NON-REACTIVE GAS DYNAMICS IN THE PISCATAQUA ESTUARY INLET

BY

TAKASHI KALANI BROWN
B.A., University of Hawaii, 2002

THESIS

Submitted to the University of New Hampshire
in Partial Fulfillment of
the Requirements for the Degree of

Master of Science
in
Earth Sciences – Oceanography

September, 2006
This thesis has been examined and approved.

Thesis Director, Dr. Douglas C. Vandemark
Affiliate Research Associate Professor
of Earth Sciences and Research Associate
Professor of Earth, Oceans, and Space

Dr. Janet W. Campbell
Research Professor of Earth Sciences
and Earth, Oceans, and Space

Dr. Joseph E. Salisbury
Research Scientist III
Earth, Oceans, and Space

Date
DEDICATION

To my mother
Yoko Terada Brown
ACKNOWLEDGEMENTS

This project was made possible with the support, assistance, and guidance of many people. For my committee, I would first like to thank my advisor, Dr. Doug Vandemark, for his support of this project, his depth of knowledge, and his patience in answering all of my questions. I would like to thank Dr. Joe Salisbury for initially introducing me to the Coastal Carbon Group, for his field expertise, and his enthusiasm for the ocean sciences. Lastly, I would like to thank Dr. Janet Campbell for her comments on this thesis and constant support of this research.

I would also like to thank members of the COOA crew including: Tim Moore, Chris Manning, Mike Novak, and especially Chris Hunt for essentially teaching me how to operate all of the equipment and also for his programming help. I would also like to express gratitude to Dr. Ru Morrison for allowing me to operate in his laboratory spaces.

Additionally, I would like to recognize and express thanks to Sheldon Kono for his programming mastery, and for basically re-teaching me how to program from the ground up. Furthermore, I wish to acknowledge my fellow Earth Sciences graduate students, especially Steve Brodovicz for his science proficiency and for helping me with those tough assignments, and Joe Thouin for his hydrological perspectives on this project.

Finally, I would like to thank Noel Carlson and Dr. Hunt Howell for allowing me to operate and conduct this research at the Coastal Marine Laboratory, and the Gulf of Maine Ocean Observing System (GoMOOS) for their much appreciated supplemental buoy data.
This work was funded in part through NOAA Coastal Services Center award to
the UNH Center for Coastal Observation and Analysis (COOA, NA160C2740).
## TABLE OF CONTENTS

DEDICATION ........................................................................................................................................ iii
ACKNOWLEDGEMENTS .................................................................................................................... iv
LIST OF TABLES ............................................................................................................................. viii
LIST OF FIGURES ............................................................................................................................ ix
ABSTRACT ........................................................................................................................................ xii

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>PAGE</th>
</tr>
</thead>
</table>
| 1. INTRODUCTION .................................................................1  
1.1 Coastal and Estuarine Biogeochemistry ..............................2  
1.2 Gas Fluxes across the Air-Sea Interface ..............................4  
1.3 Study Focus ...........................................................................7 |
| 2. METHODS AND MATERIALS ....................................................9  
2.1 Study Area – The Piscataqua Estuary Inlet ............................9  
2.2 Research Facility – Coastal Marine Laboratory ..................10  
2.3 Instrumentation .....................................................................12  
2.3.1 Gas Tension Device .........................................................12  
2.3.2 Gas Tension Device Container (GTDC)............................15  
2.3.3 Oxygen Sensor ..................................................................16  
2.3.4 Conductivity Sensor .........................................................17  
2.3.5 Carbon Dioxide Sensor and Systems Operation ..............17  
2.3.6 Atmospheric Pressure Sensor ...........................................18  
2.4 Maintenance ..........................................................................19 |
LIST OF TABLES

Table 3.1  Sensor station distances .................................................................68

Table 3.2  Time lag between tidal stages (high and low) and slack water ........69

Table 3.3  Wind parameterized air-sea flux over one tidal cycle .....................70
LIST OF FIGURES

Figure 2.1 Great Bay-Piscataqua Estuary System .........................................................22
Figure 2.2 Lower Piscataqua Estuary bathymetry and shaded relief............................23
Figure 2.3 Coastal Marine Laboratory (CML) ................................................................24
Images of CML taken from the top of Ft. Constitutions’ defensive wall (a), and from the pier (b).
Figure 2.4 Seawater pumps .........................................................................................25
Figure 2.5 Seawater intake location (primary-bottom) ....................................................26
Figure 2.6 Seawater intake location (original-pier) .........................................................27
Figure 2.7 Laboratory seawater header tanks ...............................................................28
Figure 2.8 Gas Tension Device (GTD) .........................................................................29
Figure 2.9 Gas Tension Device plenum schematic .........................................................30
Figure 2.10 Sensor systems layout ..............................................................................31
The full systems operational layout included: (a) the GTDC, (b) the Licor (CO₂), (c) the CO₂ equilibrator, (d) the water source (header tank), and (e) the laptop for recording data.
Figure 2.11 Sampling container (GTDC) sensors ..........................................................32
Seawater entered from an inlet in the container (not pictured) on the right, and was be measured by: (a) the GTD, which was forced water by the bilge pump (b), the Optode (c), and the conductivity sensor (d). Then the water would exit through the GTDC outlet (e).
Figure 2.12 Sampling container (GTDC) chambers .......................................................33
Figure 2.13 Oxygen sensor ..........................................................................................34
Figure 2.14 Conductivity sensor .................................................................................35
Figure 3.1 Additional sensor stations ..........................................................................71
Figure 3.2 Salinity record .................................................................................................. 72
(a) Full record; (b) full record removed.

Figure 3.3 Salinity comparisons ..................................................................................... 73

Figure 3.4 Gulf of Maine modeled salinity field ............................................................. 74

Figure 3.5 Total drainage into the Great Bay–Piscataqua Estuary (estimate) ............... 75

Figure 3.6 Temperature record ....................................................................................... 76

Figure 3.7 All recorded gas data ....................................................................................... 77
(a) Total dissolved gas pressure (mb); (b) oxygen concentration (mmol/kg); (c) nitrogen concentration (mmol/kg); (d) oxygen and nitrogen percent saturation; (e) carbon dioxide concentration (mmol/mol).

Figure 3.8 Nitrogen and oxygen saturation ..................................................................... 78

Figure 3.9 Nitrogen concentration .................................................................................. 79

Figure 3.10 Modeled nitrogen saturation concentration .................................................. 80

Figure 3.11 Seasonal overturning of the water column at Buoy B ................................ 81

Figure 3.12 Air temperature (a) with nitrogen concentration (b) .................................... 82

Figure 3.13 Wind speed (a) and wave height (b).............................................................. 83

Figure 3.14 Carbon dioxide concentration (aqueous) .................................................... 84

Figure 3.15 Oxygen concentration .................................................................................. 85

Figure 3.16 Oxygen saturation ......................................................................................... 86

Figure 3.17 Western Gulf of Maine temperature profile (Buoy B) ................................. 87

Figure 3.18 Chlorophyll (Buoy A) .................................................................................. 88

Figure 3.19 Oxygen saturation (a) and wave height (b) ................................................ 89

Figure 3.20 Nitrogen flux (ocean model) ........................................................................ 90

Figure 3.21 Nitrogen flux (estuary model) ..................................................................... 91

Figure 3.22 Oxygen flux (ocean model) ......................................................................... 92
Figure 3.23  Oxygen flux (estuary model).................................................................93

Figure 3.24  Wind-wave Episode 1 (variable composite)............................................94

Figure 3.25  Wind-wave Episode 2 (variable composite)............................................95

Figure 3.26  Wind-wave Episode 3 (variable composite)............................................96

Figure 3.27  Wind-wave Episode 4 (variable composite)............................................97
ABSTRACT

NON-REACTIVE GAS DYNAMICS IN THE PISCATAQUA ESTUARY INLET

by

Takashi Kalani Brown

University of New Hampshire, September, 2006

For 135 days, from late autumn 2005 to the mid-spring 2006, continuous measurements of dissolved nitrogen, oxygen, and carbon dioxide in near surface seawater were recorded at the interface between the Great Bay-Piscataqua Estuary and the western Gulf of Maine. These surface measurements were made to investigate air-sea gas fluxes and identify the primary controls over gas dynamics in a macrotidal estuary entryway, the estuary inlet. Wind-parameterized air-sea flux estimations were calculated using published flux models and were evaluated to determine their appropriateness in the estuary inlet. Also, using supporting sea-state measurements from buoys (wind speed and wave height), the effects of severe weather on dissolved gas concentrations were explored, and a determination was made as to the conditions required for air-injected dissolved gas increases. Measuring two non-reactive gases (nitrogen and oxygen) with different solubilities allowed for differentiation of two bubble-mediated processes. It was determined that the dominant bubble-mediated gas transfer in the near shore is bubble exchange and not bubble injection. Finally, we were able to record the effects of the spring bloom on oxygen levels, and compare those levels with oxygen measurements taken in the Gulf.
CHAPTER 1

INTRODUCTION

This thesis involves observation of dissolved gases made in the coastal waters of the Gulf of Maine from 2005 to 2006. In particular, the central focus is upon measurement of dissolved nitrogen and its potential for use as an inert tracer of atmosphere-ocean gas exchange and water mass mixing. The motivation for this work stems from ongoing research here at the University of New Hampshire aimed at monitoring of oceanic carbon dioxide and oxygen levels and at understanding the controls upon observed signal dynamics at time scales spanning hours to years. These two gases are intimately involved in biologically-mediated coastal ocean ecosystem processes (i.e. respiration and photosynthesis). But both are also subject, as are all gases, to thermodynamic physical controls. The following study evolved from the desire to evaluate the use of nitrogen measurements for discrimination between these abiotic and biotic controls on seawater gas dynamics. As will be discussed, the resulting efforts led to development of an extended time series measurement data set collected at a coastal estuary inlet. Background information follows to further motivate this work, to describe the measurement setting and anticipated controlling process, and to outline the specific study objectives.
1.1 Coastal and Estuarine Biogeochemistry

Estimating air-sea gas flux is one of the central uncertainties of investigations into global biogeochemical cycles, and by being able to quantify this flux, researchers would be better able to understand the role of the oceans in mediating greenhouse and trace gases and hence global climate change (Nightingale et al., 2000). A significant unknown within global estimates of air-sea gas flux comes from the fact that the coastal ocean has been largely ignored, with focus to date mainly on the open ocean (Borges, 2005). The coastal ocean receives the vast majority of the ocean’s inputs of nutrients and organic matter from the land. It exchanges this matter and energy with the open ocean and with the biosphere, and it is one of the most biogeochemically active systems on the planet (Gattuso et al., 1998). The coastal ocean is roughly defined as the area of the continental shelf from the shore, including estuaries, out to the continental shelf break (Kennett, 1982). Water depth is usually defined as less than 150 m (Pinet, 2003). While the continental shelf only represents about 7% of the global ocean surface area and less than 0.5% of the volume, as much as 20% of total global marine primary production occurs on the shelf (Gattuso et al., 1998). Much of this biogeochemical activity is made possible from land-derived particulate and dissolved substances brought to the coastal ocean from rivers by way of estuaries.

Estuaries are the transition zones between land water and the coastal ocean. In simple terms, an estuary is any area where salt water and fresh water interact (Dyer, 1973). By this definition, river plumes would be included. However, a more rigid definition of estuary is given by Cameron and Pritchard (1963), where “an estuary is a semi-enclosed coastal body of water which has a free connection to the open sea and
within which sea water is measurably diluted with fresh water derived from land drainage.” Under this definition the river plume is not included. The lower limit is geographical with respect to the coast, corresponding to the entryway, inlet, or mouth, and the upper limit is the area up river where tides cease to have an influence.

Additionally, because of bathymetry, land chemistry, and atmospheric controls (i.e. rain, wind, temperature), estuaries are quite diverse in terms of geochemistry, geomorphology, drainage discharge, and tidal influence. All of these factors have a substantial impact on biogeochemistry and nutrient cycling. The interaction between these processes makes estuaries very difficult to study. Since an estuary may never be in steady state, researchers can never be sure if they are observing a general estuarine principle or simply an estuary-specific detail (Dyer, 1973).

Biologically, estuaries are generally considered to be net heterotrophic systems, where total respiration exceeds gross primary production. Thus, in general, estuaries are organic matter sinks while being sources for inorganic carbon to the coastal ocean and carbon dioxide to the atmosphere (Borges, 2005). Dissolved inorganic carbon input into the coastal ocean is especially problematic for greenhouse gas reduction potential since it reduces the ability of the coastal ocean to act as a sink for atmospheric carbon dioxide (McNeil et al., 2006a). Additionally, human activity only makes studying these biological estuarine processes more difficult.

Acting as natural harbors by providing shelter for anchorages and navigational access, estuaries have become centers of human development (Dyer, 1973). Today many of the world’s population centers and seaports are on estuaries and with this comes increased industry. This, in turn, means increased waste water discharge and hence
increased pollution and sewage. In some population centers, like that of the eastern seaboard of the United States, municipal and industrial waste water has had such a severe effect on local estuary ecosystems that hypoxic and even anoxic conditions have occurred (Clark et al., 1995). With the increases of waste water in these estuaries, the coastal ocean is being called upon to assimilate these pollutants indefinitely. Because of that, understanding estuarine-coastal ocean transports is one of the most important challenges in the environmental sciences (Bilgili et al., 2005).

