions (equation 3) and reduce the CO$_3^{2-}$ ions available to bind with Ca$^+$ ions. Ocean acidification has the potential to decrease CaCO$_3$ saturation rates and increase dissolution rates, thereby decreasing the CO$_2$ uptake efficiency of the ocean (Doney et al., 2009).

A region is characterized as a CO$_2$ sink when input of CO$_2$ from the atmosphere exceeds output to the atmosphere. North America has been identified as both a significant source and sink for CO$_2$ emissions. Nearly 25% of global CO$_2$ emissions are from North America, with sinks offsetting approximately 30% of these emissions (Sabine
et al., 2004; CCSP, 2007). There are two major sinks for atmospheric CO$_2$: the terrestrial sink (primarily forest regrowth) and the oceanic sink (CCSP, 2007). Carbon cycling in coastal regions is a crucial link between terrestrial and oceanic carbon sinks (Robbins et al., 2009).

Approximately 1.8 billion Gt C per year is transferred to the oceans (CCSP, 2007), with the surface ocean absorbing nearly 1/3 of excess CO$_2$ (Sabine et al., 2004; Doney et al., 2009). The Pacific Ocean has the smallest net uptake due to a balance between mid-latitude uptake and equatorial release (Feely et al., 2001). The high-latitude North Atlantic region has the highest uptake per unit area due to low sea surface temperature (SST) and high photosynthetic activity, wind speeds, and alkalinity (Takahashi et al., 2009).

Compared to the wealth of information available for the open ocean, there is much less CO$_2$ flux data available for coastal margins. This can be attributed to the difficulty of quantifying fluxes in these regions due to high spatial and temporal variability (Boehme et al., 1998). There is often disagreement as to whether these regions are sinks or sources for CO$_2$ because of this high variability (Robbins et al, 2009). Despite these uncertainties, coastal margins are important as potential localized sinks for atmospheric CO$_2$. Due to the highly variable biogeochemistry in coastal margins, these regions may vary seasonally as sources and sinks (Borges et al., 2006; CCSP, 2007; Wanninkhof et al., 2009; Lohrenz et al., 2010). Air-sea fluxes in coastal margins are estimated through direct measurements of the air-sea difference in the partial pressure of CO$_2$ ($p$CO$_2$) and gas transfer velocity and solubility estimates (McGillis et al, 2001; Signorini & McClain, 2002).
Coastal margins in the northern Gulf of Mexico (GOM) region are river-dominated margins characterized by high freshwater, organic matter, and nutrient input from terrestrial sources (CCSP, 2007). According to the 2007 US Climate Change Science Program (CCSP), the GOM is a net source of CO$_2$ to the atmosphere with small localized sinks including the northern GOM region.

**Bulk CO$_2$ Flux Equation**

The bulk equation for calculating air-sea CO$_2$ flux rates has three components:

$$ FCO_2 = ks\Delta pCO_2 $$  

(eq. 6)

where $k$ is the gas transfer velocity, $s$ is the solubility of CO$_2$ in seawater, and $\Delta pCO_2$ is $pCO_{2\text{seawater}} - pCO_{2\text{air}}$ (McGillis et al., 2001; Wanninkhof et al., 2007; Lohrenz et al., 2010). Solubility of CO$_2$ in seawater is dependent on sea surface temperature and salinity (Weiss, 1974). The gas transfer velocity is a function of wind speed, with turbulence, boundary layer stability, surfactants, bubbles, and fetch also being influential (Wanninkhof, 1992).

**Gas Transfer Velocity**

Arguments exist for using both a cubic and a quadratic relationship between wind speed and gas transfer velocity. Some think a quadratic relationship may not be strong enough based on covariance flux measurements performed during the Gas Ex-98 cruise (Wanninkhof & McGillis, 1999; McGillis et al., 2001). Wanninkhof and McGillis (1999) argue that gas transfer is hindered by surfactants at low to intermediate wind speeds and by bubble enhancement at high wind speeds. They further argue that a cubic relationship more accurately quantifies these effects. Further work using the Gas Ex-98 measurements confirmed that a cubic relationship satisfied the global bomb $^{14}$C oceanic
uptake constant found in the previous 1999 study (McGillis et al., 2001). Two different
algorithms were generated to calculate gas transfer using a cubic relationship with wind
speed. The first equation for short-term wind speeds, hence forward referred to as
WM99, is from the Wanninkhof and McGillis (1999) study:

\[ k = 0.0283u^{3}_{10} (Sc^*)^{-1/2} \]  (eq. 7)

where \( u \) is wind speed adjusted to a height of ten meters in m/s and \( Sc^* \) is the Schmidt
number normalized for CO\( _2 \) in seawater at 20°C. The second algorithm, hence forward
referred to as M01, is from McGillis et al. (2001):

\[ k = 3.3 +0.026u^{3}_{10} (Sc^*)^{-1/2} \]  (eq. 8)

The averaging period for wind speed measurement is critical because short-term
averaged winds cause a weaker dependence of gas transfer on wind speed than long-term
averaged winds (Wanninkhof, 1992). Wanninkhof argued that based on relationships
between gas transfer and wind speeds determined using wind tunnels and invasion of
bomb C\(^{14} \) into the ocean, a quadratic dependence on wind speed is appropriate. The
algorithm generated from the Wanninkhof 1992 study, hence forward referred to as W92,
is:

\[ k = 0.31u^{2}_{10} (Sc^*)^{-1/2} \]  (eq. 9)

Results from the SOLAS Air-Sea gas Exchange Experiment (SAGE) showed
linear and cubic relationships between wind speed and gas transfer were inconsistent at
higher wind speeds (Ho et al., 2006). Through use of the \(^3\)He/SF\(^6 \) duel tracer technique
with SAGE wind measurements, Ho et al. determined that a quadratic relationship
between wind speed and gas transfer is more accurate than a cubic relationship. The
algorithm generated from the Ho et al. (2006) study, hence forward referred to as H06, is:
Air-sea CO₂ flux calculations are generally performed using gas transfer velocities calculated from wind speeds relative to fixed geographic coordinates. Water masses are not stationary; therefore, in order to achieve greater accuracy in CO₂ flux estimates, it would be beneficial to instead use wind speeds relative to surface water. This would account for the movement of water across the surface. This can be achieved by subtracting the components of the surface current vector from the components of the wind vector, which will be addressed further in Chapter II.

**Partial Pressure of CO₂**

Environmental variables influencing $pCO₂$ concentrations in seawater include temperature, salinity, biogeochemical processes, and water column mixing (Bates et al., 1996; Boehme et al., 1998; Borges et al., 2006). Both biological activity and temperature can significantly influence $pCO₂$ concentration (Takahashi et al., 2002). Sea surface temperature (SST) is regulated mostly by physical processes such as solar energy input, heat exchange between the air and the water surface, and the thickness of the mixed layer (Takahashi et al., 2002). Takahashi et al., 1993 determined that for every $16°C$ increase in surface water temperature, $pCO₂$ concentration in surface waters doubles according to the equation:

$$\frac{\partial \ln pCO₂}{\partial T} = 0.0423°C^{-1}$$  \hspace{1cm} (eq. 11)

It has also been noted that seasonal changes in SST and $pCO₂$ are closely in phase at the BATS site near Bermuda suggesting changes in $pCO₂$ are primarily regulated by changes in SST (Bates, 2001). CO₂ is more soluble in seawater at lower SST’s, and as SST increases CO₂ becomes less soluble in seawater.
Biological activity also plays an important role in regulating $p$CO$_2$ concentrations (Takahashi et al., 2002). For example, seasonal phytoplankton blooms can drawdown atmospheric CO$_2$, while increases in respiration release CO$_2$ to the atmosphere (Borges et al., 2006). The largest of these blooms generally occurs in the spring when the water column becomes stratified due to increased freshwater discharge and surface temperatures. Losses of phytoplankton to grazing is also low during this period of time. Primary production then decreases due to depletion of available nutrients within surface waters in the late spring and early summer months. Grazing activity and decomposition also increases during these months, and remains higher throughout the summer. Small intermittent blooms may occur throughout the summer months if nutrients from deeper layers are mixed up to the surface through storm activity. A less intense fall bloom may also occur due to a decrease in grazing activity and increased nutrient input from increased wind strength mixing the water column. Nutrient input through mixing continues throughout the winter months, but limited illumination keeps biological activity low (Miller, 2004).

**Study Region and CenGOOS Buoy**

*Study Region*

The GOM covers more than 1.9 million square kilometers and is a semi-enclosed subtropical/tropical sea with inflow from 33 major river systems (Robbins et al., 2009). Nearly 20% of the basin is continental slope, with another 20% being comprised of abyssal plains (Robbins et al., 2009). The average depth is 1600 meters, and the maximum depth is 4000 meters (Robbins et al., 2009). Major carbon pathways to the GOM include terrestrial inputs, shelf-ocean exchange, and air-sea flux.
The northern GOM is strongly influenced by the Mississippi-Atchafalaya River system (Lohrenz et al., 2010). Draining nearly 41% of the United States, the average annual freshwater discharge from this system is approximately 580 km$^3$ (Guo et al., 2009). As a result, surface salinity values in this region are relatively low (Robbins et al., 2009). The Mississippi-Atchafalaya river system delivers $21 \times 10^{12}$ g C yr$^{-1}$ of DIC, $1.2 \times 10^{12}$ to $3.8 \times 10^{12}$ g C yr$^{-1}$ of POC, and $1.8 \times 10^{12}$ to $3.1 \times 10^{12}$ g C yr$^{-1}$ of DOC to the region annually (Guo et al., 2009).

In addition to the Mississippi-Atchafalaya system, the Choctawhatchee, Escambia-Concuh, Mobile, Pascagoula, Pearl River and other similar systems (Figure 2) contribute freshwater to the northern GOM region (Robbins et al., 2009). These river systems are particularly important to the Mississippi Bight region (MBR). Total mean monthly discharge from each system can be found in appendix A. Nearly 13 Mt C is delivered to the northern GOM annually as dissolved CO$_2$ (Cai, 2003). Factors influencing flux rates in the MBR include topography, tidal mixing (tides are strongly diurnal but relatively weak), turbulence, freshwater input, and biological productivity (Robbins et al., 2009). Biological productivity is often elevated along coastal margins in the northern GOM, as observed in the Mississippi River plume region (Lohrenz & Cai, 2006).