Receiving these natural and anthropogenic land constituents, estuaries are constantly processing and altering these products before they are exported to the ocean. Since many of these land constituents have gas phases, understanding the processes that govern their exchange with the atmosphere is a necessity for determining estuarine and coastal biogeochemical budgets (Zappa et al., 2003). The exchange or transport of the gases involved in primary respiration (i.e. oxygen and carbon dioxide), other biological volatile gases like dimethyl sulfide, methane, nitrous oxide, and volatile pollutants like polychlorinated biphenyls or mercury, is controlled to some degree by their air-sea flux rates. Thus monitoring this key process is essential to understanding ecosystem metabolism and the effects of waste and/or pollution entering the coastal ocean (McNeil et al., 2006a, Zappa et al., 2003).

1.2 Gas Fluxes across the Air-Sea Interface

Due to difficulties in actually measuring gas exchange across the air-sea boundary, observational research typically focuses on determining the mass flux with the aid of models. While other conceptual models exist like Film or Boundary-Layer models
(Liss and Merlivat, 1986), most often, research focuses on transfer across the air-sea interface being dependent on molecular diffusion and the mechanisms that renew the surface boundary layer via this process. At the air-sea interface, where molecular diffusion dominates, transfer of slightly soluble gases is restricted and their transport is controlled by the aqueous side of the marine boundary layer (Jahne and Haussecker, 1998, Hahm et al., 2005). The flux of slightly soluble gases across an air-water interface is usually expressed as a simple function relating flux (F) to a concentration gradient (ΔC):

\[ F = k \Delta C = k(C_w - C_a), \]  

where k is the transfer coefficient (or “piston velocity”), C_w is the gas concentration of the bulk water, and C_a is assumed to be surface water concentration with respect to atmospheric equilibrium. The greatest restriction separating the bulk water from the air is the aqueous side of the marine boundary layer. The magnitude of the piston velocity (k) depends on the thickness of the aqueous boundary layer, a layer which varies between 10-100 µm. Its thickness is controlled by near surface turbulence such that by increasing near surface turbulence, the aqueous boundary layer thickness decreases, thereby increasing k (Zappa et al., 2003).

Due to difficulty in actually measuring near surface turbulence, piston velocity is usually parameterized in terms of a more robust measurement, such as the wind speed. In the open ocean, wind speed is usually assumed to be the dominant control, since it influences other turbulence-generating parameters like waves and breaking waves (Wolf, 1997). Although not as common today, much of the earlier studies in calculating k were done in wind-wave tank experiments (e.g. Jahne et al., 1987a, Wanninkhof and Bliven, 2005).
Today most investigations are performed in the field. Piston velocity is usually estimated using a simple relationship involving wind speed (u) and the gas specific Schmidt number (Sc). The Schmidt number is defined as the kinematic viscosity of water divided by the diffusion coefficient of the gas. The most frequently cited example of a wind speed parameterized piston velocity is Wanninkhof (1992), where:

\[ k = 0.31u^2(Sc/660)^{-0.5}. \]  

(2)

Some others that are also often used are Liss and Merlivat (1986), Wanninkhof and McGillis (1999), and Nightingale et al. (2000).

Unlike the open ocean, where it appears that wind speed adequately parameterizes piston velocity, in the coastal ocean, an area of limited fetch and shallow depth, different physical processes can strongly affect exchange rates. These include mixing, waves, white capping, Langmuir circulation, bottom stress, and surfactants (McNeil et al., 2006a). This situation becomes even more complicated in the estuary environment, especially with the addition of tidal activity. A comparison of published, observationally-based predictive models of estuarine piston velocities showed a general lack of agreement between parameterized piston models. This is largely because there are too few direct measurements of the possible physical controls on gas exchange (Raymond and Cole, 2001). Until greater understanding is developed in estuarine gas transfer processes, model-aided gas transfer estimations will be difficult to use in estuarine studies (Raymond and Cole, 2001).
1.3 Study Focus

This thesis work focused on the generation and preliminary evaluation of a 135-day long time series using relatively new generation instrumentation to monitor and record non-reactive (not chemically reactive with water or air) dissolved gas concentrations and their temporal evolution as measured at a macrotidal estuary inlet, the entryway into the Great Bay-Piscataqua Estuary system. One motivation for this data set was to improve understanding of the physical controls that govern the gas dynamics measured at the interface between a large estuary system and the coastal ocean. The two gases of focus in this study were dissolved oxygen and nitrogen. Although not actually a noble gas, nitrogen’s reactivity in sea water is so low that most science texts deem it as inert (e.g. Pilson, 1998, Broecker and Peng, 1982, Millero, 2005). Because of this, an estuarine mass balancing approach (Clark et al., 1992, Elsinger and Moore, 1983, Hartman and Hammond, 1984) was taken using nitrogen as a tracer to directly measure air-sea flux. Also, unlike the previous tracer studies that were based on a monthly or even yearly sampling schedule, this study benefited from having significantly higher temporal resolution since sensors recorded data continuously at a 1 Hz rate.

As previously mentioned, continuously recorded measurements were made using newer generation techniques, one being Gas Tension Device (GTD) technology. Prior to GTD technology, nitrogen measurements were limited by the number of bottle samples one could collect in the field and then analyze in the laboratory using mass spectrometry (e.g. Hamme and Emerson, 2002). The GTD allows for the continuous estimation of nitrogen using sensor data only. Although the GTD has been in use and has been commercially available for a few years now, this study is the only known use of GTD
technology in an estuary system. All known previous work using GTD technology occurred at sea either on ships (McNeil, 2006, McNeil et al., 2005, Katz, 2005), as part of a floating instrument package (Farmer et al., 1993, McNeil et al., 2006b, McNeil and D’Asaro, 2006, D’Asaro and McNeil, 2006), or moored to a buoy (McNeil et al., 2006a, McNeil et al., 1995, Emerson et al., 2002). The only two non-sea uses were Anderson and Johnson (1992), a laboratory study, and McNeil et al. (2006c), a lake study.

Lastly, although not the original and primary air-sea flux study goal, arguably the most important and tractable part of this project turned out to be the development of an understanding of the observed dissolved gas dynamics at the estuary inlet (river-estuary mouth). While near shore air-sea exchange is an important process to understand, without understanding the general estuary gas dynamics first, it is apparent that any such air-sea investigations will become increasingly difficult, if not unfeasible. Ultimately, data analysis centered on three objectives: the first being the investigation of dissolved gas dynamics over the study period, the second being an attempt to quantify the actual air-sea gas exchange and a determination of the appropriateness of existing flux models in the Piscataqua Estuary, and the third being an investigation of the effects of severe weather events on dissolved gases from estuary inlet measurements.
CHAPTER 2

METHODS AND MATERIALS

2.1 Study Area - The Piscataqua Estuary Inlet

The Piscataqua Estuary is the lower part of the Great Bay-Piscataqua Estuary System (Figure 2.1), a tidally dominated estuary embayment complex, located on the New Hampshire-Maine Border; it encompasses the Great Bay, the Little Bay and the Piscataqua River-Estuary (Short, 1992a). Although rock formation dates to Devonian and Ordovician geologic periods (Ward, 1992), the Great Bay-Piscataqua Estuary in its current geomorphology is a drowned river valley, dating to the area’s most recent deglaciation approximately 14,500 years ago (Short 1992a). The estuary is generally shallow, but it does have deep channels, with fast currents, and extensive tidal mud flats (Bilgili et al., 2005).

The Great Bay-Piscataqua Estuary has a drainage area of 2409 km², reflecting the drainage confluence of 7 rivers: the Lamprey, Squamscott, and Winnicut, draining into the Great Bay, the Billamy and Oyster into the Little Bay, and the Cocheco and Salmon Falls into the Piscataqua River-Estuary. Additionally, the Great Bay-Piscataqua Estuary is the drainage area for a number of smaller creek-tributaries. On average, total fresh water input into the estuary is on the order of less than 1% (Erturk et al., 2002, Swift and Brown, 1983), to 2% (Bilgili et al., 2005), of the tidal prism. Tidally, with typical sea level excursions of 2.5 m, and tidal currents reaching up to 2.3 m/s, about 40 percent of
the volume of the Great Bay exchanges with the Gulf of Maine every tidal cycle (Erturk et al., 2002). Due to tidal currents being so strong, vertical variability in the estuary is negligible, making the Great Bay-Piscataqua Estuary-System a well-mixed system (Bilgili et al., 2005).

The upper, or inner, estuary (Great Bay and Little Bay) connects to the western Gulf of Maine by way of the Piscataqua River-Estuary. The Piscataqua River-Estuary is ocean dominated and uniform vertically (Bilgili et al., 1996), and is part of the New Hampshire-Maine border flowing through Portsmouth Harbor. The interface between the Great Bay-Piscataqua Estuary System and the Gulf of Maine is the Piscataqua Estuary Inlet, the sampling location for this study.

2.2 Research Facility - Coastal Marine Laboratory

Data for this study were collected at the University of New Hampshire’s (UNH) Coastal Marine Laboratory (CML) (43.07 N, 70.17 W), located on the Fort Point Peninsula, in the Mines Building of the historical Fort Constitution on the island town of New Castle, New Hampshire (Figure 2.2). The Coastal Marine Laboratory (Figure 2.3) is located just under one nautical mile from the ‘model open boundary’ (Erturk et al. 2002), the theorized demarcation between the lower estuary and the near shore Gulf (Figure 2.1). Although the focus of the Coastal Marine Laboratory is mainly in support of the University’s aquaculture, zoological and biological research programs, their flow-through sea water system was suited for this study.

The Coastal Marine Laboratory’s flow-through seawater pump was the source of all water measurements recorded in this study. The seawater pump is actually two
independent impeller pumps (Figure 2.4), each pumping approximately 570 liters of sea water per minute from the intakes (Figure 2.5) into the laboratory. Early in this study, December 15, 2005 to January 13, 2006, the seawater intakes were located at the pier (Figure 2.6), approximately 0.67 m from the surface during low tide (2.5 m from the bottom), and about 3 meters from the surface during high tide. On January 13, 2006, because of upcoming U.S. Coast Guard plans to dredge the channel between the pier and the laboratory, the intakes were moved to a new location, where the intakes remained until the end of this study on April 28, 2006. In their new location, about 20 meters away from Ft. Constitution’s defensive wall, the intakes are 0.5 meters off the bottom, and approximately 6 m from the surface during high tide and 3.5 m during low tide. In this configuration, the entire distance from the intakes, through the pump, and eventually to the laboratory header tanks (Figure 2.7) is estimated to be 70 m.

From these header tanks, seawater is constantly distributed throughout the facility. Although there are two pumps, only one is in operation at any time - the other one being a backup. Also, by completely shutting off one of the pumps, and sealing it off from the pumping system, bio-fouling is minimized, since an anoxic environment is eventually created in that closed pump line.

From the header tanks, the bulk of the water is piped to the first floor, supplying seawater to the biological aquatic systems: fish pools, aquaculture tables, etc., but the water analyzed in this study was piped in directly into the instrumentation package from the header tanks, a distance of about 1.5 m through 0.5 inch Tygon® tubing.
2.3 Instrumentation

Over the course of this study, December 15, 2005 to April 28, 2006, the following variables were measured and recorded: total dissolved-gas pressure (TDG), dissolved oxygen concentration, dissolved oxygen saturation, water temperature, conductivity (salinity), atmospheric pressure, and dissolved and atmospheric carbon dioxide concentration. Total dissolved gas pressure, oxygen measurements, temperature, and conductivity were measured by sensors placed in a thermally insolated pool, which will be referred to as the gas tension device container (GTDC) (‘sampling container’ in McNeil et al., 2005). Carbon dioxide and atmospheric pressure measurements were made using independent systems.

2.3.1 Gas Tension Device

The total dissolved gas pressure, or gas tension, is the pressure of the sum of all the gases, including water vapor, dissolved in a volume of water. This measurement is based on Dalton’s Law of Partial Pressure where:

\[ P_T = \Sigma \text{(partial pressure of each gas)}, \]

and for this study,

\[ P_T = P_{N2} + P_{O2} + P_{H2O} + P_r, \]

where \( P_T \) is the total dissolved gas pressure, \( P_{N2} \) is the partial pressure of nitrogen, \( P_{O2} \) is the partial pressure of oxygen, \( P_{H2O} \) is the partial pressure of water vapor, and \( P_r \) is the partial pressure of the remaining trace gases, mainly argon. Since the trace gas is mainly argon, the trace gas solubility is assumed to be equal to that of argon, and assuming \( X_{N2} \) and \( X_{\text{TRACE}} \) are the atmospheric mixing ratios, reforming equation (4), nitrogen is calculated by:

\[ P_{N2} = X_{N2} P_{N2,\text{atm}} \]
\[
\text{PN}_2 = \frac{(P_T-P_{O2} - P_{H2O})}{(1+(X_{\text{TRACE}}/X_{N2}))}
\]
(McNeil et al., 2005). Oxygen solubility is taken from Garcia and Gordon (1992), and nitrogen and argon solubility are taken from Hamme and Emerson (2004). Nitrogen concentration (\(C_{N2}\)) is calculated according to Henry’s law by:

\[
C_{N2} = P_{N2} \times S_{N2},
\]

where \(S_{N2}\) is the solubility coefficient (Katz, 2005).

Total dissolved gas pressure was measured using a gas tension device (GTD) (Pro-Oceanus Systems Inc., Halifax, NS, Canada), based on the design initially described in McNeil et al. (1995). The GTD’s dissolved gas pressure sensor has a manufacturer’s quoted absolute accuracy of ±0.1 mbar, a precision of 0.02 µbar, and a drift rate less than 0.2 mbar per year (McNeil et al., 2006a).