Surface currents within the Mississippi Bight are controlled by multiple forces including wind, buoyancy, and tides (Finnegan, 2009). Freshwater input and Loop Current intrusions also influence current flow (Finnegan, 2009). Mean along-shore current flow within the Mississippi Bight is generally westward, with a less defined pattern during the summer months, and mean offshore current flow appears to have a
weak mean northward flow (Dinnel et al., 1997; Finnegan, 2009). Mean alongshore current velocity ranges from approximately 2 to 14 cm s$^{-1}$ and mean offshore current velocity ranges from approximately -5 to 9 cm s$^{-1}$ (Dinnel, 1997).

Fig. 2. Map of major river systems influencing the MBR region with locations of USM CenGOOS buoy, and NDBC buoys 42007 and 42012. River systems from left to right are the Mississippi, Pearl, Pascagoula, Mobile Bay, Escambia-Conecuh, and Choctawhatchee.

The GOM is the single largest North American coastal ocean source of CO$_2$ to the atmosphere (Robbins et al., 2009). The mean annual air-sea CO$_2$ flux rates in the GOM and Caribbean Sea range from approximately $9.4 \pm 24$ g C m$^{-2}$ yr$^{-1}$ in coastal regions, up to $13 \pm 20$ g C m$^{-2}$ yr$^{-1}$ in offshore regions (CCSP, 2007). The GOM appears to be a net CO$_2$ source on average, with the northern GOM being a localized net CO$_2$ sink (Robbins et al., 2009; Wanninkhof et al., 2009). In a recent study the northern GOM region was a net sink during the month of August (Lohrenz et al., 2010). Flux measurements from the spring and fall suggested that the entire region was a net source, with values ranging from
3.5 to 5.8 mmol m$^{-2}$ d$^{-1}$ (Lohrenz et al., 2010). Lohrenz and Cai (2006) also found the Mississippi River plume region to be a CO$_2$ sink, with regions outside of the river plume having had flux rates indicative of a weak source. Wanninkhof et al. (2009) estimated an average annual flux rate of -0.92 mol m$^{-2}$ yr$^{-1}$ for the entire northern GOM region from April 2008 through March 2009.

**CenGOOS Buoy**

The primary data source for this study was the USM Central Gulf Ocean Observing System (CenGOOS) buoy. This 3-meter discus buoy was located due south of Pascagoula within the MBR at 30.0424 $^\circ$N, 88.6473 $^\circ$W and was approximately 25 nautical miles (~46 km) from shore (Figure 2). The buoy was located in waters which were 20 meters in depth. Instrumentation onboard the buoy included a Gill Windsonic anemometer, an RM Young anemometer, a Seabird Microcat CTD, a Valsalia barometer, a Rotronic temperature and humidity sensor, an RD Instruments ADCP, a Novatel GPS, and a NOAA MAPCO$_2$ instrument package.

**Objectives/Hypothesis**

There were two primary objectives for the present study. The first was to perform a time series analysis of air-sea CO$_2$ flux rates within the northwest MBR using data collected by the USM CenGOOS buoy. From the flux analysis the importance of different environmental factors were determined. Environmental factors included wind, SST, sea surface salinity (SSS), and biological activity. The second objective was to examine the effects of using wind speed relative to surface water rather than wind speed relative to fixed geographic coordinates to determine the sensitivity of wind-based calculations on air-sea CO$_2$ flux rates.
The following four hypotheses were tested:

1.) The northwest MBR is a weak net sink for CO$_2$.

2.) An alternative hypothesis is that the northwest MBR is a net source that varies seasonally.

   This hypothesis was only tested for summer and fall, however, as the dataset is comprised of data from May through December only.

3.) Classification of the entire GOM as either a source or a sink is dependent upon the flux rates within the coastal northern GOM region.

   If the uptake rate of CO$_2$ per unit area in the northern GOM significantly exceeds the release of CO$_2$ per unit area from the open Gulf, the northern GOM may be a determining factor in the overall classification of the GOM as either a net source or a net sink.

4.) Surface currents have an appreciable effect on relative wind speeds, and therefore alter air-sea CO$_2$ flux rates throughout the region.
CHAPTER II
METHODS

Bulk CO$_2$ Flux Equation

A time series analysis of air-sea CO$_2$ flux rates was conducted from May 13, 2009 through December 21, 2009. The bulk CO$_2$ flux equation (equation 6) was used to calculate mean daily, monthly, and seasonal CO$_2$ flux rates. The gas transfer velocity ($k$) was calculated assuming short-term/steady wind speeds. Short-term wind speeds are defined as those averaged over a time period of less than a month (Wanninkhof & McGillis, 1999). Both cubic and quadratic gas transfer algorithms (equations 7-10) were used to calculate the gas transfer velocity. The units of the gas transfer coefficient were cm/h and wind speeds were measured in m/s. Wind speeds were adjusted to a height of 10 meters using the power-law wind profile:

$$U_{10} = u_1(z_2/z_1)^P$$  \hspace{1cm} (eq. 12)

where $u_{10}$ is the wind speed adjusted to a height of 10 meters ($z_2$), $u_1$ is the wind speed measured at 5 meters ($z_1$) and the exponent $P$ has the pre-determined value of 0.11 (Hsu et. al., 1994). The sampling rate of the wind data was decreased to match the 3-hour sampling rate of the pCO$_2$ sensor by using the downsampling function in MATLAB. Mean daily and monthly wind headings were estimated using the methods outlined in the NCAR Earth Observatory Laboratory’s Wind Direction Quick Reference (Appendix B).

The dimensionless Schmidt number ($s_{c*}$) in equations 7-10 is the kinematic viscosity of water divided by the molecular diffusivity of CO$_2$ in seawater (Wanninkhof, 1992; Wanninkhof & McGillis, 1999). The kinematic viscosity is the dynamic viscosity of water divided by the density of water (Johnson, 2010). The dynamic viscosity was
calculated using the `sw_viscosity` function located in the Massachusetts Institute of Technology’s *Seawater Thermophysical Properties Library* for MATLAB (http://web.mit.edu/seawater/). Density of seawater was calculated using the `sw_dens0` function in the *Seawater Library* for MATLAB (Morgan & Pender, 2006). Molecular diffusivity was calculated using the equation of Jahne et al. (1987):

\[
D = A e^{-\frac{E_a}{RT}} \tag{eq. 13}
\]

where \( A = 5019 \times 10^{-5} \text{ cm}^2/\text{s} \), \( E_a \) (activation energy) = 19.51 KJ/mol, \( R \) (universal gas constant) = 8.3145 J/mol K, and \( T \) is SST in degrees Kelvin. \( E_a \) and \( A \) were both predetermined experimentally (Jahne et al., 1987).

The Schmidt number was normalized to a value of 660, which is the Schmidt number of \( \text{CO}_2 \) in seawater at 20\( ^\circ \text{C} \) (Wanninkhof, 1992). The -0.5 exponent on the Schmidt number (equations 7-10) is representative of turbulent mixing (McGillis et al., 2001; Johnson, 2010). This exponent is generally used for regions where bubbles at the surface are an influencing factor, as opposed to regions with smooth surfaces where the exponent is -0.66 (Wanninkhof & McGillis, 1999; McGillis et al., 2001). Pressure, SST, and SSS datasets were all necessary to calculate the Schmidt number. Like wind speed, the sampling rates of SST and SSS data had to be decreased to match the 3-hour sample rate of the \( p\text{CO}_2 \) sensor. Pressure was measured by the \( p\text{CO}_2 \) sensor at the 3-hour sample rate.

Solubility \( (s) \) of \( \text{CO}_2 \) in surface waters was calculated using the equation found in the appendix of the 1992 Wanninkhof paper:

\[
s = \exp(-60.2409 + 93.4517*(100/T) + 23.3585 * \ln(T/100) + S* \left[0.023517 + 0.023656*(T/100) + 0.0047036*(T/100)^2\right]) \tag{eq. 14}
\]
where T is the SST in degrees Kelvin and S is the SSS. The resulting solubility was in mol/L atm. Units were converted to mol m$^{-3}$ atm$^{-1}$ by dividing by 0.001 m$^3$ (1 Liter).

The difference between $p_{CO_2_{seawater}}$ ($p_{CO_2_{sw}}$) and $p_{CO_2_{air}}$ ($p_{CO_2_a}$) was determined from mole fractions of CO$_2$ ($X_{CO_2_a}$ and $X_{CO_2_{sw}}$) measured every three hours by the NOAA MAPCO$_2$ sensor onboard the USM buoy. Mole fractions were converted to partial pressure as outlined in the papers by Sabine et al. (2000) and Wanninkhof et al. (2007):

$$p_{CO_2}=X_{CO_2}(P-p_{H_2O}) \quad (\text{eq. 15})$$

In equation 15, P is the barometric pressure and $p_{H_2O}$ is the water vapor pressure at 100% humidity. Vapor pressure was calculated using the Weiss and Price (1980) equation:

$$\ln (p_{H_2O}) = 24.4543 - 67.4509(100/T) - 4.8489 \ln(T/100) - 0.000544(S) \quad (\text{eq. 16})$$

where T is the SST in Kelvin, S is the SSS, and $p_{H_2O}$ is in $\mu$atm.

Data Sources and Missing Data

The primary data source for this study was the USM CenGOOS buoy, with NDBC buoys 42007 and 42012 serving as alternative data sources when the USM buoy went offline. Figure 3 displays a timeline of USM buoy (and alternate NDBC buoy 42007) operations for the duration of the study. The USM CenGOOS buoy began collecting all data on May 12, 2009. The $p_{CO_2}$ sensor onboard the buoy (including pressure) collected data continuously through December 21, 2009, with the exception of a brief period from December 10 to December 15 when the sensor was temporarily disabled. Data collection by all other equipment onboard the buoy ceased on September 29, 2009 when the power source failed. Data for all equipment except the $p_{CO_2}$ sensor
was also missing for the period from July 7 to July 12, 2009 when a communications error occurred. The buoy was retrieved from the water for repairs on December 21, 2009.

![Buoy timeline](image)

Fig. 3. Buoy timeline.

Wind and SST data was extracted from NDBC buoy 42007 to supplement all missing data in the USM buoy dataset. Buoy 42007 is a 3-meter discus buoy previously located approximately 22 nautical miles (nm) south/southeast of Biloxi, MS at 30.090 °N, 88.769 °W and approximately 7 nm northwest of the USM buoy (Figure 4).