A moored-mode GTD requires an operational depth of a few meters to hydrostatically keep the internal membrane from distorting in supersaturated waters. It also has a response time that can be on the order of hours (McNeil et al., 1995, Emerson et al., 2002). Although our study was stationary, since the moored GTD design (McNeil et al., 1995, Emerson et al., 2002, McNeil et al., 2006a) was not suitable, due to technical and response time issues, our study benefited from use of a GTD modified for shipboard operation (McNeil et al. 2005)(Figure 2.8). The shipboard GTD was required because this study focused on surface waters in a location of routine dissolved gas supersaturation. This would be a problem because our GTD’s operational depth within the GTDC was only a few centimeters. Also, since sampling in a dynamic environment, a fast flowing estuary inlet with tidal phase changes every six hours, we required a GTD with a much faster response time than those used in moored-mode. The shipboard GTD
differs from the moored-mode GTD through the addition of a flow-through plenum, replacing the moored-mode endcap (Fig. 2.8). The plenum modification allows for a decreased and constant response time. Since the baffle allows, or increases, turbulent flow over the sensor membrane, it decreases the thickness of the diffusive boundary layer over the surface of the membrane (Katz, 2005).

In addition to the decreased response time, the plenum’s screen also provides mechanical support for the membrane, preventing the membrane from bulging in shallow and supersaturated waters (McNeil et al., 2005). Furthermore, the plenum’s screen protects the membrane from much of the sediment and other debris which would otherwise clog, or damage, the membrane. This was crucial in this study, since much of the sampled water was filled with sediment and debris. Ultimately, the plenum modification significantly reduces the response time of the GTD down to 11±2 minutes, while at the same time maintaining the accuracy of the GTD to better than ±0.07% (0.7 mbar) (McNeil et al. 2005).

The plenum modification requires a source of constant water flow, and in this study that flow came from the use of a bilge pump (GTD pump) (Rule-Industries, Inc., Model 24). The pump is the flow generator forcing the water to flow against the baffle, increasing turbulent flow (Figure 2.9). The GTD pump also served a secondary, but important, function, and that was to stir the water within the GTDC to circulate the water throughout. Although, a plenum modified GTD could collect data out of water, since flow could be pumped directly into the intake, this could potentially cause unknown errors due to thermal heating (i.e. solubility change) since the GTD could possibly be operating at a different temperature than the water it is sampling. Due to this temperature
consideration, the GTD was operated in a thermally insulated container, the Gas Tension Device Container (GTDC).

2.3.2 Gas Tension Device Container (GTDC)

The GTDC in this study differs from the 5 gallon water cooler described in McNeil et al. (2005) and Katz (2005). The GTDC used in this study (Figure 2.10), was a 30 gallon cooler (Igloo Products Corp., Model 44011), and selected over the type used in previous studies for three reasons. First, since our project used a different oxygen sensor, and as well as an added conductivity sensor within the GTDC, additional space was needed (Figure 2.11). Second, to minimize the effects of bubble injection into the sampling reservoir of the GTDC, the GTDC was separated into two chambers (Figure 2.12), an empty fore-chamber, on the seawater inflow side, to allow bubbles to rise to the top, and an aft-chamber (sampling reservoir) where the measurements were taken. The two chamber approach came about in order to minimize the chances of bubbles coming into contact with the GTD pump and being ground up and dissolved into the water, affecting dissolved gas measurements. This was accomplished by dividing the first quarter of the GTDC by using 1.5 inch rigid polystyrene (foam) insulation. This barrier had two 2 cm holes on the bottom which would allow the passage of water. This barrier was far enough away from the seawater inflow to allow intruding bubbles to rise to the top in the fore-chamber, thereby keeping the aft-chamber bubble free.

Third, in order to minimize air intrusion (air-water interaction) within the GTDC, foam insulation was added to the water level tops of both chambers, reducing the surface skin of the water, thereby decreasing the area for air contact. Holes in this top insulation were to allow bubbles to escape from the fore-chamber, and for space to fit the sensor
data cables. This concern of air-water gas exchange is also discussed in McNeil et al. (2006c), but in that study wax paper, not foam insulation, was used. Operationally, due to the height of the seawater outlet, the displacement of the instruments, and the displacement of insulating foam divider, the water volume of the GTDC was approximately 40 L. The GTDC was supplied with water directly from the header tank at a rate of 11 to 13 L/min, thus an approximate residence time of 3 to 4 minutes.

Along with the GTD, the GTDC also contained two other sensors (oxygen and conductivity) and was the initial source of water for a third sensor (carbon dioxide), not contained in the GTDC. Initially, it was important to link the sensors to the same water source to insure that all of the sensors were sampling the same water, minimizing the effects of thermal contamination.

2.3.3 Oxygen Sensor

The dissolved oxygen sensor used in this study was an Oxygen Optode, model 3835, manufactured by Aanderaa Instruments Inc. (Figure 2.13). An Optode is an in situ dissolved oxygen optical sensor, and operates on the principle of dynamic luminescence, or fluorescence, quenching. With this quenching technology, Optodes do not consume or remove oxygen from the water, unlike electrochemical sensors, and because of this, Optodes are not flow sensitive, and have minimal performance drift from normal wear, as claimed by the manufacturer (ACT, 2004). The claim of no performance drift was confirmed by the Alliance for Coastal Technologies (ACT, 2004); in their laboratory studies, they found no appreciable sensor drift. However, in field studies, ACT (2004) found that the Optode would drift if the sensing foil (membrane) became covered, due to bio-fouling. According to the manufacturer’s specifications, Optode performance enfolds
a concentration range of 0-500 µM, with a concentration resolution <1µM, a
collection accuracy < 8µM or 5% (whichever is greater), a saturation range 0-120%,
and a response time of <25 seconds. The complete specifications for Optodes can be
found at www.aanderaa.com. Since Optodes contain an internal thermistor, Optodes are
able to measures absolute saturation. However, without the incorporation of salinity, the
dissolved concentration values are expressed with respect to fresh water. Thus to correct
this, salinity values are also required.

2.3.4 Conductivity Sensor

Salinity was calculated with the use of a conductivity sensor, Aanderaa
Conductivity Sensor 3919A, manufactured by Aanderaa Instruments Inc. (Figure 2.14).
The conductivity sensor measures in situ conductivity and temperature, and from that,
real time calculations of salinity and density are produced. Since this sensor operates
under the principle of induction, it can provide measurements without the use of
electrodes, which often foul in the field. Aanderaa’s conductivity sensor 3919
specification data sheet reports that the sensor has a conductivity accuracy of ±0.005 S/m,
a resolution of 0.0002 S/m, and a response time < 3 seconds. The temperature accuracy is
reported as ±0.1°C, with a resolution of 0.01°C, and a response time (63%) of < 10 sec.

2.3.5 Carbon Dioxide Sensor and Systems Operation

Although not contained within the GTDC, a fourth sensor that used the GTDC as
its water source was the carbon dioxide sensor (Figure 2.10). The CO2 sensor used was a
LI-840, manufactured by LI-COR Inc., and its operation was consistent with the methods
described in Salisbury et al. (2006). Initially, for about the first third of this study
(December 23, 2005 – February 7, 2006), in order to insure that the Licor sensor was
sampling the same water as the other sensors, water was pumped out of the GTDC to the Licor using a second bilge pump (Rule-Industries, Model 24) through 0.5 inch Tygon® tubing. However, out of practical concerns, after February 7, 2006, flow to the Licor was pumped directly from the header tanks. The main concern was the fear that all the water in the GTDC would be pumped out if seawater inflow was ever temporarily stopped into the GTDC. Temporary inflow stoppages occur during header tank, or sea pump, maintenance. Although pumping all the water out of the GTDC, in itself is not a problem, since all the instruments can operate in air, but operating in air would cause unknown anomalies in the data set, as well as an offset to occur in the GTD measurements. Once seawater inflow was restored, while the other sensors would return to normal operation, the GTD would need to be re-primed, or re-pressurized, to remove this offset.

2.3.6 Atmospheric Pressure Sensor

The final recorded variable in this study was atmospheric pressure, measured using a Vaisala BAROCAP PTB210 Digital Barometer, manufactured by the Vaisala Group (Helsinki, Finland). According to the manufacturer, the barometer has a total accuracy of ±0.25 hPa (1hPa=1mbar), and a long term stability of ±0.10 hPa/year. Although the Coastal Marine Laboratory is not climate controlled, the outside pressure was measured by connecting a 1/8 inch BEV-A-LINE® tube, with one end outside a window, directly to the barometer. Also, like the Licor, since the barometer was not a critical measurement for GTD calculations, unlike the Optode and the conductivity sensor, it was removed from this study on occasion, normally when needed for unrelated cruise operation, usually just a few days a month. Gaps in the atmospheric pressure data were of low concern, since atmospheric pressure is measured at several nearby locations,
including an NDBC location at the Isles of Shoals (IOSN3), New Hampshire, and GoMOOS Buoy B, located on the western Maine shelf.

2.4 Maintenance

Since all of the GTDC sensors (GTD, Optode, Conductivity Sensor) are ‘moor-able’ (i.e. designed to withstand deployment on moorings), GTDC sensor maintenance was minimal. Also, since the GTDC reservoir was not exposed to light, autotrophic bio-fouling was minimized. However, although bio-fouling was not an issue, sedimentation was. Sampling at an estuary inlet, especially after mid-January, when the sea pump’s intakes were moved from the pier to the bottom, fine sediment collected on the bottom of the GTDC. Larger sediment and/or debris had difficulty entering the GTDC since most of it would settle in the header tanks, so only fine sediment could flow in.

In the initial planning, since sediment build up was a concern, steps were taken to minimize its effects on the sensors. The Optode and Conductivity sensor were caged to keep the sensors off the bottom (Figure 2.11), as well as orienting the Optode’s sensor foil to face the bottom to eliminate the possibility of sediment build up on the sensor foil. For the first three months of this study during periodic inspections, about once per week, when the GTDC was opened, the water would be clear and the sediment had settled in the areas of the GTDC where circulation was light; the water had to be manually be stirred to re-suspend the sediment. Even though the system appeared not to be affected by the sedimentation, during inspections the GTDC was flushed. The GTDC was opened, the insulation barriers were removed, the seawater valve was shut off and tap water was hosed in. This served several purposes, first to flush out the sediment and as much biotic
material as possible, and to rinse the sensors with fresh waster, and since sensors were kept on, viewing tap water measurements was a quick way to visually inspect the responses of the sensors.

This GTDC tap water flush usually lasted about 30 minutes, enough time to flush out all of the sediment and debris, as well as time for the salinity to stabilize near zero. At this time the tap water was turned off and air stones connected to aquarium pumps was added to the GTDC, aerating the water to create a saturated water bath, for the purpose of monitoring possible Optode sensor drift, as described by the manufacturer’s calibration procedure. After about an hour, the air stones were removed, the foam barriers were repositioned, and the GTDC was closed, completing the weekly GTDC maintenance procedure.

Unlike the sensors contained within GTDC, with the Licor not being a moored-type instrument, it required much more attention. The Licor requires a continuous supply of drying gas, thereby needing drying gas tank changes every 2 to 3 days. Also, the Licor needs to be constantly calibrated with a set of gas tanks, a zero and a span. Ultimately, because of the logistical issues of ordering drying and calibration gas tanks, waiting for their arrival, switching them with those at CML, and physically being at CML to perform theses calibrations, Licor operation suffered. For most of the study period, the Licor operated with unacceptable levels of moisture, as well as sensor drifts of up to 6%. For this reason, although relative values were acceptable for present analyses, the absolute values measured by the Licor will require future attention.
2.5 Deployment and Data System

Excluding times of systems and sensor maintenance, malfunction, and/or repair, and during times when various sensors were needed in unrelated science experiments, total dissolved gas pressure, oxygen concentration, oxygen saturation, water temperature, conductivity (salinity), atmospheric- and water-side carbon dioxide concentration, and atmospheric pressure were continuously measured, at a sampling rate on the order of once per second in the Piscataqua Estuary Inlet, as measured from the Coastal Marine Laboratory, from December 15, 2005 to April 28, 2006.