![Location of USM CenGOOS buoy and NDBC buoys 42007 and 42012](image)

Fig. 4. Location of USM CenGOOS buoy and NDBC buoys 42007 and 42012.
An ANOVA analysis within *MATLAB* showed no significant difference in data for wind speed (r = 0.8217) and direction (r = 0.7351) between buoy 42007 and the USM buoy, validating the use of 42007 to supplement missing wind data (Figure 5). NDBC buoy 42007 was disestablished on December 9, 2009. At this time data from NDBC buoy 42012 was used to supplement missing wind and SST data through December 21, 2009. Buoy 42012 is a 3-meter discus buoy located approximately 12 nm south of Orange Beach, AL at 30.065°N, 87.555°W and approximately 57 nm east of the USM buoy (Figure 4).

Fig. 5. Comparison of wind data for all three buoys from May through August, 2009 with a one-way ANOVA of wind direction for all three buoys (a) and a one-way ANOVA of wind speed for all three buoys (b). In both plots the red lines in the boxes show the median, the top of the boxes are the 25th percentile of the dataset, the bottom of the boxes are the 75th percentile of the dataset, the “whiskers” are the range of values (excluding outliers), and the plus signs represent outliers.
Again, an ANOVA analysis confirmed the validity of using this data source for missing wind speed \( (r = 0.6732) \) and direction \( (r = 0.6340) \) data (Figure 5).

![SST for all 3 buoys May-August](image)

\[ a. \]

![USM SST vs 42007 SST for May-August, 2009](image)

\[ b. \]

![USM SST vs 42012 SST for May-August, 2009](image)

\[ c. \]

Fig. 6. Comparison of SST for all three buoys from May 13 through August 30, 2009. One-way ANOVA of SST for all three buoys (a), SST correlation between USM buoy and 42007(b), and SST correlation between USM buoy and 42012 (c).
ANOVA analysis of SST data from both NBDC buoys and the USM buoy for the same time periods yielded a p-value of 0; indicating values were significantly different (Figure 6a). Further investigation, however, revealed SST data from both NDBC buoys to be a valid supplement to the missing USM buoy data (Figures 6b & 6c). SST from May 13 through August 30, 2009 was compared between the USM buoy and buoy 42012 and between the USM buoy and buoy 42007 (Figure 6). There was a strong correlation between USM and 42007 SST ($r= 0.9707$) and between USM and 42012 SST ($r = 0.9356$). The results also showed there was less than a 1°C difference between the USM buoy and buoy 42012 for approximately 76% of the data. For approximately 97% of the data there was less than a 2°C difference between these buoys, with the mean difference having been 0.687°C. Only 3% of the 42007 data varied from the USM buoy by more than 1°C, and only 0.2% of that data varied by more than 2°C. The mean SST difference between 42007 and the USM buoy was 0.307°C.

Pressure and $pCO_2$ data were missing for a brief period from December 10 to December 15, 2009. Interpolation in *MATLAB* was used to fill in this missing data. Interpolation was also used to fill in missing SSS data from July 7 to July 12 and September 29 and 30. SSS for October through December was estimated using linear regression (Appendix C) of climatological SST and SSS data obtained from NOAA’s National Coastal Data Development Center. Climatological data was obtained from the region enclosed within 30.5424°N, 29.5424°N, -89.1473°W, and -88.1473°W. A One-way ANOVA indicated the linearly regressed SSS was not significantly different from the measured CenGOOS SSS (Figure 7).
Regression SSS vs CenGOOS SSS from May-September, 2009

Fig. 7. One-way ANOVA of measured CenGOOS SSS and linearly regressed SSS for May through September, 2009.

CO₂ Flux Rates

Time series analyses were conducted from the results of the bulk flux equation above (equation 6). CO₂ flux rates were calculated at the 3-hour sampling rate of the $pCO₂$ sensor for a total of 8 values each day. From these values average daily, monthly, and seasonal CO₂ flux rates were determined. All four gas transfer algorithms (equations 7-10) were used to provide a range of flux rates. Flux rates calculated from the quadratic W92 algorithm (equation 9) were used for comparisons of flux with other variables. This algorithm, along with the WM99 algorithm, is based on an average wind speed of 7.4 m/s. The H06 and M01 algorithms are based on higher average wind speeds. The W92 algorithm was selected because in addition to being based on an average wind speed closest to that of this study (5.83 m/s), it also yielded the strongest relationship between wind speed and gas transfer ($k_{600}$) at low to intermediate wind speeds (Figure 8).
Average net CO₂ uptake for the entire northern GOM region (Figure 9) was estimated by applying the overall mean flux rates from each algorithm to the total area of the region. The northern GOM region was defined as the continental shelf region at latitudes above 28°N from the eastern Texas coast to the western coast of Florida. The area (in m²) was estimated through area calculations of polygons drawn on a map of the region. A map with markers at the corners of each polygon can be found in Appendix D.

The northern GOM area was estimated at approximately 2.04 x 10¹¹ m², while the area of the entire GOM has been estimated at approximately 1.9 x 10¹² m² (Robbins et al., 2009). To compare the northern GOM region with the remaining GOM, the area of the northern region was subtracted from the area of the entire GOM. The mean annual CO₂ flux rate from Robbins et al. (2009) (9.4 ± 24 to 13 ± 20 g C m⁻² d⁻¹) was applied to the resulting area to estimate mean net flux for the remainder of the GOM. This allowed for comparison of the northern GOM net CO₂ flux rate with the net flux rate for the remainder of the GOM. With this comparison the role of the northern GOM in the classification of the entire GOM as a source or sink for atmospheric CO₂ could be
examined. The estimate of mean net flux for the northern GOM region was based on the assumption that CenGOOS flux rates were applicable to the entire region; therefore, the overall mean rate (for all four algorithms) from the northwest MBR was extrapolated throughout the entire region. Likewise, the estimate of mean net flux for the remainder of the GOM was based on the assumption that the Robbins et al. flux rates were applicable to that entire region.

Fig. 9. Map of region used to estimate area of northern GOM. Region is outlined in white circles.

Influence of Surface Currents on CO$_2$ Flux Rates

In order to determine the influence surface currents have on the air-sea exchange of CO$_2$, surface currents were factored into the flux equation. For the purpose of this study wind speed relative to water was referred to as “Lagrangian,” and wind speed relative to a fixed geographic location was referred to as “Eulerian,” even though these frames of reference are not the standard. Wind speed relative to water was determined by subtracting the surface current vector from the wind vector in the following manner:

$$V = \sqrt{(u_w-u_c)^2 + (v_w-v_c)^2}$$

(eq. 17)
In equation 17, $uw$ is the eastern component of the wind vector, $vw$ is the northern component of the wind vector, $uc$ is the eastward component of the current vector, and $vc$ is the northward component of the current vector. Surface currents data was measured by the CenGOOS buoy from May through September only, as the Acoustic Doppler Current Profiler (ADCP) went offline at the end of September when the buoy’s power source failed.

Additional surface currents data for the MBR was obtained from three CenGOOS Coastal Ocean Dynamics Applications Radar (CODAR) Stations: SGRV located at 30.3339°N, -88.5690°W, OBSP located at 30.2496°N, -87.6683°W, and HBSB located at 30.3830°N, -86.4327°W. Data from June 30 to November 9 was used, as this was the only data available within the CO$_2$ flux analysis sampling period. Data were only available from the 1-3 and the 22-30 for the month of September and the 29-31 for the month of October. CO$_2$ flux rates were then calculated for the region within the CODAR range by replacing $u$ (cubic or quadratic) in the gas transfer velocity equations (equations 7-10) with $V$ from equation 17. The boundaries of the CODAR region were 30.1997°N, -85.8501°W, 28.7853°N, and -88.8263°W (Figure 10). CO$_2$ flux relative to surface water was calculated based on the assumption that all variables necessary for the calculation (pressure, SSS, SST, wind speed & direction, and $p$CO$_2$), except for the surface currents, did not vary spatially. The same variables were therefore used to calculate the Lagrangian flux rates as were used to calculate the Eulerian flux rates. This was accomplished through interpolation of the CenGOOS datasets to match the hourly sampling rate of the CODAR surface currents and to match the CenGOOS data to every grid point within the sampling region.
Fig. 10. Map of CODAR sampling region boundaries. Green triangles mark CODAR stations, the red diamond marks NDBC buoy 42012, blue diamond marks the USM CenGOOS buoy, and the cyan diamond marks NDBC buoy 42007.

Productivity Data

The location of the USM buoy corresponds with one of the sampling stations (station 8) of the Northern Gulf Institute (NGI) project *Monitoring and Assessment of Coastal and Marine Ecosystems in the Northern Gulf*. Limited nutrient and chlorophyll data were available from this station from May through December, 2009. As an additional source, net primary productivity (NPP) data estimated using the Eppley VGM algorithm was obtained through MODIS satellite imagery from Ocean Color’s Ocean Productivity Page. NPP was plotted using GMT (http://www.soest.hawaii.edu/gmt/) for the region located within 28.5°N, -90.0°W, 31.0°N, and -87.0°W.
CHAPTER III
ANALYSIS OF CENGOOS BUOY DATA

Environmental Variables

As indicated previously, the CenGOOS buoy measured SSS, SST, pressure, wind speed, and wind direction. Figure 11 illustrates plots of daily and monthly averages of these variables from May 13 through December 21, 2009. A summary of mean values for each variable is outlined below.

Mean daily SSS ranged from a minimum value of 21.06 in May to a maximum value of 36.96 in October, with an overall mean value of 30.54. Mean SSS for the summer months (May-August) was 29.49, and the mean fall (September-December) value was 31.58. Mean daily SST ranged from a minimum value of 14.9°C in December to a maximum value of 31.71°C in June, with an overall mean value of 25.97°C. Mean SST for the summer was 28.52°C, and the mean fall SST was 23.45°C. Mean daily wind speed ranged from a minimum of 0 m/s in November to a maximum of 19.64 m/s also in November, with an overall mean of 5.83 m/s. The mean summer wind speed was 5.09 m/s, and the mean fall wind speed was 6.85 m/s. Wind direction was highly variable, but was northeasterly on average. Summer winds were southwesterly on average, and fall winds were northeasterly on average. Mean daily pressure had low variability and ranged from a minimum of 0.9809 atm in December to a maximum of 1.0085 atm in October, with an overall mean of 0.9809 atm. Mean monthly SSS, SST and wind values can be found in Table 1.
Table 1. Mean monthly SSS, SST (°C), wind speed (m/s), and wind direction (degrees) measured from true north.

<table>
<thead>
<tr>
<th></th>
<th>SSS</th>
<th>SST</th>
<th>W Speed</th>
<th>W Direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>May</td>
<td>25.42</td>
<td>26.02</td>
<td>6.76</td>
<td>92.28</td>
</tr>
<tr>
<td>June</td>
<td>26.17</td>
<td>28.69</td>
<td>4.95</td>
<td>241.47</td>
</tr>
<tr>
<td>July</td>
<td>32.49</td>
<td>28.84</td>
<td>4.89</td>
<td>229.16</td>
</tr>
<tr>
<td>August</td>
<td>32.19</td>
<td>29.56</td>
<td>4.40</td>
<td>157.86</td>
</tr>
<tr>
<td>September</td>
<td>29.89</td>
<td>28.57</td>
<td>5.54</td>
<td>122.65</td>
</tr>
<tr>
<td>October</td>
<td>34.44</td>
<td>25.57</td>
<td>6.61</td>
<td>23.03</td>
</tr>
<tr>
<td>November</td>
<td>32.83</td>
<td>20.15</td>
<td>6.38</td>
<td>68.79</td>
</tr>
<tr>
<td>December</td>
<td>27.97</td>
<td>17.70</td>
<td>8.52</td>
<td>60.67</td>
</tr>
</tbody>
</table>

Fig. 11. Average SSS, SST, pressure, and wind measured by the CenGOOS buoy (and NDBC buoys). Figures on the left represent time series of daily averaged values, and figures on the right represent monthly averaged values.
**Biological Activity**

Mean overall NPP for the region located within 28.5°N, -90.0°W, 31.0°N, and -87.0°W ranged from a minimum of ~165.86 mg C m⁻² d⁻¹ in November to a maximum of ~301.55 mg C m⁻² d⁻¹ in July, with a mean of approximately 223.04 mg C m⁻² d⁻¹ (mean values were obtained from 8-day averages). Mean summer NPP was ~250.16 mg C m⁻² d⁻¹ and mean fall NPP was ~197.86 mg C m⁻² d⁻¹. October had the lowest monthly mean NPP and July had the highest mean monthly NPP. Processed MODIS imagery of 8-day and monthly averaged NPP can be found in appendix E. Figure 12 illustrates 8-day and monthly averaged net primary productivity from May through December, 2009.

![8 day averages of NPP](image1)

![Mean Monthly NPP](image2)

**Fig. 12.** Eight day averages (left) and mean monthly values of NPP in mg C m⁻² d⁻¹ estimated from MODIS satellite imagery for the region located within 28.5°N, -90.0°W, 31.0°N, and -87.0°W.

All nutrient concentrations with the exception of silicate were below one µM.

The mean chlorophyll concentration was approximately 2.54 µg / L. Mean nutrient values (µM) were 0.02 for ammonium, 0.01 for nitrate, 0.04 for nitrite, 0.07 for phosphate, and
7.60 for silicate. Chlorophyll and silicate concentrations both peaked in June at 5.18 μg/L and 18.33 μM respectively. Nitrate and nitrite remained at or near zero throughout the study period. Ammonium peaked in August at 0.33 μM. Phosphate peaked in May at 0.11 μM. The highest nutrient concentrations and lowest chlorophyll concentration in August corresponded to one of the highest NPP values. Nutrient and Chlorophyll data from NGI station 8 can be found in Figure 13.

Fig. 13. NGI Chlorophyll and nutrient data from station 8 for the months of May, June, August, and November of 2009. Data was not available for all other months from May through December.

$p_{CO_2}$ and CO$_2$ Flux Rates

$p_{CO_2a}$ ranged from a minimum of 365.79 μatm in September to a maximum of 420.29 μatm in November, with a mean value of 388.73 μatm. Mean summer $p_{CO_2a}$ was 386.98 μatm, and the mean fall value was 390.47 μatm. $p_{CO_2sw}$ ranged from a minimum of 104.45 μatm in May to a maximum of 485.43 μatm in July, with a mean value of 335.36 μatm. Mean summer $p_{CO_2sw}$ was 341.80 μatm, and the mean fall value was 328.99 μatm. Figure 14 illustrates mean daily and monthly $p_{CO_2}$ and CO$_2$ flux rates.
from May 13 through December 21, 2009. Mean monthly $pCO_2$ values are listed in Table 2.

Table 2. Mean monthly $pCO_2$ ($\mu$atm) and $CO_2$ flux rates (mmol m$^{-2}$ d$^{-1}$).

<table>
<thead>
<tr>
<th>Month</th>
<th>$pCO_2$$_{air}$</th>
<th>$pCO_2$$_{sw}$</th>
<th>$CO_2$ flux (W92)</th>
<th>$CO_2$ flux (H06)</th>
<th>$CO_2$ flux (WM99)</th>
<th>$CO_2$ flux (M01)</th>
</tr>
</thead>
<tbody>
<tr>
<td>May</td>
<td>390.68</td>
<td>257.10</td>
<td>-15.76</td>
<td>-13.52</td>
<td>-12.48</td>
<td>-11.56</td>
</tr>
<tr>
<td>June</td>
<td>388.77</td>
<td>292.11</td>
<td>-8.29</td>
<td>-7.11</td>
<td>-4.98</td>
<td>-4.64</td>
</tr>
<tr>
<td>July</td>
<td>385.61</td>
<td>411.07</td>
<td>1.45</td>
<td>1.25</td>
<td>0.84</td>
<td>0.79</td>
</tr>
<tr>
<td>August</td>
<td>384.35</td>
<td>372.52</td>
<td>-0.65</td>
<td>-0.56</td>
<td>-0.35</td>
<td>-0.33</td>
</tr>
<tr>
<td>September</td>
<td>382.75</td>
<td>333.73</td>
<td>-3.47</td>
<td>-2.98</td>
<td>-1.97</td>
<td>-1.84</td>
</tr>
<tr>
<td>October</td>
<td>387.83</td>
<td>330.24</td>
<td>-7.16</td>
<td>-6.15</td>
<td>-5.65</td>
<td>-5.20</td>
</tr>
<tr>
<td>November</td>
<td>395.97</td>
<td>317.27</td>
<td>-7.93</td>
<td>-6.80</td>
<td>-6.40</td>
<td>-5.90</td>
</tr>
<tr>
<td>December</td>
<td>397.53</td>
<td>337.11</td>
<td>-11.49</td>
<td>-9.86</td>
<td>-10.49</td>
<td>-9.68</td>
</tr>
</tbody>
</table>

Overall the region was a net sink for atmospheric $CO_2$ from May through December, 2009. The overall mean flux rate ranged from -4.23 to -5.96 mmol m$^{-2}$ d$^{-1}$ (-1.54 to -2.17 mol m$^{-2}$ yr$^{-1}$) depending on which gas transfer algorithm was used. Mean summer $CO_2$ flux rates ranged from -3.11 to -4.71 mmol m$^{-2}$ d$^{-1}$ (-1.13 to -1.72 mol m$^{-2}$ yr$^{-1}$). Mean fall flux rates ranged from -5.34 to -7.19 mmol m$^{-2}$ d$^{-1}$(-1.95 to 2.62 mol m$^{-2}$ yr$^{-1}$), indicating the region was a stronger sink for atmospheric $CO_2$ during the fall months than it was during the summer months. Mean monthly flux rates were negative (region was a sink) for all months except the month of July. In July the mean rate ranged from 0.79 to 1.45 mmol m$^{-2}$ d$^{-1}$, indicating the region was a weak net source during this time. The region was strongest as a sink during the month of May, followed by December (Figure 14). Mean monthly $CO_2$ flux rates from each algorithm can be found in Table 2.
Flux rates from each gas transfer algorithm were statistically different (p < 0.01), and quadratic flux rates were statistically different than cubic flux rates (p < 0.01). On average the cubic algorithms (WM99 and M01) yielded weaker flux rates than the quadratic algorithms (W92 and H06). The W92 algorithm produced the strongest flux rates followed by the H06 algorithm, then the WM99 algorithm, and finally the M01 algorithm produced the weakest flux rates.

*Estimated Net Flux for Entire Northern GOM*

The estimated net annual flux rate for the entire northern GOM region (as defined in Chapter II and Figure 9) ranged from -3.78 to -5.33 Mt C yr$^{-1}$ depending on the algorithm used. The estimated mean annual CO$_2$ flux rate for the remainder of the GOM,
using the estimates of Robbins et al. (2009), ranged from 14.33 to 19.82 Mt C yr\(^{-1}\). All estimates were based on a single range of mean annual CO\(_2\) flux rates which were extrapolated throughout the entire region. Based on the estimates of CO\(_2\) flux rates in the northern GOM from CenGOOS data, the coastal northern GOM region was not a strong enough sink to control the classification of the entire GOM as either a source or a sink. The northern GOM region did, however, reduce the net annual release of CO\(_2\) to the atmosphere in the GOM by approximately 27%.

*Published CO\(_2\) Flux Rates for the Northern Gulf of Mexico*

Mean CenGOOS CO\(_2\) flux rates were comparable to several previously published values. Lohrenz et al. (2010) estimated mean August 2004 rates of 0.186 to 0.230 mmol m\(^{-2}\) d\(^{-1}\) for the Louisiana shelf region between 89\(^{\circ}\)W and 90\(^{\circ}\)W outside of the Mississippi River plume. In October 2005 estimated mean flux rates were 2.71 to 3.32 mmol m\(^{-2}\) d\(^{-1}\) for the same region (Lohrenz et al., 2010). Both the mean August and October rates were similar to the 2009 CenGOOS rates (-0.33 to -0.65 mmol m\(^{-2}\) d\(^{-1}\) for August and -5.20 to -7.16 mmol m\(^{-2}\) d\(^{-1}\) for October); however, the signs are different. This is due to the proximity of the Lohrenz et al. study to the Mississippi River plume, which has much higher inputs of organic matter. Lohrenz et al., (2010) attributed the low August rates to low river discharge during the sampling period, which was preceded by high river discharge. October flux rates were attributed to decreased primary production resulting from decreased river discharge, as well as increased mixing due to the passing of two major storm events (Lohrenz et al., 2010).

Lohrenz and Cai, (2006) estimated mean June 2003 flux rates of -2.7 to -5.5 mmol m\(^{-2}\) d\(^{-1}\) in the same Mississippi River plume region as Lohrenz et al. (2010). These
rates were similar to the CenGOOS 2009 rates of -4.64 to -8.29 mmol m\(^{-2}\) d\(^{-1}\).