The data acquisition system consisted of a multi-port serial to USB converter and a laptop computer running a continuously logging serial stream recording program that recorded a new data file for each sensor once every hour. Post processing involved data conversion and time tagged merge of all data into one continuous data file. Although measurements were recorded at a rate of one measurement per second, in post processing this continuous file was sub-sampled to one measurement per minute. Additionally, this continuous file incorporated supporting measurements from GoMOOS, NDBC, and USGS data. The ultimate data file consisted of 153 columns and nearly 200,000 rows.
Figure 2.1 Great Bay – Piscataqua Estuary System

The Coastal Marine Laboratory (CML) is located on the bottom right of this figure. The dashed line is the conceptual demarcation between the estuary and the open ocean. (Reproduced from Erturk et al., (2002))
Figure 2.2 Lower Piscataqua Estuary bathymetry and shaded relief
(Courtesy of B. Calder, CCOM, UNH)
Figure 2.3  Coastal Marine Laboratory (CML)

Images of CML taken from the top of Ft. Constitutions’ defensive wall (a), and from the pier (b).
Figure 2.4 Seawater pumps

These impeller pumps pull in seawater from the intakes, and pump water to the header tanks at a rate of 150 gal/min each.
Figure 2.5 Seawater intake location (primary-bottom)

The two white floats in the center-right of this image mark the location of the intakes. The intakes were here for most of the study after being moved from their original pier location.
Figure 2.6 Seawater intake location (original-pier)

Original location of intakes before being moved due to channel dredging.
Figure 2.7 Laboratory seawater header tanks

Pumped seawater is distributed throughout the facility from these header tanks. The GTDC can be seen on the right.
Figure 2.8 Gas Tension Device (GTD)

A GTD with the addition of the plenum for shipboard use. The moored mode endcap is also shown. (Reproduced from McNeil et al. (2005))
Figure 2.9 Gas Tension Device plenum schematic

As the entering sea water is forced past the baffle, the development of Laminar flow is greatly reduced above the membrane surface. (Reproduced from McNeil et al. (2005))
Figure 2.10  Sensor systems layout

The full systems operational layout included: (a) the GTDC, (b) the Licor (CO2), (c) the CO2 equilibrator, (d) the water source (header tank), and (e) the laptop for recording data. Missing from view is the atmospheric barometer.
Figure 2.11 Sampling container (GTDC) sensors

Seawater entered from an inlet in the container (not pictured) on the right, and was be measured by: (a) the GTD, which was forced water by the bilge pump (b), the Optode (c), and the conductivity sensor (d). Then the water would exit through the GTDC outlet (e). The brown matter is the accumulation of sediment after one week.
The sampling reservoir was covered and sectioned to minimize air-water interaction and bubble intrusion.
Figure 2.13 Oxygen Sensor

Optode Model 3835 by Aanderaa Inc. (www.aanderaa.com)
Figure 2.14 Conductivity Sensor

Conductivity sensor model 3919A by Aanderaa Inc. (www.aanderaa.com)
CHAPTER 3

OBSERVATIONS AND DISCUSSION

Between December 15, 2005 and April 28, 2006, the following measurements were recorded in the Piscataqua Estuary Inlet: salinity, water temperature, oxygen concentration, total dissolved gas pressure, atmospheric pressure, and carbon dioxide concentration, and from these measurements, excluding the CO₂, nitrogen concentration was also calculated. In addition to our collected field measurements, this study relied upon relevant monitoring data from the western Gulf of Maine. These sources included buoy measurements from the Gulf of Maine Ocean Observing System (GoMOOS), specifically Buoy B (Western Maine Shelf; 43.18°N, 70.43°W), Buoy C (Casco Bay; 43.57°N, 70.06°W), and Buoy A (Massachusetts Bay; 42.52°N, 70.57°W) (Figure 3.1). Although Buoy B is the closest to the study site, Buoys C and A were necessary because they contain sensors (oxygen and chlorophyll) not on Buoy B. Additional sources were: meteorological data from the National Buoy Data Center’s (NBDC) Isle of Shoals station (IOSN3) (42.97°N, 70.62°W), and United States Geological Survey (USGS) river discharge and tidal data. Distances between sensor stations have been tabulated (Table 3.1). Although there are monitoring programs within the Great Bay – Piscataqua Estuary (e.g. Great Bay Coastal Buoy), unfortunately these programs were not in operation during this project, or the data were not yet publicly available.
The constant mixing of end member waters at the estuary inlet suggests that water mass mixing will play a substantial role in dictating the observed gas dynamics. Thus the proceeding analysis first addresses physical water properties at the Piscataqua Estuary Inlet. In effect, the impacts and influence of oceanside and estuarine end members need to be evaluated. Additionally, the estuary itself can quickly alter certain physical water properties, like temperature. Water temperature is the primary control on gas solubility and thus any long term estuarine gas study must first consider this effect.

For the ocean end member (ocean side) data, this study will make some use of an existing coastal buoy network (GoMOOS). However, buoy distances from our site (order 20-80 km, see Table 3.1), their offshore distance (roughly 15km), and depth (about 60 m) all leave enough uncertainty in their applicability that these buoy data will be used in qualitative comparisons to our chosen ocean end member which will be high tide waters. We do not have a freshwater end member data set for the Great Bay. Thus we take the tidal extremes (high and low) to be the assumed near shore and estuarine representative end member measurements. With this in mind, observed state variables like salinity and temperature are first evaluated to determine appropriate end member values, and to assess the general state of the estuary. These data can then be used to model expected gas solubility effects on observed gas dynamics. Both the tidal and seasonal variations in the hydrography are addressed.
3.1 Salinity

3.1.1 Tidal Salinity

Salinity data from the estuary inlet are presented in Figure 3.2. This figure reveals something unusual about Piscataqua Estuary, the tidal high, the time when the water level is highest at the inlet, is not the same as the salinity maximum. Usually at high tide in estuaries, the tide is highest because the full tidal prism has entered the estuary ending the flood phase. The epoch between the flood and ebb phase is a tidal current slack period (slack ebb-begin), a time when the tide changes directions, so the water level is highest because sea water volume is greatest, and typically salinity is also at its maximum.

However, that is not the case in the Piscataqua Estuary. Due to the bathymetry of the Great Bay-Piscataqua Estuary, although a water volume maximum has been reached at the inlet (high tide), the flood tidal current continues for about 80 additional minutes before finally stopping and changing direction (slack-ebb begin). Despite reaching a high tide volume, until the flood tidal current ends (slack ebb-begin), sea water is still entering the estuary, and as a result, salinity continues to increase. This difference between high tide and the current slack is visible in the salinity data. Figure 3.2 shows that the salinity high does not correspond to the tidal high but to the slack in current (ebb-begin).

An analogous situation occurs for the other salinity extreme, except the time difference between low tide and the changing of tidal current (slack-flood begin) is even more pronounced. At the estuary inlet, the tidal low precedes the tidal current slack (flood begin) by approximately 200 minutes. This increased time separation is reflected in the large salinity difference of Figure 3.2 where the tidal low is significantly higher than for
current slack (flood begin). Tabulated time differences between the tidal stages and current stages are shown in Table 2.

These tidal stage to current stage lags occur because of the bathymetry of the Great Bay-Piscataqua Estuary. Since tidal flow in the lower Piscataqua Estuary are more dissipative than that of the Great and Little Bays, the confluence of the lower Piscataqua, upper Piscataqua and Little Bay at Dover point (Figure 2.1) causes Dover Point to act like a hydraulic choke point (Swift and Brown, 1983, Erturk et al., 2002). Essentially, choke points like this cause water in the Great Bay-Piscataqua Estuary to pile up in places since the tidal current is exceeding the capacity of these hydraulic choke points, thereby becoming out of phase with the tidal currents.

Physically, since the tidal salinity cycle is the proxy for ocean influence in the estuary, and because the maximum and minimum ocean influence is reflected by ebb- and flood- current slacks, and not tidal stages, hereafter, tidal variation in the Piscataqua Estuary is discussed with respect to the slack-ebb begin and slack-flood begin. The “high” and “low” tides are now with respect salinity cycles (current slacks) only, not tidal water volume.

3.1.2 Seasonal Salinity Dynamics

Salinity changes at the inlet occur due to the different water masses involved, fresher river-estuary water versus near shore ocean water, and because of that the temporal history will be discussed with respect to the slack-ebb begin (“high tide”) for the tidal salinity high, slack-flood begin (“low tide”) for the tidal salinity low. In Figure 3.3, for most of the study period during high tide, salinity remained between 30-32 psu, only briefly dropping below during high discharge events, as seen with the lowered
salinity measurements during low tide. Generally high tide salinity follows the surface (1m) salinity at Buoy B. The 1 to 2 psu offset between the inlet and Buoy B reflects that even though Gulf impact is greatest at high tide, fresh water influence is never zero. Being in the estuary inlet, our measurements are impacted by the fresh water input into the estuary. Also, in addition to the local drainage area fresh water input into the estuary system, the Gulf water entering the estuary is influenced by other fresh water sources, primarily the large rivers north of the inlet.

This is confirmed when looking at the GoMOOS salinity model for the western Gulf of Maine (Figure 3.4). Over much of the study period, along the coast between Casco Bay and Cape Ann there is a belt of lower salinity ranging between 0.2-2.0 psu, most likely influenced by the fresh water coming out of the large coastal Maine rivers, like the Kennebec River, and flowing to the south-southwest along the coast as part of the Western Gulf Coastal Current (Geyer et al., 2004). Additionally, on occasion, due to south winds, water from the large outer Merrimack Estuary (river plume) is blown up the coast lowering the near coastal salinity. Lastly, the York River, although often classified as a tidal stream, being just five miles up the coast from the Piscataqua Estuary Inlet, could possibly “freshen” the near shore waters entering the Piscataqua Estuary from the ocean side. Lastly, the converging of high tide inlet and Buoy B salinity values around day 95, is associated mainly with decreases in river discharge (Figure 3.5) into the estuary, and increased evaporation in the estuary with the onset of spring.

Unlike inlet salinity at high tide with its fairly small range, over the study period, low tide salinity is much more dynamic (Figure 3.3). Throughout the study period, the low tide salinity ranged from 20.5 to 29.5 psu. While the high tide salinity generally
followed the movement of Buoy B surface salinity, low tide salinity is likely responding much more to land water discharges. When compared to river discharge (Figure 3.5), all of the large drops in low tide inlet salinity correspond to large increases in river discharge.

Although the Great Bay-Piscataqua Estuary is the depository of several rivers, we chose to use the Lamprey River USGS gauge for a discharge surrogate, since the Lamprey River historically has the largest discharge and was the only river to not have persistent gauge malfunctions over the winter. Lamprey River data were used to estimate total Great Bay-Piscataqua discharge by:

$$\text{Total Discharge} = \text{Lamprey Discharge} \times \left( \frac{\text{Total Area}}{\text{Lamprey Area}} \right).$$  \hspace{1cm} (7)

Due to the frequency of these discharges, it appears that observed inlet salinity consistently increases until the next elevated discharge event. Thus, over the course of this study, there were no recordings of significant periods of constant low tide salinities. Since river input is less than 2% of the tidal prism, and 40% of the volume of the Estuary is exchanged out every tidal cycle, the estuary is constantly increasing in salinity, approaching near shore levels, until river discharge events “re-freshen” (decrease salinity) the estuary.

### 3.2 Water Temperature

Inlet and Buoy B surface temperatures for the study period are displayed in Figure 3.6. In the estuary, since high tide is the period of the tidal cycle of greatest ocean influence, the winter inlet temperature tidal maximum reflects the warmer ocean temperatures. Initially, at low tide with ocean volume minimized, inlet water temperature
reflects the added cold fresh water flowing from the land into the estuary. Also, because of the greater surface area to volume ratio of the estuary, winter atmospheric temperatures cause the estuary colder than the Gulf.

As discussed earlier, it was around day 95 when the separation between Buoy B and the inlet high tide salinities became small. In Figure 3.6, just after day 80, in the first week of March, inlet tidal max temperatures (high and low) began to approach each other, initially intersecting each other on day 87, a day when inlet high tide, inlet low tide and Buoy B surface temperatures were all the same. For nearly a week, until day 95, land and land water temperatures were making estuary temperature warmer than surface Gulf temperatures. Finally, just before day 100, in late March, both the estuary and the Gulf began to increase in temperature, and the estuary tidal temperature inversion for spring/summer begins. For the remaining days, estuary temperatures (temperatures at low tide) exceed the Gulf temperature (temperature at high tide).

3.3 Dissolved Gases

Three gas variables were measured in this study, total dissolved gas pressure (TDG), dissolved oxygen, and carbon dioxide. Additionally, from TDG and oxygen concentration, the concentration of a fourth gas variable, nitrogen, was determined (Figure 3.7). Often, when dealing with tidal data, a common processing approach is to “de-tide” the data, thereby removing the tidal signature in order to focus in on a more dominant signal (e.g. McNeil et al., 2006a). Removing the tidal signature can include taking the tidal mean, running some type of smoothing function, or possibly a Fourier transform analysis approach. However, while these methods may be appropriate for
situations where the tidal impact is minimal, simply causing noise in the data, that is not the case in the Piscataqua Estuary Inlet. As seen in the temperature plot (Figure 3.6), and as will be explained in the nitrogen concentration plot (Figure 3.7), the changing tide reflects the dominant water body currently influencing the inlet. In the estuary during high tide, with the fresh water input being less than 2% of the tidal prism, water at the inlet is essentially near shore western Gulf water. During the low tide, when the tidal current at the inlet is zero (slack), estuary influence is maximal and the ocean influence is minimal. So essentially, low tide is uncontaminated Piscataqua Estuary water as measured at the inlet. Since the inlet itself is not the generator of physical change, at the tidal extremes, the inlet allows us to measure two different water bodies, the near shore western Gulf of Maine, and the Great Bay-Piscataqua Estuary, and in between the tidal extremes, there is nothing more than simple mixing and tidally induced changing ratios.

Due to the tidal changes experienced at the inlet, this study will require several approaches in displaying continuous dissolved gas data. Most often, dissolved gas data are displayed in terms of percent saturation (e.g. McNeil 2006, McNeil et al., 2005, McNeil et al., 2006a, Emerson et al., 2002, McNeil et al., 1995, Katz 2005) to represent dissolved gas concentration with respect to solubility. However, since the inlet represents mixing between the estuary and the near shore western Gulf, the inlet continuously reflects two commingling water bodies with two differing percent saturations, so any changes seen in the percent saturation measured at the inlet, could be attributed to either source. Also, since these two different bodies have different temperatures and salinities, the mixing of these two bodies at the inlet would consistently cause a temporary disequilibrium in gas saturation; because of the non-linearity of temperature dependent
gas solubilities, when mixing two different water masses, the change in solubility will exceed the rate of re-equilibration of the gases. Thus, in the new pre-equilibrated mixture, percent saturation will reflect an un-equilibrated state (Pilson, 1998, McNeil et al., 2006a). Lastly, with this macrotidal estuary being a system where temperature and salinity change significantly with the M2 tidal phase, and each water body possibly being at a different physical state, an inlet specific saturation value is a representation of a process one degree away. For example, if there was a sudden spike in the inlet gas saturation data, one would need to investigate if the spike was caused by a sudden change in the gas concentration of the ocean, of the estuary, both, or neither. In the neither case for example, since percent saturation is with respect to solubility, a substantial temperature change in the water, which is feasible in an estuary, would cause percent saturation to quickly change, even though there is no change in dissolved gas concentration, and it would not be until gas re-equilibration that true percent saturation is achieved.