Wanninkhof et al, 2009 also estimated CO\(_2\) flux rates in the northern GOM similar to those of the CenGOOS rates. The mean annual rate of Wanninkhof et al. from April 2008 to March 2009 was -0.92 mol m\(^{-2}\) yr\(^{-1}\), while the mean annual CenGOOS rate ranged from -0.94 to -1.33 mol m\(^{-2}\) yr\(^{-1}\). It should be noted that the CenGOOS annual rate was calculated based on the number of days in the study period; therefore 223 days were used instead of 365 days to calculate the annual rate.

Influence of Environmental Variables on CO\(_2\) Flux Rates

As mentioned previously, SSS, SST, wind speed, wind direction, atmospheric pressure, and \(pCO_2\) all contribute to CO\(_2\) flux rates. In an attempt to determine which of these variables were most strongly influencing CO\(_2\) flux rates, correlation coefficients were calculated using MATLAB. All of the above variables had a statistically significant correlation with flux rates, with the exception of atmospheric pressure and wind direction. The variables which had the strongest correlations with CO\(_2\) flux rates were \(\Delta pCO_2\) and \(pCO_{2sw}\) (\(r = 0.72 \& r = 0.70, p = 0\)) followed by wind speed (\(r = -0.58, p = 0\)). This was not surprising, as wind and \(\Delta pCO_2\) are major components of the bulk CO\(_2\) flux equation (equation 6).

A summary of trends between CO\(_2\) flux rates and each variable follows. As \(pCO_{2sw}\) increased, CO\(_2\) flux into surface waters decreased, and as \(\Delta pCO_2\) increased CO\(_2\) flux into surface waters increased (Figure 15). As wind speed increased CO\(_2\) flux into surface waters increased (Figure 16). In addition to \(\Delta pCO_2\), \(pCO_{2sw}\), and wind speed, NPP also had a rather strong, statistically significant, correlation with CO\(_2\) flux rates (\(r = 0.69, p = .0001\)).
Fig. 15. Relationships between CO$_2$ flux rates and $p$CO$_{2\text{air}}$, $p$CO$_{2\text{sw}}$, and $\Delta$pCO$_2$.
Correlation coefficients for each relationship were as follows: $p$CO$_{2\text{air}} = -0.3939$, $p$CO$_{2\text{sw}} = 0.6969$, and $\Delta$pCO$_2 = 0.7180$.

NPP and CO$_2$ flux were inversely correlated, and as NPP increased CO$_2$ flux into surface waters decreased (Figure 17). Overall, simple correlations of each variable with CO$_2$ flux indicated $\Delta$pCO$_2$ had the strongest correlation with flux rates, followed by $p$CO$_{2\text{sw}}$, NPP, and then wind speed. The correlations with $p$CO$_2$ and wind speed are apparent. The strong correlation between NPP and CO$_2$ flux rates are likely due to strong correlations between NPP and $p$CO$_2$, which will be discussed momentarily.

Fig. 16. Time series of daily averaged wind speed and CO$_2$ flux rates from May through December, 2009.
Fig. 17. Time series of eight-day averages and monthly averages of NPP and CO₂ flux rates from May through December, 2009.

An additional method which was employed to try to determine which environmental variables were most influential on CO₂ flux rates was a sensitivity analysis. Each variable was altered by adding 1, 5, 10, 20, 30, 40 or 50 to the measured values, with the exception of atmospheric pressure. Because ranges of pressure at the air-sea interface are generally small, pressure was altered by adding 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, or 0.5.

When CO₂ flux rates were calculated from the in situ values of each variable the mean rate was -6.06 mmol m⁻² d⁻¹ (W92). Based on the analysis, CO₂ flux rates were most sensitive to changes in wind speed (Figure 18). A change in wind speed of only 1 m/s in either direction altered CO₂ flux rates by approximately 29% (Table 3). A more extreme change in wind speed of 50 m/s produced CO₂ flux rates seventy times that of those estimated from in situ values.
Fig. 18. Results of sensitivity analysis of changes in wind speed on CO\textsubscript{2} flux rates. The blue lines are flux rates calculated from \textit{in situ} values and the red lines are flux rates with the indicated alterations. Changes in winds speed are shown above each subplot.

Table 3. Results of sensitivity analysis showing percent increase/decrease in CO\textsubscript{2} flux rates when variables were changed by the values indicated. For pressure values were divided by 100 (0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5).

<table>
<thead>
<tr>
<th>Variable</th>
<th>+1%</th>
<th>+5%</th>
<th>+10%</th>
<th>+20%</th>
<th>+30%</th>
<th>+40%</th>
<th>+50%</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔpCO\textsubscript{2}</td>
<td>2%</td>
<td>9%</td>
<td>17%</td>
<td>35%</td>
<td>52%</td>
<td>69%</td>
<td>87%</td>
</tr>
<tr>
<td>Pressure</td>
<td>1%</td>
<td>5%</td>
<td>10%</td>
<td>20%</td>
<td>30%</td>
<td>40%</td>
<td>50%</td>
</tr>
<tr>
<td>SST</td>
<td>0.3%</td>
<td>2%</td>
<td>5%</td>
<td>9%</td>
<td>20%</td>
<td>44%</td>
<td>76%</td>
</tr>
<tr>
<td>SSS</td>
<td>0.5%</td>
<td>3%</td>
<td>5%</td>
<td>11%</td>
<td>16%</td>
<td>20%</td>
<td>25%</td>
</tr>
<tr>
<td>Wind Speed</td>
<td>29%</td>
<td>190%</td>
<td>490%</td>
<td>1421%</td>
<td>2792%</td>
<td>4604%</td>
<td>6856%</td>
</tr>
</tbody>
</table>

After wind speed, CO\textsubscript{2} flux rates were most sensitive to changes in ΔpCO\textsubscript{2} (Appendix F). A change in ΔpCO\textsubscript{2} of 1 µatm in either direction altered CO\textsubscript{2} flux rates by approximately 2%, while a change of 50 µatm in either direction altered flux rates by approximately 87% (Table 3).

Of the remaining three variables, CO\textsubscript{2} flux rates were most sensitive to changes in pressure (Appendix F). Overall flux rates were least sensitive to changes in SSS and SST (Appendix F). When pressure was increased or decreased by only 0.01 atm CO\textsubscript{2} flux
rates were altered by approximately 1%, while a change of 0.5 atm altered flux rates by approximately 50% (Table 3). A change in SST and SSS of 1 altered CO$_2$ flux rates by less than 1% (Table 3). CO$_2$ flux rates had greater sensitivity to more extreme changes in SST (>30), and sensitivity was actually greater than that of pressure for these extremes. Changes in flux rates resulting from changes in SSS remained lower than all other variables (Table 3).

Because $\Delta p$CO$_2$ was the second most influential variable, an examination of the effects of variables on $p$CO$_2$ values was necessary. The analysis of the relationships between $p$CO$_2$ and all other variables indicated NPP and SSS correlated most strongly with both $\Delta p$CO$_2$ ($r=.63$ for NPP & $r=.60$ for SSS) and $p$CO$_2$$_{sw}$ ($r=.60$ for NPP & $r=.60$ for SSS), while $p$CO$_2$$_a$ correlated most strongly with NPP ($r=-.47$) and SST ($r=-.63$) (Figures 19 and 20 and Appendix F). $p$CO$_2$$_a$ was inversely correlated with both SST and NPP and both correlations were statistically significant at the 0.01 level (Figures 19 and 20). Increased SST generally reduces the solubility of CO$_2$ in surface waters; therefore, one would expect to observe an increase in $p$CO$_2$$_a$ with an increase in SST. This was not what was observed in this case. SST can increase rates of photosynthesis (Miller, 2004), which could increase drawdown of atmospheric CO$_2$. Whereas, no direct measurements of the rates of photosynthesis were made, this is a possible explanation for the observed decrease in $p$CO$_2$$_a$ with increased SST. The inverse correlation between $p$CO$_2$$_a$ and NPP lends support to this possible explanation, as drawdown of $p$CO$_2$$_a$ concentrations appeared to increase when NPP concentrations increased.

As indicated in the preceding paragraph, changes in SST affect the solubility of CO$_2$ in surface waters. For this reason, a stronger correlation between $p$CO$_2$$_{sw}$ and SST
would be expected. The actual observed correlation was rather weak and not statistically significant ($r=.12, p >0.05$). This suggests the changes in SST may not have been large enough to outweigh the SSS and NPP correlations. $pCO_{2sw}$ was positively correlated with SSS and NPP at the 0.01 level. As SSS and NPP increased, $pCO_{2sw}$ also increased (Figures 19 and 20). These relationships are not surprising, as SSS is positively correlated with alkalinity, which affects $pCO_{2sw}$. Increased NPP can serve as a mechanism for increased drawdown of atmospheric CO$_2$. The maximum mean monthly NPP and $pCO_{2sw}$ values observed in July suggest increased NPP may have been contributing to increased $pCO_2$ in surface waters, causing the small release of CO$_2$ to the atmosphere observed during this time.

Fig. 19. Time series of wind speed, SST, SSS, and $\Delta pCO_2$ from May through December, 2009.
Fig. 20. Mean monthly NPP plotted with $\Delta pCO_2$, $pCO_{2a}$, and $pCO_{2sw}$.

$\Delta pCO_2$ correlated most strongly with NPP and SSS ($p<.001$), and as NPP and SSS increased $\Delta pCO_2$ decreased. Again, with increased SSS alkalinity likely also increased; therefore, $pCO_{2sw}$ increased which decreased the difference between $pCO_{2sw}$ and $pCO_{2a}$. It can also be assumed that increased NPP would increase $pCO_{2sw}$, as increased rates of photosynthesis would increase drawdown of atmospheric CO$_2$. The increase in $pCO_{2sw}$ would decrease the difference between $pCO_{2sw}$ and $pCO_{2a}$.

To summarize the importance of environmental factors on CO$_2$ flux rates, simple correlations between each variable indicated CO$_2$ flux rates correlated most strongly with $\Delta pCO_2$, NPP, and wind speed in that order. A sensitivity analysis showed CO$_2$ flux rates were most sensitive to changes in wind speed, followed by $\Delta pCO_2$, and then pressure. Flux rates were least sensitive to changes in SST and SSS. An examination of $pCO_2$ indicated $\Delta pCO_2$ had the strongest correlation with CO$_2$ flux rates, followed by $pCO_{2sw}$ and then $pCO_{2a}$. $pCO_{2a}$ correlated most strongly with SST and NPP, and $pCO_{2sw}$
correlated most strongly with SSS and NPP. \( \Delta p_{\text{CO}_2} \) had the strongest correlations with NPP and SSS. Overall, NPP had the strongest correlation with CO\(_2\) flux rates, followed by wind and SSS.

**Synthesis of Maximum and Minimum CO\(_2\) Flux Rates**

Mean monthly CO\(_2\) flux into surface waters was strongest for the month of May. Rates weakened through June and in July surface waters were a weak net source of CO\(_2\) to the atmosphere. After July surface waters became a net sink for CO\(_2\) again and flux rates continuously strengthened through December. Figure 21 shows mean monthly CO\(_2\) flux rates and mean monthly values of the variables which had the strongest influences on those rates (\( p_{\text{CO}_2}, \) SSS, SST, NPP, and wind speed).

The lowest mean monthly SSS was observed during the month of May when river discharge to the MBR was greatest. (Appendix A). This low SSS together with mid-level NPP corresponded to the lowest mean monthly \( p_{\text{CO}_{2\text{sw}}} \) value. A slightly higher \( p_{\text{CO}_2a} \) value together with the lowest \( p_{\text{CO}_{2\text{sw}}} \) value resulted in the highest \( \Delta p_{\text{CO}_2} \) value. This high \( \Delta p_{\text{CO}_2} \) together with the highest observed mean wind speeds likely contributed to May having the strongest mean monthly uptake of atmospheric CO\(_2\) by surface waters.

In July mean SSS was much greater than it was in May which was likely due to a large decrease in river discharge to the region. Mean NPP also increased to its maximum value at this time, as did \( p_{\text{CO}_{2\text{sw}}} \). It can be assumed that the increased \( p_{\text{CO}_{2\text{sw}}} \) was related to increased uptake rates of atmospheric CO\(_2\), which may have been due to increased NPP. Mean SST increased, and \( p_{\text{CO}_2a} \) decreased. As alluded to earlier, this decrease in \( p_{\text{CO}_2a} \) could be related to increased rates of photosynthesis from increased SST. \( p_{\text{CO}_{2\text{sw}}} \) was highest in July which correlated with the highest NPP value. Mean
$\Delta p\text{CO}_2$ greatly decreased due to the large increase in $p\text{CO}_{2\text{sw}}$, and was positive for the only time during the analysis. The positive mean $\Delta p\text{CO}_2$ and a decrease in wind speeds likely contributed to weakened CO$_2$ flux rates and a small release of CO$_2$ to the atmosphere for the month of July.

Fig. 21. Monthly averages for CO$_2$ flux rates and most influential environmental variables.
CHAPTER IV

ANALYSIS OF LAGRANGIAN CO$_2$ FLUX RATES

All CO$_2$ flux rates discussed in the previous chapter were calculated from wind speed relative to fixed geographic coordinates. Friction created as winds blow across surface waters transfers momentum and sets surface currents in motion. Due to the strong relationship between wind and surface currents, CO$_2$ flux rates could be significantly altered by using wind speed relative to surface waters (a Lagrangian reference). A discussion of CO$_2$ flux rates estimated using a Lagrangian reference frame follows.

CenGOOS Buoy Data

Daily mean $u$ component surface current speeds ranged from -22.63 to 11.40 cm/s with an overall mean westward flow of -2.37 cm/s (Figure 22a). Daily mean $v$ component surface current speeds ranged from -18.81 to 14.95 cm/s with an overall mean northward flow of 1.03 cm/s (Figure 22b).
When CO$_2$ flux was calculated using a Lagrangian reference frame the mean rate ranged from -2.76 to -4.39 mmol m$^{-2}$ d$^{-1}$ (mean flux for May through September) depending on the gas transfer algorithm used. Compared to the mean Eulerian flux rate from May through September (-2.86 to -4.49 mmol m$^{-2}$ d$^{-1}$), this was a mean difference of 2.18 to 3.59%. The mean percent difference suggests uptake of CO$_2$ by surface waters was decreased by 2.18 to 3.59% on average when a Lagrangian reference frame was used to calculate CO$_2$ flux rates. A one-way ANOVA of buoy flux rates, however, indicated flux rates calculated using a Lagrangian reference frame were not significantly different from flux rates calculated using a Eulerian reference frame ($p > 0.01$). Figure 23 illustrates mean monthly CO$_2$ flux rates calculated from CenGOOS buoy data with and without the influence of surface currents.
Mean monthly percent differences ranged from a minimum of 0.018 to a maximum of 5.82, depending on the gas transfer algorithm used. Mean percent difference in cubic flux rates was greatest for the month of June, and mean percent difference in quadratic flux rates was greatest for the month of September (Figure 24). For all algorithms the smallest mean percent difference in flux rates occurred during August when the mean percent difference was near zero (Figure 24). Percent differences were positive for all months except September (and August for the cubic algorithms). Positive differences indicate uptake or release of CO$_2$ into or out of surface waters was decreased when a Lagrangian reference frame was used. When differences were negative in September (and August), use of a Lagrangian reference frame increased both uptake and release of CO$_2$ by surface waters.
Fig. 24. Mean monthly CenGOOS percent differences between Eulerian and Lagrangian flux rates (Eulerian-Lagrangian). Flux rates calculated from all four gas transfer algorithms were included. Negative differences indicate uptake or release of CO$_2$ by surface waters increased when a Lagrangian reference frame was used, and positive differences indicate uptake or release decreased.

Mean monthly trends in differences between flux rates calculated from Eulerian and Lagrangian references (dflux) correlated most strongly with trends in $p$CO$_2$ and SSS. When dflux was greatest during the months of May and June (-0.28 and -0.30 mmol m$^-2$ d$^-1$), $\Delta$pCO$_2$ was also greatest (-133.57 and -96.66 µatm) due to $p$CO$_2$$_a$ being much greater than $p$CO$_2$$_sw$ (Figure 25). SSS was lowest during these months (Figure 25).

Correlations between mean monthly dflux and mean monthly SSS and between mean monthly dflux and mean monthly $\Delta$pCO$_2$ were significant at the 0.01 and 0.05 levels respectively. When differences in $p$CO$_2$$_sw$ and $p$CO$_2$$_a$ were high, differences in flux rates were also high. As $\Delta$pCO$_2$ decreased, dflux also decreased. Conversely, when SSS was low, dflux was high.
Fig. 25. CenGOOS mean monthly difference in flux rates (dflux), SSS, and ΔpCO₂.
dflux and SSS had an r-value of 0.9539 (p= 0.01) and dflux and ΔpCO₂ had an r-value of
0.8987 (p <0.05).

CODAR Data

**Summary of Surface Currents**

Daily mean u component surface current speeds ranged from -16.42 to 23.39 cm/s
with an overall mean eastward flow of 2.65 cm/s (Figure 26a). Daily mean v component
surface current speeds ranged from -26.82 to 18.96 cm/s with an overall mean southward
flow of -0.97 cm/s (Figure 26b).
Fig. 26. Mean monthly CODAR surface current speeds for June through November 2009. For the $u$ component (a) positive values indicate eastward flow while negative values indicate westward flow. For the $v$ component (b) positive values indicate northward flow while negative values indicate southward flow.

**Lagrangian Flux Rates**

When CO$_2$ flux rates were calculated using a Lagrangian reference frame the mean rate ranged from -1.20 to -2.02 mmol m$^{-2}$ d$^{-1}$ (mean flux for June 30 through November 9) depending on the gas transfer algorithm used. Compared to the mean Eulerian flux rate from this time period (-1.23 to -2.06 mmol m$^{-2}$ d$^{-1}$), this was a mean difference of 2.06 to 2.84 %. The mean percent difference indicates uptake of CO$_2$ by surface waters was decreased by 2.06 to 2.84% when a Lagrangian reference frame was used to calculate CO$_2$ flux rates. A one-way ANOVA indicated this slight decrease in CO$_2$ flux rates was statistically significantly (p <0.01); however, the decrease in CO$_2$ flux rates for the northwest MBR was trivial. Figure 27 illustrates mean monthly CO$_2$ flux rates calculated from CODAR data with and without the influence of surface currents.
Fig. 27. CODAR mean monthly CO\textsubscript{2} flux rates from June through November calculated with (blue dashed line) and without (red solid line) surface currents data.

Mean monthly percent differences ranged from a minimum of -0.038 to a maximum of 5.346, depending on the gas transfer algorithm used. Mean difference in flux rates was greatest for the month of September and smallest for the month of August when the mean difference was near zero (Figure 28). Percent differences were positive for all months except August when differences were just below zero (-0.038 to -0.242). Positive differences indicate uptake or release of CO\textsubscript{2} by surface waters was decreased when a Lagrangian reference frame was used. When differences were negative in August, use of a Lagrangian reference frame slightly increased uptake of CO\textsubscript{2} by surface waters.

The margin of error for mean CO\textsubscript{2} flux rates was calculated using a 95% confidence interval, and was approximately ± 0.84 for the W92 algorithm, ± 0.72 for the H06 algorithm, ± 0.60 for the WM99 algorithm, and ± 0.55 for the M01 algorithm.
Ranges of CO₂ flux rates were therefore -1.21 to -2.90 for the W92 algorithm, -1.04 to -2.49 for the H06 algorithm, -0.72 to -1.92 for the WM99 algorithm, and -0.68 to -1.79 for the M01 algorithm. Lagrangian CO₂ flux rates for each algorithm fell within these margins of error.

Fig. 28. CODAR Mean monthly percent differences between Lagrangian and Eulerian flux rates. Flux rates calculated from all four gas transfer algorithms are included. Negative differences indicate uptake of CO₂ by surface waters increased when a Lagrangian reference frame was used, and positive differences indicate uptake or release decreased.