Due to the issues involved with inlet gas saturation, an additional approach will need to be employed. Dissolved gas data, especially for nitrogen, will be plotted and discussed with respect to concentration, in the context of 100% saturation concentration. 100% saturation concentrations are modeled using temperature and salinity for the low tide (estuary), high tide (near shore western Gulf), and Buoy B surface cases.

3.3.1 Dissolved Nitrogen

Since nitrogen is inert and is the assumed proxy for physical control processes over weakly soluble gases, including the abiotic component for biologically active gases like oxygen, it is discussed first. As seen in Figure 3.8, at the very beginning of the study,
nitrogen started out at just slightly above 100% saturation in the surface layer (Well and Roether, 2003, Pilson, 1998, Broecker and Peng, 1984). In the early days of the study, the fluctuations in the nitrogen concentration (Figure 3.9) which may appear as noise, are in fact the inlet concentration oscillating between the different concentrations of the Piscataqua Estuary and the near shore Gulf, governed by swing of the tide. In Figure 3.9, the nitrogen concentration is simply switching between the saturation concentration extremes of the high tides and the low tides, with simple mixing occurring between those two extremes. So in Figure 3.9, the range of the concentration signal is simply the six hour difference between the tidal extremes.

3.3.1.1 Modeled Saturation

Removing the measured concentration, and just leaving the 100% saturation concentration models (Figure 3.10), a general observation about the Piscataqua Estuary can be made. The inlet at low tide (estuary dominated), has the higher saturation concentration over much of the record because the low tide is the time of the tidal cycle with the coldest and freshest water, conditions favoring increased gas solubility (Pilson, 1998). On the opposite extreme, for much of the study, the surface saturation concentration at Buoy B is the lowest, reflecting the warmer, more saline waters of the Gulf, conditions for decreased gas solubility. Lastly, between those two extremes, lies the high tide saturation concentration, reflecting the near shore Gulf waters and the constant mixing between the Gulf water and the estuary occurring at the inlet. Also, in an estuary where the average fresh water input is less then 2% of the tidal prism, and the high tide being the period of maximum ocean influence, the high tide saturation concentration values are situated much more closely to that of Buoy B. However, since the inlet is still
part of the estuary, and the ocean is more stable with respect to temperature and salinity, major changes in the estuary have greater apparent control over high tide saturation dynamics. In Figure 3.10, while high tide saturation concentrations are much closer to the values of Buoy B, all of the major saturation concentration changes on the estuary side (low tide) are also seen in the high tide.

Although, river and land water input do have a significant impact on high tide saturation concentrations, it may not be the only control mechanism. Even if the tidal prism was uncontaminated by fresh or estuarine waters, winter time saturation concentrations would still be higher in the estuary because the estuary is colder in winter than the ocean, due to its larger surface area to volume ratio and increased heat loss.

Lastly, since the study began in very late autumn, although not the coldest time of this study, it is the time of greatest winter thermal separation between the estuary waters and the Gulf waters, which is why the concentration saturation difference is greatest in the beginning of the study. With the onset of the cooler temperatures of autumn, culminating in the overturning of the water column (Wallace and Wirick, 1992) on October 9th (Figure 3.11), land and the water from the land cooled the estuary faster than the ocean could be cooled and as a result, the saturation concentration was greatest at the beginning but then decreased throughout the remainder of the study before overlapping at around day 100 (March 24, 2006), the beginning of spring (Figure 3.10). At that time, the saturation concentrations of all three bodies were approximately the same, until about day 125, when they began to separate again. Thereafter, presumably until autumn, with the estuary being warmer than the ocean, the estuary saturation concentration was below Gulf levels.
3.3.1.2 First Nitrogen Period

Returning to nitrogen concentrations (Figure 3.9), the data set can be seen to represent two separate and fairly distinct periods. For the first 55-65 days, nitrogen concentration follows the expected 100% saturation levels through their respective tidal cycle (high-low). However, starting around day 65, this relationship breaks down. From day 65 until the end of the study, while still somewhat following the general movement of the end member (high and low tides) saturation concentrations, there was a significant undersaturation of nitrogen for both the ocean and estuary sides. Also, while end member tidal variation diminished throughout the entire study period, it was during the second period that nitrogen’s tidal variation collapsed to just a couple percent. Since the processes controlling nitrogen concentration appear to be different for the two periods, nitrogen evolution will be treated as two separate periods.

During the first 55 to 65 days (first period) of the study, nitrogen tidal extremes correlate strongly with their tidal end members, reflecting that the inlet is the location of mixing between estuarine and near shore waters. While there were several instance of slight supersaturation (less than 1%), only once between day 0 and day 65 did the nitrogen concentration exceed 1% above an end member saturation concentration. On day 19, the concentration was 2.3% above saturation concentration on the estuary side, or a percent saturation of 102.3%. This instance of supersaturation was preceded by 3 days of supersaturation, although smaller in magnitude, during the low tides.

With essentially inert gases like nitrogen, instances of super- or under- saturation are the result of some physical process. Sudden instances of thermal heating or cooling would change water temperature faster than gas flux, and until air-sea gas equilibration
occurred, the gas would be super- or under- saturated, respectively (McNeil, et al., 2005). The data suggests that thermally driven undersaturation on the estuary side occurred on days 21-26, when atmospheric temperatures significantly dropped to near zero degrees, and on days 54-61, when air temperatures suddenly dropped 10 degrees to sub-zero conditions (Figure 3.12). Additionally, gas supersaturation events in surface waters can also occur because of severe wind-wave activity that mechanically forces air into the water through bubble mediated processes (Woolf and Thorpe, 1991, Wallace and Wirick, 1992).

Returning to the supersaturation period of days 16-19, although this increase does correspond to increased wind-wave activity (Figure 3.13), since there appears to be little visible change on the ocean side (high tide) (Figure 3.9) and the supersaturation occurred on the estuary side, wind-wave activity may not be the only process causing this supersaturation event. While speculative, another process which may have caused the estuarine supersaturation was ice formation. This period of supersaturation corresponded with a period of air temperatures of less than -2 °C (Figure 3.12), as well as a discharge event (Figure 3.5), likely snow. If estuarine waters froze or were freezing, nitrogen would have been excluded from the ice matrix, supersaturating the remaining water. Although not a general property of all gases, some gases like nitrogen are excluded from ice during formation (Hamme and Emerson, 2002). At ice-water interfaces, large supersaturations of certain dissolved inert gases like nitrogen and argon have been observed (Burton, 1981, Hood et al., 1998), while inert gases like helium and neon are substantially undersaturated (Craig et al., 1992, Hood et al., 1998). Thus, over this period, the estuary’s discharge event (snow) and the possibility of ice formation could possibly explain the
observed supersaturation. This is why the supersaturation was seen during the lower low tide, when the ocean influence was at its daily minimum.

During high tide (near shore component), nitrogen concentration was essentially undersaturated for the entire length of the first period. The overarching process governing this undersaturation is that seasonal cooling was out pacing gas re-equilibrium (McNeil et al. 2005); a warm season analog to this is discussed in detail in McNeil (2006), and McNeil et al. (2006a). Essentially, since the ocean is cooling over this entire period, and heat flux out is exceeding gas flux in, the general condition will be one of undersaturation. Basically, during the first period, the observed nitrogen evolution can be explained based on conditions of heat fluxes, winter mixing, and the assumption of non-reactive gases being in constant equilibrium with the atmosphere (Pilson, 1998). However, these concepts or assumptions are no longer fully applicable during the second period.

3.3.1.3 Second Nitrogen Period

At the beginning of the second period (Days 60 to 135), data interpretation becomes much more uncertain. Nitrogen departs from its expected behavior of near 100% saturation. Day 65 marks the beginning when nitrogen concentration becomes undersaturated on both the estuary and ocean side (Figure 3.9). Initially, this change is small, 0.8% undersaturated on day 66, but as time progressed, 3.4% on day 76, before reaching 4.3% on day 112, the maximum undersaturation of this study. During the second period, nitrogen continued to be undersaturated especially on the high tide, and this deviation continuously increased through the end of the study.
A major feature of the second period is the shrinking of the high-low tide variation, and its eventual collapse on day 115. In the beginning of the study, difference between tidal extreme saturation levels were controlled by the solubility differences between the colder, fresher waters of the estuary and the warmer, more saline waters of the near shore Gulf. This led to the observed maximum dissolved gas fluctuation during each tidal cycle. In the second period, starting around day 100, and likely lasting until autumn, conditions were in place for minimum tidal saturation differences. On day 100, although the land water and estuary temperatures were significantly warmer than near shore (high tide) waters (Figure 3.6), the land water was also the fresher water. These conditions offset each other with respect to solubility. While this may explain the decrease in tidal difference, it does not explain the general undersaturation of the second period.

The large estuarine undersaturation event of days 65 – 82 (Figure 3.9), the longest observed in winter, occurred for a similar reason as the thermal undersaturation events of period 1. This event was initiated by a 22 degree temperature drop (Figure 3.12) and between days 65 and 82, temperatures averaged sub-zero levels, the coldest period of the entire study. This atmospheric condition caused the greatest disequilibrium between heat flux and gas transfer, thus the greatest undersaturation of this study. Also, the associated re-equilibration would be the reason for the supersaturation event of day 82-85, with the sudden increase in atmospheric temperature increasing water temperature causing a solubility decrease.

Finally, starting around day 86 (mid March), atmospheric temperatures soared to 16 degrees (Figure 3.12). This initiated the spring thaw, and although not as distinct this
year (Figure 3.5), the snow melt could have caused the state of undersaturation recorded out to the end of the study. As previously discussed, since nitrogen is excluded from ice formation, water from melted ice would be extremely undersaturated in nitrogen. Depending on discharge, this water entering the estuary could be a substantial process causing estuarine undersaturation. This process is demonstrated in on days 90 and 110, where significant decreases in nitrogen concentration correspond to discharge events (Figure 3.5).

3.3.1.4 Biological Nitrogen

In addition to the physical controls over the nitrogen (N$_2$) concentration, the biological influence on N$_2$ concentration was also considered. In the ocean, N$_2$ is usually considered abiotic (Broecker and Peng, 1982, McNeil et al., 2005); even in ideal conditions, maximum rates of N$_2$ fixation are negligible when compared to the effects of air-sea exchange (Emerson et al., 2002). Also, since at no time in our study were anoxic conditions measured, denitrification was not an issue of consideration (Pilson, 1998). For these reasons, and the fact that N$_2$ does not undergo any measurable chemical reactions, most ocean researchers consider N$_2$ to be inert (Broecker and Peng, 1982, Pilson, 1998), putting it in the same category as the noble gases (Millero, 2005).

The situation was on the estuarine side. Historically, with no evidence of hypoxia or anoxia ever being reported in the Great Bay-Piscataqua Estuary system (Short, 1992b), denitrification in the river-estuary system was unlikely (Allen, 1995). Moreover, nitrogen fixation is considered to be negligible in estuary surface waters and would be severely limited in the near freezing waters observed for most of this study (Marsho et al., 1975). Lastly, with the estuary being so heavily ocean dominated and the river input being so
small (less than 2% of the tidal prism), any significant impact from biotic nitrogen processes in Piscataqua Estuary Inlet are unlikely.

3.3.2 Dissolved Oxygen

Whereas assumptions could be made about nitrogen saturation being in approximate equilibrium with the atmosphere (Pilson, 1998, Broecker and Peng, 1982), Figure 3.8 suggests that the same assumptions may not fully explain observed oxygen. In theory, the nitrogen discussion can be applied to the abiotic oxygen component. However, this requires taking into account certain physical differences like oxygen being twice as soluble as nitrogen (Pilson, 1998, Broecker and Peng, 1982). Processes like collapsing air-bubble injection would favor insoluble gases like nitrogen (Hamme and Emerson, 2002), but non-collapsing bubbles would actually favor the more soluble gases like oxygen, enriching the air bubble with the less soluble gas like nitrogen (Millero, 2005). However, in looking at Figure 3.8, it is quite apparent that even in winter, the controls over the dynamics of oxygen are well beyond that of the physical (abiotic, nitrogen proxy), leaving the biological component as an equal, if not dominant, control.

Unlike in the nitrogen discussion, where assumptions had to be made to assess the likely controls of heat flux and ice melt discharge, the oxygen analysis had the benefit of additional supporting measurements. The dissolved carbon dioxide measurement (Figure 3.14) was taken for the purpose of aiding in oxygen analysis. Additionally, data from oxygen sensors on Buoys A and C, at 50 (m), and 20 (m), respectively, as well as a chlorophyll sensor on Buoy A (3m) were used to aid analysis.

Regarding biological control, the oxygen time series can be viewed as having two time periods. The first period runs from day 0 to 85, the winter or pre-spring bloom
period, and the second period, starting on day 85 and extending to the end of the study, the spring bloom period. The annual spring bloom is the single largest productivity event in the Gulf of Maine (Townsend et al., 1992). Since oxygen dynamics are apparently more dependent on biological controls (Figure 3.8), plotting concentrations along with 100% saturation concentrations (Figure 3.15), as done for the nitrogen analysis is not as meaningful. There appears to be much lower agreement between inlet concentrations levels and their respective saturation levels (Figure 3.9 and 3.15). Moreover, oxygen’s biological control appears to be ocean (not estuary) driven.

Regarding the use of buoy oxygen data, although Buoy A is slightly closer to CML than Buoy C (Table 3.1), Buoy C is the preferred buoy since its location places it up current with respect to the usual Western Gulf Coastal Current flow. Equally important is that Buoy C’s oxygen sensor is at 20 m depth, whereas Buoy A’s sensor is at 50 m, well below the surface layer.