Some of the global ocean’s strongest sources of CO₂ to the atmosphere occur within the equatorial region and the northwest Pacific, while the global ocean’s strongest sinks occur between 40°N to 60°N and between 40°S to 60°S (Takahashi et al., 2002). Mean CO₂ flux rates have been estimated at -0.39 Pg C yr⁻¹ for the region north of 50°N, -0.92 Pg C yr⁻¹ for the region between 14°N and 50°N, 1.07 Pg C yr⁻¹ for the region between 14°N and 14°S, -1.51 Pg C yr⁻¹ for the region between 14°S and 50°S, and -0.47 Pg C yr⁻¹ for the region south of 50°S (Takahashi et al., 2002).
Assuming a universal difference in flux rates of 2.06 to 2.84% for the entire global ocean with use of a lagrangian reference frame, release of CO$_2$ to the atmosphere in source regions would decrease. Uptake of atmospheric CO$_2$ in sink regions would also decrease. Flux rates in the equatorial region (between 15°S and 15°N) would likely experience little to no change due to wind speed relative to surface waters being irrelevant when dealing with the doldrums. The global ocean’s mean CO$_2$ flux rate is currently estimated to be approximately -2.22 Pg C yr$^{-1}$ (Takahashi et al., 2002). The inclusion of surface currents in the calculation of flux rates would reduce the mean estimated uptake of atmospheric CO$_2$ by 0.068 to 0.093 Pg C yr$^{-1}$ (1.55 x 10$^{12}$ to 2.11 x 10$^{12}$ mol yr$^{-1}$), resulting in a mean global oceanic uptake of -2.15 to -2.13 Pg C yr$^{-1}$. This reduction in uptake is equivalent to approximately 1% (based on IPCC 2000 to 2005 estimates) of the annual global CO$_2$ emissions from fossil fuels (IPCC, 2007).

*Trends in Flux Differences*

Trends in dflux can be related to both wind and surface currents direction. In regions where differences in flux rates were most strongly negative, wind coincided with surface currents (Figure 29c). This was in agreement with the overall pattern of negative differences in regions where wind and currents coincided and positive differences in regions where winds opposed currents (Figures 29 and 30). To demonstrate this relationship more clearly, data from the CenGOOS buoy was examined. This data exhibits a clearer relationship, as wind data used in determining CODAR flux rates was assumed to be uniform throughout the region and therefore did not vary spatially. Figure 30 illustrates the relationship between wind, surface currents, and differences in flux rates from the CenGOOS buoy.
Fig. 29. Contour plot of mean $d$flux (a). The black arrows represent mean surface currents. Mean wind speed and direction is indicated to the right of each plot. Values were averaged over the time period from June 30 to November 9, 2009. Regions where the difference in flux rates was positive are represented by red and yellow shading and are displayed in a magnified portion of the plot to the left (b). Below is a contour plot of hourly wind, surface currents, and flux differences from hour 1 of August 1, 2009 (c). Negative differences are represented by green and blue shading.

The strongest relationships were observed between Julian days 133 and 181 (May and June) when $d$flux was most negative. During this time, the above mentioned
relationship between dflux and winds was observed. Additional hourly and monthly contour plots can be found in Appendix G.

Fig. 30. Mean daily CenGOOS buoy winds, surface currents, and differences in flux rates from May through September 2009.

On average, during the months of June and July, positive differences in flux dominated (data was only available for the 30th in June). As the months progressed, positive differences become less frequent. In August the frequency of positive differences was nearly equal to that of negative differences. The months of September, October, and November had negative differences dominating over positive differences. It should be noted, however, that limited data were available during the months of September, October, and November. SSS and ΔρCO₂ values correlated most strongly with these observed trends as discussed below (Figure 31).
Fig. 31. CODAR mean monthly dflux, SSS, and ΔpCO₂. dflux and SSS had an r-value of 0.5176 (p<0.01) and dflux and ΔpCO₂ had an r-value of 0.9379 (p<0.01).

Mean monthly trends in CODAR dflux correlated most strongly with trends in pCO₂ and SSS. When dflux was greatest during the months of October and November (-0.15 and -0.12 mmol m⁻² d⁻¹), differences in pCO₂ were also greatest (-57.10 and -59.71 µatm) due to pCO₂a being greater than pCO₂sw (Figure 31). When differences in pCO₂sw and pCO₂air were high, differences in flux rates were also high (Figure 31). As ΔpCO₂ decreased, dflux also decreased. SSS was lowest during September when the difference in flux rates was highest (Figure 31).
CHAPTER V

CONCLUSIONS

From May through December 2009, $p$CO$_2$, SST, SSS, wind, pressure, and currents data were collected by the USM CenGOOS buoy located in the NW MBR. During this time the MBR was overall a net sink for atmospheric CO$_2$, with a mean flux rate of -4.23 to -5.96 mmol m$^{-2}$ d$^{-1}$ (-1.54 to -2.17 mol m$^{-2}$ yr$^{-1}$). Net annual uptake for the entire northern Gulf of Mexico region was estimated at -3.78 to -5.33 Mt C yr$^{-1}$. Estimates were based on the range of mean annual CO$_2$ flux rates estimated from CenGOOS buoy data which were extrapolated throughout the entire region. Mean monthly flux rates were all negative with the exception of July when the region was a weak net source of CO$_2$ to the atmosphere. The strongest CO$_2$ flux rates occurred during the month of May, and the weakest rates occurred during August.

The classification of the region as either a source or a sink did not vary seasonally from summer to fall. Both seasons were net sinks for atmospheric CO$_2$, with the fall months being a stronger net sink than the summer months. Net annual uptake for the northern GOM region was estimated at approximately -3.78 to -5.33 Mt C yr$^{-1}$. The estimated net annual CO$_2$ flux for the entire GOM minus the defined northern region ranged from 14.33 to 19.82 Mt C. All net flux estimates were based on a single range of mean annual CO$_2$ flux rates which were extrapolated throughout the entire region. Based on the estimates of CO$_2$ flux in the northern GOM from CenGOOS data, the coastal northern GOM region was not a strong enough sink to control the classification of the entire GOM as either a source or a sink. The northern GOM region did, however,
reduce the net annual release of CO$_2$ to the atmosphere in the GOM by approximately 27%.

The MBR CO$_2$ flux rates were similar to previously published rates for the northern GOM region. Wanninkhof et al. (2009) estimated a mean annual rate of -0.92 mol m$^{-2}$ yr$^{-1}$ from April 2008 to March 2009. Lohrenz and Cai (2006) estimated mean flux rates of -2.7 to -4.9 mmol m$^{-2}$ d$^{-1}$ near the Mississippi River plume during June, 2003. Lohrenz et al. (2010) estimated mean flux rates for the same region at 0.186 to 0.230 mmol m$^{-2}$ yr$^{-1}$ for August 2004 and 2.71 to 3.32 mmol m$^{-2}$ yr$^{-1}$ for October 2005. The CenGOOS overall mean flux rate was -0.94 to -1.33 mol m$^{-2}$ yr$^{-1}$ for May through December 2009, which corresponds to the Wanninkhof et al. (2009) rate. The mean CenGOOS August rates were fairly similar to the Lohrenz et al. (2010) rates at -0.33 to -0.65 mmol m$^{-2}$ d$^{-1}$. The mean October rates were also similar to the Lohrenz et al. rates at -5.20 to -7.16 mmol m$^{-2}$ d$^{-1}$. The CenGOOS signs, however, for both the August and the October mean rates were different. This was attributed to the proximity of the Lohrenz et al. study to the Mississippi River plume and the different biogeochemistry associated with that region. The Mean June CenGOOS rate was -4.64 to -8.29 mmol m$^{-2}$ d$^{-1}$, which was comparable to the mean Lohrenz and Cai (2003) rate.

Simple correlations between each environmental variable and CO$_2$ flux rates indicated CO$_2$ flux rates correlated most strongly with $\Delta p$CO$_2$, NPP, and wind speed in that order. A sensitivity analysis showed CO$_2$ flux rates were most sensitive to changes in wind speed, followed by $\Delta p$CO$_2$. An examination of $p$CO$_2$ indicated $\Delta p$CO$_2$ had the strongest correlation with CO$_2$ flux, followed by $p$CO$_{2sw}$ and then $p$CO$_{2a}$. $p$CO$_{2a}$ had the strongest correlations with SST and NPP, and $p$CO$_{2sw}$ had the strongest correlations with
SSS and NPP. $\Delta p\text{CO}_2$ was correlated most strongly with NPP and SSS. Overall, NPP had the strongest correlation with CO$_2$ flux rates, followed by wind and SSS.

Calculating mean daily CO$_2$ flux rates using wind speed relative to surface water (Lagrangian) rather than wind relative to fixed geographic coordinates (Eulerian) decreased flux rates by 2.06 to 2.84%. Both uptake of atmospheric CO$_2$ by surface waters and release of CO$_2$ to the atmosphere decreased for all months except August. In August the cubic flux algorithms produced negative differences between the Eulerian and Lagrangian flux rates, indicating uptake of atmospheric CO$_2$ by surface waters increased when a Lagrangian reference frame was used. While these differences in flux rates were statistically significant, they were rather trivial for the northwest MBR.

Assuming a universal difference in flux rates of 2.06 to 2.84% for the entire global ocean with use of a lagrangian reference frame, release of CO$_2$ to the atmosphere in source regions would decrease. Uptake of atmospheric CO$_2$ in sink regions would also decrease. Flux rates in the equatorial region (between 15°S and 15°N) would likely experience little to no change due to wind speed relative to surface waters being irrelevant when dealing with the doldrums. The global ocean’s mean CO$_2$ flux rate is currently estimated to be approximately -2.22 Pg C yr$^{-1}$. The inclusion of surface currents in the calculation of flux rates would reduce the mean estimated uptake of atmospheric CO$_2$ by 0.068 to 0.093 Pg C yr$^{-1}$, resulting in a mean oceanic uptake of -2.15 to -2.13 Pg C yr$^{-1}$.

As anthropogenic input of CO$_2$ to the atmosphere continues to rise, constraints on the global CO$_2$ budget are increasingly important. The global ocean is one of the two major sinks for excess CO$_2$ in the atmosphere. Coastal oceans represent a large
uncertainty in uptake of atmospheric CO$_2$; therefore continued CO$_2$ flux work in these regions is critical for increased understanding of future levels of both atmospheric and oceanic CO$_2$. 
APPENDIX A

RIVER DISCHARGE

Fig. A-1. Mean monthly river discharge for all major rivers influencing the MBR.

Table A-1. Mean monthly river discharge (m$^3$/s) for all major rivers contributing to MBR from May to December, 2009.