In comparing the time series of inlet oxygen percent saturations with that of Buoy C (Figure 3.16), it is clear that over both records a percent saturation increase is the general trend. In the beginning of the study, the significant undersaturation shows that oxygen was not in equilibrium with the atmosphere, and this was occurring for both the estuary and near shore end members (Figure 3.15). Although oxygen is expected to be depleted at depth due to respiration (Broecker and Peng 1982, Millero 2005) throughout the world’s oceans the GEOSECS program found oxygen to be about 3% supersaturated even in cold, near zero degree surface waters (Broecker and Peng, 1982). Thus, the deviation from a surface state of slight supersaturation, as seen in the first 25 days of this
study, would suggest either significant surface respiration or, more likely, a mixing of surface waters with undersaturated bottom waters.

As discussed in Wallace and Wirick (1992), with the winter overturning of the water column occurring on October 9th (Figure 3.11), as long the surface waters are mixing down and being replaced with undersaturated water from depth, surface water measurements will continue to reflect undersaturated bottom waters. Over the study period, this persistent undersaturation due to mixing does not end until about day 22, and as seen in the Buoy B data (Figure 3.17), day 22 marks temporary stratification in the water column. Prior to day 22, the surface mixed layer often exceeded 50 m at Buoy B, a condition which would have mixed up oxygen depleted waters from the bottom; the water depth at Buoy B is 62 m. From day 22 until day 72, the surface mixed layer was primarily above the bottom waters of 50 m, and since undersaturated bottom water was not being mixed up, the surface oxygen concentration could return to its condition of slight supersaturation (Figure 3.16).

Starting on day 72, there was a 2 week period when the surface mixed layer depth exceeded 50m (Figure 3.17). This should have led to undersaturated surface waters. However, supersaturation was observed starting on day 72, climaxing on day 77 (Figure 3.8). Since an oxygen production event was not supported in the chlorophyll data (Figure 3.18), over this period there was a slight draw down in the CO₂ data (Figure 3.14), possibly pointing towards biological oxygen production. On day 77, there was a sharp decrease in oxygen percent saturation levels, which would be expected with the end of the conjectured oxygen production event. While there was a wave related oxygen pulse
on day 85 (to be explained later), undersaturation does not end until about day 86, with the onset of mixing depth stratification (Figure 3.17).

Finally, despite persistent undersaturation during the first period, there were several instances of supersaturation. Although not fully visible in the nitrogen data, all 8 of the sharp increases of supersaturation, starting on days 11, 14, 21, 34, 52, 59, 64, and 85, corresponded to elevated wave activity (Figure 3.19). This is fully in agreement with the findings of Wallace and Wirick (1992), where all of the sharp increases in oxygen saturation, some over 10%, corresponded to specific wave events. Wind-wave events will be discussed in a later section.

The onset of the annual spring phytoplankton bloom on day 86 marks the beginning of the second dissolved oxygen period, as seen in the chlorophyll data (Figure 3.18). Surface-bottom mixing and wave activity are no longer the primary controls over oxygen concentration. The beginning of the spring bloom marks the beginning of an oxygen upsurge sending surface oxygen to extreme levels (Figure 3.16) - actually exceeding the operational range of the sensor for a few days. As seen in Figure 3.15, during the second period, surface oxygen percent saturation was no longer at slightly saturated conditions, but responds according to phytoplankton dynamics. This can be seen by the way oxygen saturation (Figure 3.16) follows the chlorophyll trends, and by the way oxygen saturation and CO₂ are anti-correlated (Figure 3.16, Figure 3.14).

Although the spring bloom is the largest oxygen producing event in the western Gulf, it also occurs during a period when permanent seasonal stratification begins, so much of it is not recorded by the buoy oxygen sensors at depth. While the buoy sensors do show a large increase in oxygen, they never break 100% saturation for any sustained
period in our study (Figure 3.16). Finally, the bloom did slow down towards the end of
the study period, with chlorophyll levels actually dropping to below pre-bloom conditions
(Figure 3.18). However oxygen percent saturation remains substantially over saturated.

3.4 Wind Parameterized Air-Sea Gas Flux Analysis

So far the observed gas dynamics have been interpreted qualitatively by linking
deviations of expected behavior to likely controls, or by making comparisons to
secondary data sources, like buoy data. However, a framework does exist for discussing
one control on gas dynamics quantitatively, specifically, air-sea gas transfer through the
use of gas-flux modeling. Generally, the primary source for restoring weakly soluble
dissolved gas under- or super-saturation is the atmosphere through the re-equilibration of
that gas through the air-sea interface. Some of the early modeling framework for wind-
parameterized gas transfer was developed in open ocean environments through analysis
using bomb $^{14}$C (Wanninkhof, 1992). In freshwater environments like lakes and streams,
wind parameterization was developed through tracer analysis like the purposeful sulfur
hexafluoride study in lakes (Wanninkhof et al., 1985). In all these environments, gas
transfer studies have progressed to be able to predict piston (gas transfer) velocities
through physical control variables (Raymond and Cole, 2001). However, this is not the
case for river and estuarine studies, where there appears to be large disagreements on the
extent of physical forcing (Raymond and Cole, 2001). In the coastal ocean, near surface
turbulence (i.e. the primary control over piston velocity) is not only caused by wind, but
also by currents, waves, breaking waves, and bottom friction. However, despite the
disagreement in estuarine flux studies, researchers have determined wind-parameterized
flux relationships in their respective estuary studies. The appropriateness of these wind parameterized flux equations to the waters of the Piscataqua Estuary Inlet was therefore examined.

A description of flux across the air-sea interface is usually expressed as:

\[ F = k \Delta C = k(C_w - C_a) \]  

(1)

where \( F \) is the flux, \( k \) is the transfer (or piston) velocity, \( C_w \) is the gas concentration of the bulk water, and \( C_a \) is the 100% surface saturation concentration of the gas. \( \Delta C \) is the gradient, the difference between the bulk and the surface, with a negative value implying a flux into the water, or a positive value implying a flux out of the water. It is the piston velocity \( k \) that determines the speed at which this flux occurs. In marine and aquatic studies, piston velocity is normally determined using some form of wind parameterization, the most cited being Wanninkhof (1992) with:

\[ k = 0.31u^2(Sc/660)^{-0.5} \]  

(2)

where \( u \) is the wind speed, in m/s, measured at the standard 10 m height, and \( Sc \) is the Schmidt number defined as:

\[ Sc = \mu/D \]  

(8)

where \( \mu \) is the kinematic viscosity of the water, and \( D \) is the molecular diffusivity. Also, as the term piston velocity suggests, this flux model is one dimensional.

In this study, since nitrogen is inert and measured, it can be used as a natural tracer for use in a mass balance approach (Hartmond and Hammond, 1984, and Devol et al., 1987), for determining a specific transfer velocity. This would bypass the need to use of wind parameterized piston velocity since:

\[ k = F(C_w - C_a)^{-1} \]  

(9)
with flux calculated by:

\[ F = -(dM/dt)A^{-1}, \quad (10) \]

where \( dM \) is the change in mass, and \( A \) is the surface area, or alternately:

\[ F = -(dC/dt)h, \quad (11) \]

where \( dC \) is the change in concentration, and \( h \) is the mixing depth (Wanninkhof et al., 1987). However, in this study, because of fast currents and bathymetric depths ranging from 0 to 25 m over distances less than 500 m, a reliable mixed layer depth \( (h) \) could not be calculated or assumed. Also, since the surface area is not fixed, like that of a lake, \( F \) and \( k \) could not be directly calculated.

One of the initial goals of this study was to determine which of the various wind parameterized flux equations would be most appropriate at the inlet of large macrotidal estuary. At the outset, this seemed like a simple proposition. Flux can be calculated using: the dissolved gas measurements recorded at the inlet, local ocean winds calculated using the mean wind measured from Isles of Shoals and Buoy B and corrected to 10 m by using the neutral drag law as described in Smith (1988), atmospheric pressure measured at Buoy B, and various parameterized piston velocities. In this case the first piston velocity estimations looked at were Wanninkhof (1992):

\[ k = 0.31u^2(Sc/660)^{-0.5}, \quad (2) \]

and a macrotidal estuary derived linear relationship described in Borges et al. (2004):

\[ k_{600} = 4.045+2.580u. \quad (12) \]

Since the equation (12) was developed for CO\(_2\) in fresh water, it was transformed to a generalized form using the ratio of the Schmidt numbers (Jahne et al., 1987a), where

\[ k_1/k_2 = (Sc_1/Sc_2)^n, \quad (13) \]
which in this case was:

\[ \frac{k_{\text{gas}}}{k_{600}} = \left( \frac{Sc_{\text{gas}}}{600} \right)^n \]  

(Raymond et al., 2000). Also, for consistency with Wanninkhof (1992), the Schmidt number dependency (n) was kept at -0.5.

Finally, the Schmidt numbers were calculated with respect to temperature and salinity by linearly interpolating the Schmidt coefficient relationship in Wanninkhof (1992) as described in Borges et al. (2004). Wanninkhof (1992) determined coefficients using least squares third-order polynomial fits of Schmidt numbers ranging from 0 to 30 degrees for fresh (0 psu) and seawater (35 psu), derived from the experiments of Jahne et al. (1987b) and Wilke and Chang (1955). This linear interpolation method is acceptable since Schmidt numbers vary strongly with temperature and weakly with salinity (Pilson, 1998). Because of that, many researchers simply assume a 35 psu when calculating the Schmidt coefficient relationship of Wanninkhof (1992) (e.g. Olsen et al., 2005).

Nitrogen and oxygen fluxes were estimated at the inlet for the entire study period using both Wanninkhof (1992) and Borges et al. (2004) (Figures 3.20, 3.21, 3.22, 3.23). In looking at the nitrogen flux plots (Figures 3.20, 3.21), for most of the study period there was a nitrogen flux into the water, which would be the case since nitrogen was undersaturated for most of the study. Also, there does not appear to be much difference in the magnitude of the fluxes except that Wanninkhof (1992), being of a quadratic form, magnifies the higher wind events. In the oxygen fluxes (Figure 3.22, 3.23), the opposite appears to occur. For most of the study oxygen flux was positive, out of the water, with permanent out-flux with the onset of spring bloom. While, these wind parameterized fluxes were calculated and displayed in a manner consistent with many publications (e.g.
Sellers et al., 1995, Cole and Caraco, 1998, Hahm et al., 2005), closer inspection reveals a possible problem with this technique.

The problem is not inherent in the technique itself, the problem comes in the ability to verify the model. As mentioned before, these models are based on the assumption of a 1-dimensional column of water with complete horizontal homogeneity. While this condition may be possible in a laboratory, it is less likely to occur in the natural environment. Even in a lake, since wind parameterization is not applicable at low wind speeds, then most likely there would be wind driven circulation occurring (Jacobs, 1974). This 1-dimensional concept is not applicable anywhere with a current, especially not in a macrotidal estuary. Researchers sometimes assume water mass homogeneity by identifying time periods of water mass stability in density or other state variables. For example, McNeil et al. (2006a) subsets the time series by testing for closed heat and salt budgets to find periods, a few tidal cycles, of minimal horizontal advection. As previously mentioned, since our mixing depth was unknown, the same approach could not be taken in this study.

To more closely investigate individual flux values, periods of ocean stability were determined by identifying consecutive high tide periods with isopycnal stability to less than 0.1 kg/m³. High tides were assumed to be the most stable period of the tidal cycle because water is always mixing in estuaries, and estuaries are more sensitive to environmental changes, so if at anytime an assumption could be made about water homogeneity between tidal periods in an estuary inlet, it would have to be between high tides during periods of ocean stability. These time periods, as seen in Table 3.3, were examined to see how well current flux values at \( t = 1 \), the initial high tide, correlated to
the change in percent saturation values at the next tidal high \((t = 2)\). The expectation was that a flux of \(x\) into the water starting at \(t = 1\), should cause a corresponding increase in percent saturation at \(t = 2\). Results from our “stable” times are shown in Table 3.3. We found that only about half the time did the flux estimation predict a saturation change in the right direction; meaning half the time, a flux into the water still resulted in a decrease in percent saturation. The wind induced bubble correction of Woolf and Thorpe (1991) was also calculated in Table 3.3, but its corrections were small. Woolf and Thorpe (1991) will be discussed in further detail in the next section.

This finding in the estuary inlet data enables one of two determinations to be made regarding, not just wind parameterized flux estimations, but 1-dimensional flux calculations in general. First, that even during the most stable periods of the coastal ocean, as measured from the estuary inlet, gas transfer is more complicated then the simple assumption of 1-dimentional atmospheric re-equilibration as the primary control; or second, flux may occur as predicted by the models, but due to the constant moving water column, the same parcel of water cannot be re-measured. So unless some kind of floating array is employed, mass balancing oxygen or nitrogen will not be a reliable, or verifiable, technique in determining gas flux in the Piscataqua Estuary Inlet.

### 3.5 Elevated and Severe Wind-Wave Events

The final focus of this study was to examine and determine the extant of gas transfer during elevated or severe wind-wave activity (storms). What are the required conditions to elevate dissolved gas levels in the Piscataqua Estuary Inlet? Is severe wind sufficient, or is wave driven gas exchange required? Over the 135 days of this study there
were several periods of sustained elevated wind-wave activity lasting for several days, but there were also short, yet severe, wind-wave incidences that lasted less than one day. These events are explored.

Furthermore, as discussed in the dissolved oxygen section (3.3.2), while air bubble injection (complete bubble collapse) favors invasion of less soluble gases like nitrogen, bubble exchange (diffusive gas exchange through the bubble surface-water interface) favors invasion of more soluble gases like oxygen (Hamme and Emerson, 2002). The events of Episode 1, as will be seen in all wave events, support the hypothesis that the dominant exchange process during elevated wind-wave events is wave driven bubble exchange, as will be seen by the substantially greater response in the oxygen data.