<table>
<thead>
<tr>
<th></th>
<th>Mobile Bay</th>
<th>Escambia</th>
<th>Choctawatchee</th>
<th>Pearl</th>
<th>Pascagoula</th>
<th>Mississippi</th>
</tr>
</thead>
<tbody>
<tr>
<td>May</td>
<td>36.8</td>
<td>8855</td>
<td>163</td>
<td>9204</td>
<td>16960</td>
<td>912100</td>
</tr>
<tr>
<td>June</td>
<td>19.1</td>
<td>7031</td>
<td>85</td>
<td>4553</td>
<td>4876</td>
<td>824900</td>
</tr>
<tr>
<td>July</td>
<td>21</td>
<td>1339</td>
<td>90.5</td>
<td>2185</td>
<td>1812</td>
<td>471700</td>
</tr>
<tr>
<td>August</td>
<td>33.9</td>
<td>2579</td>
<td>99.1</td>
<td>3225</td>
<td>2007</td>
<td>405200</td>
</tr>
<tr>
<td>September</td>
<td>32.7</td>
<td>6946</td>
<td>97.9</td>
<td>3521</td>
<td>4190</td>
<td>331400</td>
</tr>
<tr>
<td>October</td>
<td>35.3</td>
<td>3915</td>
<td>106.6</td>
<td>21260</td>
<td>4922</td>
<td>605000</td>
</tr>
<tr>
<td>November</td>
<td>43.6</td>
<td>11230</td>
<td>114.4</td>
<td>6757</td>
<td>5256</td>
<td>858300</td>
</tr>
<tr>
<td>December</td>
<td>112.8</td>
<td>31200</td>
<td>215.2</td>
<td>28190</td>
<td>38040</td>
<td>673900</td>
</tr>
</tbody>
</table>

Table A-2. Mean climatological river discharge (m$^3$/s) for all major rivers contributing to MBR from May to December, 2009.

<table>
<thead>
<tr>
<th></th>
<th>Mobile Bay</th>
<th>Escambia</th>
<th>Choctawatchee</th>
<th>Pearl</th>
<th>Pascagoula</th>
<th>Mississippi</th>
</tr>
</thead>
<tbody>
<tr>
<td>May</td>
<td>33</td>
<td>5290</td>
<td>81</td>
<td>11300</td>
<td>10300</td>
<td>808000</td>
</tr>
<tr>
<td>June</td>
<td>36</td>
<td>5390</td>
<td>90</td>
<td>5510</td>
<td>5350</td>
<td>737000</td>
</tr>
<tr>
<td>July</td>
<td>48</td>
<td>6040</td>
<td>101</td>
<td>4620</td>
<td>5390</td>
<td>522000</td>
</tr>
<tr>
<td>August</td>
<td>35</td>
<td>4100</td>
<td>105</td>
<td>3780</td>
<td>3940</td>
<td>451000</td>
</tr>
<tr>
<td>September</td>
<td>42</td>
<td>4410</td>
<td>83</td>
<td>3160</td>
<td>3830</td>
<td>340000</td>
</tr>
<tr>
<td>October</td>
<td>31</td>
<td>4380</td>
<td>113</td>
<td>3270</td>
<td>3320</td>
<td>605000</td>
</tr>
<tr>
<td>November</td>
<td>33</td>
<td>4920</td>
<td>91</td>
<td>4390</td>
<td>5050</td>
<td>549000</td>
</tr>
<tr>
<td>December</td>
<td>37</td>
<td>7310</td>
<td>108</td>
<td>10200</td>
<td>10400</td>
<td>51100</td>
</tr>
</tbody>
</table>
APPENDIX B

MEAN WIND DIRECTION FORMULA

From the NCAR Earth Observing Laboratory Wind Direction Quick Reference

a.** U= - ws*sin(wd*pi/180) East component of wind
b.** V= - ws*cos(wd*pi/180) North component of wind
c.*** Mean direction= 270 - (atan2(V, U)*180/pi) if U < 0
    Mean direction= 90 - (atan2(V, U)*180/pi) if U > 0

** ws = wind speed (m/s)
** wd = wind direction (degrees true north)
*** Mean values of U and V are used in part c.
Linear Regression in MATLAB:

\[
\text{oct}_\text{p}=\text{polyfit(Octsst,octsss,1)} \\
\text{oct}_\text{s}=\text{oct}_\text{p(:,1).*octsst+oct}_\text{p(:,2)}; \\
\text{nov}_\text{p}=\text{polyfit(Novsst,novsss,1)} \\
\text{nov}_\text{s}=\text{nov}_\text{p(:,1).*novsst+nov}_\text{p(:,2)}; \\
\text{dec}_\text{p}=\text{polyfit(Decsst,decsss,1)} \\
\text{dec}_\text{s}=\text{dec}_\text{p(:,1).*decssst+dec}_\text{p(:,2)};
\]

\text{Octsst}, \text{Novsst}, and \text{Decsst} represent climatological SST data from NOAA’s National Coastal Data Development Center.

\text{octsss}, \text{novsss}, and \text{decsss} represent climatological SST data from NOAA’s National Coastal Data Development Center.

\text{octsst}, \text{novsst}, and \text{decss} represent combined SST data from NDBC buoys 42007 and 42012.
Fig. D-1. Map of northern Gulf of Mexico region used to calculate net annual CO$_2$ uptake. The region is outlined by the black and white circles. The yellow pins mark corners of triangles used to divide the region. Areas of each triangle were totaled to produce the final area estimate for the entire region.
Fig. E-1. Images of 8-day averaged NPP from day 137 to day 168, 2009.
Fig. E-2. Images of 8-day averaged NPP from day 169 to day 200, 2009.
Fig. E-3. Images of 8-day averaged NPP from day 201 to day 232, 2009.
Fig. E-4. Images of 8-day averaged NPP from day 233 to day 264, 2009.
Fig. E-5. Images of 8-day averaged NPP from day 265 to day 296, 2009.
Fig. E-6. Images of 8-day averaged NPP from day 297 to day 328, 2009.
Fig. E-7. Images of 8-day averaged NPP from day 329 to day 360, 2009.
May 2009 Net Primary Productivity
(mg C m\(^{-2}\) d\(^{-1}\))

Fig. E-8. Mean monthly May 2009 NPP.

June 2009 Net Primary Productivity
(mg C m\(^{-2}\) d\(^{-1}\))

Fig. E-9. Mean monthly June 2009 NPP.
July 2009 Net Primary Productivity

(mg C m\(^{-2}\) d\(^{-1}\))

Fig. E-10 Mean monthly July 2009 NPP.

August 2009 Net Primary Productivity

(mg C m\(^{-2}\) d\(^{-1}\))

Fig. E-11. Mean monthly August 2009 NPP.
September 2009 Net Primary Productivity
(mg C m\(^{-2}\) d\(^{-1}\))

Fig. E-12. Mean monthly September 2009 NPP.

October 2009 Net Primary Productivity
(mg C m\(^{-2}\) d\(^{-1}\))

Fig. E-13. Mean monthly October 2009 NPP.
November 2009 Net Primary Productivity

(mg C m\(^{-2}\) d\(^{-1}\))

Fig. E-14. Mean monthly November 2009 NPP.

December 2009 Net Primary Productivity

(mg C m\(^{-2}\) d\(^{-1}\))

Fig. E-15. Mean monthly December 2009 NPP.
Fig. F-1. Sensitivity analysis of CO₂ flux rates to changes in SST. Changes in SST are indicated above each subplot. The blue lines are flux rates calculated from in situ values and the red lines are flux rates calculated with the indicated alterations.
Fig. F-2. Sensitivity analysis of CO$_2$ flux rates to changes in SSS. Changes in SSS are indicated above each subplot. The blue lines are flux rates calculated from in situ values and the red lines are flux rates calculated with the indicated alterations.

Fig. F-3. Sensitivity analysis of CO$_2$ flux rates to changes in atmospheric pressure. Changes in pressure are indicated above each subplot. The blue lines are flux rates calculated from measured values and the red lines are flux rates calculated with the indicated alterations.
Fig. F-4. Sensitivity analysis of CO$_2$ flux rates to changes in $\Delta p$CO$_2$. Changes in $\Delta p$CO$_2$ are indicated above each subplot. The blue lines are flux rates calculated from *in situ* values and the red lines are flux rates calculated with the indicated alterations.

Fig. F-5. Time series plots of mean daily pCO$_2$sw, SST, SSS, and wind speed.
Fig. F-6. Time series plots of mean daily pCO$_2$, SST, SSS, and wind speed.
APPENDIX G

SUPPLEMENTAL CONTOUR PLOTS OF DIFFERENCES IN CO$_2$ FLUX RATES

Fig. G-1. Contour plot of mean dflux for hour 3, July, 2009. Black arrows indicate surface current speed and direction. Mean wind speed and direction is indicated in the lower right corner.

Fig. G-2. Contour plot of mean dflux for hour 19, July 21, 2009. Black arrows indicate surface current speed and direction. Mean wind speed and direction is indicated in the lower right corner.
Fig. G-3. Contour plot of mean dflux for hour 10, August 6, 2009. Black arrows indicate surface current speed and direction. Mean wind speed and direction is indicated in the lower right corner.

Fig. G-4. Contour plot of mean dflux for hour 21, November 4, 2009. Black arrows indicate surface current speed and direction. Mean wind speed and direction is indicated in the lower right corner.
Fig. G-5. Contour plot of mean monthly dflux for June, 2009. Black arrows indicate surface current speed and direction. Mean wind speed and direction is indicated in the lower right corner.

Fig. G-6. Contour plot of mean monthly dflux for July, 2009. Black arrows indicate surface current speed and direction. Mean wind speed and direction is indicated in the lower right corner.
Fig. G-7. Contour plot of mean monthly dflux for August, 2009. Black arrows indicate surface current speed and direction. Mean wind speed and direction is indicated in the lower right corner.

Fig. G-8. Contour plot of mean monthly dflux for September, 2009. Black arrows indicate surface current speed and direction. Mean wind speed and direction is indicated in the lower right corner.
Fig. G-9. Contour plot of mean monthly dflux for October, 2009. Black arrows indicate surface current speed and direction. Mean wind speed and direction is indicated in the lower right corner.

Fig. G-10. Contour plot of mean monthly dflux for November, 2009. Black arrows indicate surface current speed and direction. Mean wind speed and direction is indicated in the lower right corner.
REFERENCES


Ocean Color’s Ocean Productivity Site. http://www.science.oregonstate.edu/ocean.productivity/


Dr. Pieter Tans, NOAA/ESRL (www.esrl.noaa.gov/gmd/ccgg/trends/)