Lastly, while there is a quantitative frame work for dissolved gas analysis at high wind events (e.g. Woolf and Thorpe (1991), Keeling (1993), Woolf (1997)), these approaches may not be directly applicable to the data set of this study. For example, in Woolf and Thorpe (1991), to account for air-sea gas exchange in the surface layer caused by wind induced bubble mediated gas transfer, this transfer is parameterized using wind speed with the relationship:

\[ F = k(C_w - C_a(1 + \Delta_e)), \]  

(15)

where the coefficient:

\[ \Delta_e = 0.01(u/u_i)^2, \]  

(16)

and \( u_i \) is a gas specific constant. Equation (15) is the same as equation (1), except this flux equation has the surface bubble transfer correction \( (1 + \Delta_e) \), which attempts to account for the wind-wave induced bubble transfer. While this relationship has been criticized for insufficiently estimating the corrected surface supersaturation concentration (Farmer et
al., 1993, Wallace and Wirick, 1992), it is still in use today. Equations (1 and 15) allow for the calculation of flux with just the bulk water measurement ($C_w$). This $C_w$ measurement was part of the problem in this study.

Due to an intake depth as shallow as 3 m during low tide, 0.5 m for the first month, and just 2.5 m deeper during high tide, as well as the fact that the intakes are only 20 m from shore, during increased wind-wave events, the intakes were most likely positioned in a location with surface to bottom vertical mixing. While it is apparent in the data that we are obtaining some measure of the impacts of white capping, wave crashing, and bubble gas transfer on the active turbulent mixed layer (surface), without a subsurface bulk layer and its attendant subsaturation concentration value ($C_w$), there was no subsurface gradient to drive the flux model.

While the modeled approach of equations (1 or 15) may have been insufficient for this study, bubble mediated gas transfer is a current topic in the air-sea gas exchange community, and there are newer approaches in quantifying these processes. However, there are still substantial uncertainties with the magnitude of bubble mediated processes to account for gas transfer (Woolf, 2005), and because of that, these newer methods are beyond the scope of this project, so our analysis was qualitative in nature.

3.5.1 Episode 1

Episode 1 (Figure 3.24) actually represents a series of winter storm events. Unfortunately due to sensor malfunctions, the dissolved gas record was fragmented for this period, but what was recorded is consistent with the expected behavior as discussed in Wallace and Wirick (1992). Between days 30 and 38 (January 13 to January 21, 2006), three high wind events, starting on days 31, 34, and 37, were recorded exceeding 12 m/s
for extended periods. Of these three high wind events only one, the event beginning on
day 34, was a large wave generator, creating nearly 6 meter waves as measured from
Buoy B. Unlike the first (1.1) and third (1.3) wind events, which were offshore winds,
blowing from the northwest and west, respectively. Winds from the second event (1.2)
were generated from the southeast changing to the south and were the highest of the three
events with a peak wind of 19 m/s. Since “fully developing seas require wind to blow for
a considerable time, over a considerable area, with stronger winds requiring even more
time and an even longer fetch, than light winds” (Knuass, 1978), offshore winds do not
have sufficient fetch to develop large waves in the near coastal ocean. With event 1.2 was
an onshore wind event, large waves were generated creating the conditions for heavily
supersaturated waters.

With the large wave activity of event 1.2, oxygen percent saturation jumped
dramatically on day 34. Also, although not conclusive, event 1.2 was also possibly
demonstrated in the nitrogen data. Although small in magnitude, nitrogen also elevated to
supersaturation on day 34 before decreasing on day 35 due to the decaying wave energy.

3.5.2 Episode 2

The events of Episode 2 (days 50 – 67) (Figure 3.25) were not as severe as that of
Episode 1 but there was a full record for both gases during this period. Although not
especially high, averaging only about 9 m/s winds, these averaged winds were sustained
for 17 days. The wind events of this episode are mainly offshore winds, and are not as
distinct as those recorded in the first episode, and as such, there was not the same kind of
wave development, except for the day 60 wave crest. Although difficult to see because of
the scale, the three periods of significant increase in the oxygen data (cresting on day 53,
60, and 64) do correspond to the elevated wave activity. This can be seen better in Figure 3.19 since there is greater vertical exaggeration. This does show that sudden instances of oxygen percent saturation increases do not require extreme wave activity, waves exceeding 5 m, but can be generated with 2-3 m waves. Wallace and Wirick (1992) observed nearly the same thing. They found that percent saturation increases of up to 12% could be generated with 3 m waves. Wind event 2.2, an east-northeast wind was a wave generator, creating 6 m waves, and causing a 12% increase in the oxygen percent saturation. Also, despite wind events 2.1 and 2.3 were more land generated (offshore winds), by coming from the southwest, there was sufficient fetch to generate wave induced gas level increases nearly rivaling the increases of event 2.2.

Elevated levels in nitrogen percent saturation also corresponded to two of the three oxygen saturation increases, the first (2.1) and the third (2.3), but as discussed in section 3.3, other processes affecting estuarine nitrogen may have cancelled out any increasing effects of wave event 2.2 on nitrogen levels. Finally, a striking feature in the nitrogen data during Episode 2 were the N₂ percent saturation spikes on days 55, 61, and 62, which initially looked like anomalies since they did not correspond to the oxygen, or any specific wind-wave event; however, upon comparison with the salinity data, those spikes actually occurred on the estuary side (low tide), so processes other than wind-wave events were responsible.

3.5.3 Episode 3

The winds of Episode 3 (days 71-81) (Figure 3.26) were similar in magnitude to that of Episode 2, but this period was more dominated by offshore winds, blowing mainly from the west-northwest (nearly perpendicular to the shore) with only 2 short periods of
onshore lasting less 36 hours combined. Although these onshore winds did generate elevated wave activity, the limited duration of these winds only produced waves on the order of 1-2 m. So despite the large wind magnitude, the extremely limited fetch and limited duration of onshore led to minimal wave generation during this episode, thereby causing air-sea gas transfer to be minimal.

3.5.4 Episode 4

Episode 4 (Figure 3.27) is not a series of events, it was a single storm event, the single largest wind-wave event of this entire study, with 20 m/s southeast winds and nearly 6 m seas, but lasting less than one day. Because of that, a closer inspection is required. Episode 4 occurred on the second day of this study, December 16, 2005. Early that day winds were light, less than 2 m/s, blowing from the north and seas were less than 0.5 m. At 4 am (GMT), winds started to increase, changing directions into a southeast wind, and over the next 12 hours the winds continued to increase causing wave generation. Also, atmospheric temperatures began rising at noon, starting from zero degrees. All three would continue to rise until 7 pm, at which time the winds were at 20 m/s, the waves 5.6 m and air temperatures were 8 degrees, then all three dropped. Winds fell to 10 m/s, flowing now from the land (west-northwest), seas dropped to 2 m, and atmospheric temperature dropped back to zero, and these conditions remained like this for the next few days. From a data analysis point of view, this was almost an ideal coastal sea storm, since the event is so clean.

In the gas data, this storm caused a 4 % increase in the oxygen data on the ocean side when compared to the previous tidal high, and a 7% increase over the flood tide phase. The next day, tidal high oxygen levels returned back to the pre-storm levels. And
despite the substantial fracture in the nitrogen data on day one, there was a slight increase (0.5%), in the nitrogen percent saturation from the pre-storm high tide to the storm high tide. Also, like in the oxygen data, by the second high tide of the next day, nitrogen saturation returned to pre-storm levels.

3.5.5 Wind-Wave Summation

Overall, these events present a case for strong invasion of dissolved oxygen into the sea during events with high wave energy. The fact that this invasion can occur even in supersaturated water strongly suggests bubble processes are the dominant control. Since the nitrogen data does not show a similarly strong response suggests that the primary bubble mediated gas transfer was in fact bubble exchange (diffusion across the bubble-water interface), and not bubble injection (bubble collapse) as discussed in Hamme and Emerson (2002). Although this study is just a cursory analysis of wave induced bubble transfer, the observations are promising for future evaluation of such processes.
Table 3.1  Sensor station distances
The distances between data recording stations. Distances are measured in km. See Figure 3.1 for station locations.

<table>
<thead>
<tr>
<th></th>
<th>CML</th>
<th>IOSN3</th>
<th>Buoy B</th>
<th>Buoy C</th>
<th>Buoy A</th>
</tr>
</thead>
<tbody>
<tr>
<td>CML</td>
<td>0</td>
<td>13.7</td>
<td>26.0</td>
<td>76.7</td>
<td>62.1</td>
</tr>
<tr>
<td>IOSN3</td>
<td>13.7</td>
<td>0</td>
<td>28.6</td>
<td>81.3</td>
<td>49.5</td>
</tr>
<tr>
<td>Buoy B</td>
<td>26.0</td>
<td>28.6</td>
<td>0</td>
<td>52.7</td>
<td>74.0</td>
</tr>
<tr>
<td>Buoy C</td>
<td>76.7</td>
<td>81.3</td>
<td>52.7</td>
<td>0</td>
<td>123.5</td>
</tr>
<tr>
<td>Buoy A</td>
<td>62.1</td>
<td>49.5</td>
<td>74.0</td>
<td>123.5</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 3.2  Time lag between tidal stages (high and low) and slack water

This is a three day sample of tidal stages compared to current slacks at New Castle, New Hampshire. Data were generated using X-tide, a tide prediction software made publicly available by the University of South Carolina (http://tbone.biol.sc.edu/tide). Time lag values below differ from what is reported earlier in this study, because the software uses predicted tides and we used measured tides in this study. Measured tides are available through

<table>
<thead>
<tr>
<th>Date</th>
<th>Tidal Stage</th>
<th>Tidal Current</th>
<th>Time Difference Delay (Minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Year</td>
<td>Month</td>
<td>Day</td>
<td>Hour</td>
</tr>
<tr>
<td>2005</td>
<td>12</td>
<td>15</td>
<td>3</td>
</tr>
<tr>
<td>2005</td>
<td>12</td>
<td>16</td>
<td>9</td>
</tr>
<tr>
<td>2005</td>
<td>12</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>2005</td>
<td>12</td>
<td>16</td>
<td>22</td>
</tr>
<tr>
<td>2005</td>
<td>12</td>
<td>16</td>
<td>4</td>
</tr>
<tr>
<td>2005</td>
<td>12</td>
<td>16</td>
<td>10</td>
</tr>
<tr>
<td>2005</td>
<td>12</td>
<td>16</td>
<td>18</td>
</tr>
<tr>
<td>2005</td>
<td>12</td>
<td>16</td>
<td>22</td>
</tr>
<tr>
<td>2005</td>
<td>12</td>
<td>17</td>
<td>4</td>
</tr>
<tr>
<td>2005</td>
<td>12</td>
<td>17</td>
<td>10</td>
</tr>
<tr>
<td>2005</td>
<td>12</td>
<td>17</td>
<td>16</td>
</tr>
</tbody>
</table>
Table 3.3 Wind parameterized air-sea flux over one tidal cycle

Flux estimated from the gradient ($C_w - C_a$) at $t=1$ and the mean wind speed ($u_{10}$) over the high tide interval ($t=1$ to $t=2$) during stable ocean conditions. $F$ is the flux (mmol/m²/hr), $\Delta$Conc is the change in concentration (mmol/kg) from tide 1 ($t=1$) to tide 2 ($t=2$), and $\Delta$Sat is the change in saturation from tide 1 ($t=1$) to tide 2 ($t=2$). So a flux in (negative) should show an increase in $\Delta$Sat. Green displays failure of this happening.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (t=1)</td>
<td>$u_{10}$ (m/s)</td>
<td>Flux</td>
<td>$\Delta$ Conc.</td>
<td>$\Delta$Sat</td>
</tr>
<tr>
<td>8397</td>
<td>7.46</td>
<td>-0.29</td>
<td>2.08</td>
<td>0.01</td>
</tr>
<tr>
<td>19580</td>
<td>5.07</td>
<td>0.30</td>
<td>-4.26</td>
<td>-0.48</td>
</tr>
<tr>
<td>21040</td>
<td>5.78</td>
<td>0.74</td>
<td>-0.31</td>
<td>-1.34</td>
</tr>
<tr>
<td>22540</td>
<td>6.79</td>
<td>0.46</td>
<td>6.33</td>
<td>0.57</td>
</tr>
<tr>
<td>25540</td>
<td>2.17</td>
<td>-0.13</td>
<td>2.98</td>
<td>0.05</td>
</tr>
<tr>
<td>27030</td>
<td>7.30</td>
<td>-1.36</td>
<td>1.85</td>
<td>0.02</td>
</tr>
<tr>
<td>30050</td>
<td>5.94</td>
<td>-0.28</td>
<td>-0.79</td>
<td>-0.14</td>
</tr>
<tr>
<td>31520</td>
<td>2.69</td>
<td>0.00</td>
<td>-0.63</td>
<td>0.03</td>
</tr>
<tr>
<td>32300</td>
<td>3.55</td>
<td>-0.01</td>
<td>-0.64</td>
<td>-0.06</td>
</tr>
<tr>
<td>35260</td>
<td>3.52</td>
<td>-0.27</td>
<td>3.79</td>
<td>0.19</td>
</tr>
<tr>
<td>36040</td>
<td>4.73</td>
<td>-0.48</td>
<td>-1.06</td>
<td>-0.42</td>
</tr>
<tr>
<td>80040</td>
<td>6.79</td>
<td>-1.00</td>
<td>0.16</td>
<td>0.08</td>
</tr>
<tr>
<td>81540</td>
<td>7.05</td>
<td>-1.31</td>
<td>2.56</td>
<td>0.10</td>
</tr>
<tr>
<td>83060</td>
<td>6.07</td>
<td>-1.18</td>
<td>1.34</td>
<td>0.30</td>
</tr>
<tr>
<td>88940</td>
<td>7.62</td>
<td>-2.24</td>
<td>-1.56</td>
<td>0.42</td>
</tr>
<tr>
<td>98550</td>
<td>6.35</td>
<td>-1.40</td>
<td>-2.54</td>
<td>0.92</td>
</tr>
<tr>
<td>100048</td>
<td>5.04</td>
<td>-0.58</td>
<td>-8.11</td>
<td>-0.61</td>
</tr>
<tr>
<td>103050</td>
<td>10.69</td>
<td>-4.00</td>
<td>9.06</td>
<td>0.46</td>
</tr>
<tr>
<td>104569</td>
<td>7.61</td>
<td>-1.57</td>
<td>-1.40</td>
<td>-0.87</td>
</tr>
<tr>
<td>110530</td>
<td>8.62</td>
<td>-3.06</td>
<td>2.44</td>
<td>0.18</td>
</tr>
<tr>
<td>111280</td>
<td>6.03</td>
<td>-1.31</td>
<td>-2.64</td>
<td>-0.57</td>
</tr>
<tr>
<td>112040</td>
<td>7.28</td>
<td>-2.10</td>
<td>3.17</td>
<td>0.68</td>
</tr>
<tr>
<td>114270</td>
<td>10.56</td>
<td>-3.87</td>
<td>7.69</td>
<td>1.12</td>
</tr>
<tr>
<td>115760</td>
<td>8.19</td>
<td>-1.80</td>
<td>9.16</td>
<td>1.16</td>
</tr>
<tr>
<td>117250</td>
<td>5.22</td>
<td>-0.49</td>
<td>4.54</td>
<td>1.05</td>
</tr>
<tr>
<td>123280</td>
<td>8.62</td>
<td>-0.38</td>
<td>4.25</td>
<td>1.68</td>
</tr>
<tr>
<td>124910</td>
<td>4.54</td>
<td>-0.01</td>
<td>-16.32</td>
<td>-2.60</td>
</tr>
<tr>
<td>127730</td>
<td>4.16</td>
<td>-0.32</td>
<td>-3.48</td>
<td>-0.53</td>
</tr>
<tr>
<td>128470</td>
<td>4.24</td>
<td>-0.23</td>
<td>-6.33</td>
<td>-0.97</td>
</tr>
<tr>
<td>132880</td>
<td>9.27</td>
<td>-2.76</td>
<td>1.43</td>
<td>-0.28</td>
</tr>
<tr>
<td>140290</td>
<td>5.59</td>
<td>-1.36</td>
<td>2.04</td>
<td>0.38</td>
</tr>
<tr>
<td>143290</td>
<td>3.38</td>
<td>-0.44</td>
<td>-5.33</td>
<td>-0.20</td>
</tr>
<tr>
<td>144780</td>
<td>4.77</td>
<td>-0.80</td>
<td>-4.23</td>
<td>-0.40</td>
</tr>
<tr>
<td>146280</td>
<td>5.59</td>
<td>-1.18</td>
<td>4.38</td>
<td>0.87</td>
</tr>
<tr>
<td>152300</td>
<td>5.33</td>
<td>-0.83</td>
<td>-5.81</td>
<td>-0.84</td>
</tr>
<tr>
<td>157490</td>
<td>4.12</td>
<td>-0.44</td>
<td>-9.84</td>
<td>-1.46</td>
</tr>
</tbody>
</table>
Figure 3.1 Additional sensor stations

CML data was supplemented with data from GoMOOS Buoys (A,B,C) and NDBC station (IOSN3) on the Isles of Shoals
Figure 3.2 Salinity Record

(a) Full record; (b) full record removed.
Figure 3.3 Salinity comparisons

Measured salinity with the addition of buoy salinity measurements.
Figure 3.4 Gulf of Maine modeled salinity field

An example of the general circulation in the western Gulf of Maine; this is a surface salinity and velocity model created by the University of Maine SMS Ocean Circulation Modeling group for GoMOOS. Usually between Casco Bay and Cape Ann there is a band of less saline water, and it is this lower salinity water that usually enters the Piscataqua Estuary. (Available at www.gomoos.org/buoy/circulation.html)
Figure 3.5 Total drainage into the Great Bay-Piscataqua Estuary (estimate)
Figure 3.6 Temperature record

Measured temperature for the entire study period with the addition of Buoy B surface temperatures
Figure 3.7 All recorded gas data

(a) Total dissolved gas pressure (mb); (b) oxygen concentration (mmol/kg); (c) nitrogen concentration (mmol/kg); (d) oxygen and nitrogen percent saturation; (e) carbon dioxide concentration (mmol/mol).
Figure 3.8 Nitrogen and oxygen saturation
Figure 3.10 Modeled nitrogen saturation concentration
Figure 3.11  Seasonal overturning of the water column at Buoy B

This period precedes the beginning of the CML record, starting in October 2005.
Figure 3.12  Air temperature (a) with nitrogen concentration (b)
Figure 3.13 Wind speed (a) and wave height (b)
Figure 3.14 Carbon dioxide concentration (aqueous)
Figure 3.15 Oxygen concentration
Figure 3.16 Oxygen saturation
Figure 3.17 Western Gulf of Maine temperature profile (Buoy B)
Figure 3.18 Chlorophyll (Buoy A)
Figure 3.19 Oxygen saturation (a) and wave height (b)

Until day 100, all sudden increases in O2 saturation (a) correspond to elevated wave events (b).
Figure 3.20 Nitrogen Flux (ocean model)
Figure 3.21 Nitrogen flux (estuary model) Estimated using Borges et al. (2004).
Figure 3.22: Oxygen Flux (ocean model)
Figure 3.23 Oxygen flux (estuary model)

Estimated using Borges et al. (2004).
Figure 3.24 Wind-wave Episode 1 (variable composite)

Day 26 is Jan 9, 2006. The green line is measured from Buoy B surface (1m). “U Direct BB” is wind direction measured from Buoy B, and “Wave BB m” is the wave height (m) measured from Buoy B.
Figure 3.25 Wind-wave Episode 2 (variable composite)

Day 46 is Jan 29 2006. The green line is measured from Buoy B surface (1m). “U Direct BB” is wind direction measured from Buoy B, and “Wave BB m” is the wave height (m) measured from Buoy B.
Day 67 is Feb 19, 2006. The green line is measured from Buoy B surface (1m). “U Direct BB” is wind direction measured from Buoy B, and “Wave BB m” is the wave height (m) measured from Buoy B.
Figure 3.27 Wind-wave Episode 4 (variable composite)

Day 0 is Dec 15, 2005. The green line is measured from Buoy B surface (1m). “U Direct BB” is wind direction measured from Buoy B, and “Wave BB m” is the wave height (m) measured from Buoy B.
CHAPTER 4

CONCLUSION

This study was borne out of an interest to assess the gas tension device technology and its ability to derive dissolved nitrogen measurements in seawater. From a scientific perspective the interests were the assessment of air-sea gas fluxes via evaluation of oxygen, carbon dioxide, and this inert nitrogen tracer. The present time series study took place at a near shore UNH facility (CML) where an existing suitable seawater intake system operates nearly continuously. The potential for obtaining a Piscataqua Estuary Inlet data set afforded the opportunity to investigate the effects of tidal, seasonal, and severe weather on dissolved gas measurements. The resulting 135 days of nearly continuous data collection of dissolved-gas evolution in the Piscataqua Estuary Inlet bore this promise out and provide a baseline data set to evaluate this site’s potential for future UNH Coastal Carbon Group research.

Interpretation of these estuary inlet observations without supporting measurements from offshore and upper estuary endmembers is not trivial. However, this study was able to use our single site’s temperature, salinity, and dissolved gas measurements to show that the estuary inlet behavior often adheres well to continuous water mass mixing model between the high and low tide endmembers. Although not completely intuitive in first evaluation of the dissolved gases, this became logical. The inlet of the estuary is not in itself a physical control system, but simply a location of
conservative mixing, one governed and dominated by predictable tidal currents and estuary discharge. Inlet measurement of gas variability at tidal time scales reflects the mixture of both bodies of water along varying tidal phases. This would likely not be the case if, for example, the Piscataqua Estuary Inlet was below a spillway where mechanical forcing could supersaturate levels by up to 40% (Geldert et al., 1998). Under these conditions the inlet would be a location of active physical change, and not just passive mixing.

Although Gulf measurements were incorporated in this study, the closest buoy (Buoy B) is 26 km away, and oxygen and chlorophyll buoy data come from even farther distances. Also, while there are Great Bay Estuary monitoring programs (e.g. Great Bay Coastal Buoy), unfortunately these programs did not extend through the winter and/or their data were not publicly available as of yet. Fortunately, tidal predictability and the Great Bay’s large tidal prism-to-discharge ratio does, for the most part, allow for reasonable inferences and assumptions about endmember values.

Regarding the analyses and quantification of air-sea fluxes, with certain key variables unknown like the mixing depth and bulk water concentrations, during elevated wind-wave activity, flux values could not be determined with any certainty. Essentially, this location with its dynamic bathymetry, strong currents, and tidal water mass mixing does not adhere well to existing one-dimensional flux models, nor most conceptual models for field evaluation of air-sea mass flux. Without the mixed layer depth, a direct bulk mass balance flux determination based on inert nitrogen concentration change could not be done. The same goes for the wind-wave event flux estimation because of the shallowness of the intake depth and/or vertical mixing to the bottom at this location.
While it is apparent in the data that we are obtaining some measure of the impacts of white capping, wave crashing, and bubble gas transfer on the active turbulent mixed layer (surface), without a subsurface bulk layer and its attendant subsaturation concentration value there is no subsurface gradient to drive the flux model. This study demonstrates that a new conceptual model is needed for this and similar sites that are judged to lie beyond the scope of the present analyses.

In addition to difficulties in direct flux determinations and wind-wave flux estimations, the strong tidal current mixing confounds wind-parameterized flux estimation even in calm conditions, since there was never a time when we could assume a static time-evolving water column. Even on the ocean side (high tide) during the most isopycnally stable time periods in the western Gulf, the fact that our wind-parameterized flux values (Table 3.2) were going in the wrong direction half the time suggests that other processes are involved (e.g. upwelling, currents, wave activity, mixing). Another unresolved possibility is that there was significant spatial diel variation in coastal gas concentrations. This work highlights the problems associated with gas flux estimates in the presence of strong horizontal advection. In this study the inability to track advective effects made air-sea natural gas mass-balance flux estimates in the Piscataqua Estuary difficult. The floating dome approach (e.g. Kremer et al., 2003, Marino and Howarth, 1993) may be a way to directly measure discrete gas fluxes despite the moving currents. However, this approach is limited to short term use, requiring active involvement by the researcher, and is only viable in calm conditions. A longer-term study would most likely involve a purposeful dual tracer approach, with one tracer being non-volatile (Nightingale et al., 2000). With a non-volatile in use, an arbitrary area could be used, since dilution
could be accounted for, so budget calculating would be possible despite the currents. Also, this technique could be applied under any weather condition. A possible problem with this technique is its detection limit. Since 40% of the volume of the Great Bay Estuary is exchanged every tidal cycle any forced tracer addition would quickly dilute down, and thus there would be a limit on the technique’s usefulness.

Although the air-sea flux portion of this study proved inconclusive, there were some significant findings. As measured from the inlet, the Great Bay-Piscataqua Estuary system does behave and interact predictably with the western Gulf of Maine during the winter season. During the winter months, nitrogen dynamics are governed by seasonal and temporary heat fluxes more than anything else. Oxygen is primarily controlled by surface and lower water column mixing, bringing undersaturated water up from depth. This occurs until the spring bloom when primary production oxygen creation dominates over all else. Additionally, with respect to elevated wind-wave events, it is observed that wind speed is not the strongest correlative with observed gas dynamics and observed oxygen supersaturation. Rather it is the wind generated wave activity which best explains significant storm event increases. Finally, combined oxygen and nitrogen results strongly suggest that wave activity in the near shore Gulf contributes to bubble exchange and not bubble injection. Dissolved oxygen’s much greater response to wave activity is one clear observational result that we hope to build on in future analyses using carbon dioxide in addition to these two gases.
LIST OF REFERENCES


Borges, A.V., 2005. Do we have enough pieces of the jigsaw to integrate CO2 fluxes in the coastal ocean?. Estuaries, Vol. 28, No. 1, 3-27.


wind oligotrophic lake measured by the addition on SF$_6$. Limnology and
Oceanography, 43(4), 647-656.


of Marine Systems, Submitted.

Devol, A.H., Quay, P.D., Richey, J.E., and L.A. Martinelli, 1987. The role of gas-
exchange in the inorganic carbon, oxygen and $^{222}$Rn budgets in the Amazon.
Limnology and Oceanography, 32, 235-248.


Elsinger, R.J., and W.S. Moore, 1983. Gas exchange in the Pee Dee River based on
$^{222}$Rn evasion. Geophysical Research Letters, 10, 443-446.

Emerson, S., Stump, C., Johnson, B., and D.M. Karl, 2002. In situ determination of
oxygen and nitrogen dynamics in the upper ocean. Deep-Sea Research I, 49, 941-
952.

wetting and drying. Journal of Geophysical Research, 107, No. C5, 3038,


equations. Limnology and Oceanography, 37(6), 1307-1312.

metabolism in coastal aquatic ecosystems. Annual Review of Ecology and
Systematics, 29, 405-433.

below a spillway plunge pools. Journal of Hydraulic Engineering, 124(5), 513-
521.


